is a metastable state such as $^3\Delta_u$ at 3.21 eV[20] with a long lifetime and stability toward collisions with $N_2$ or $D_2$.

*Photochemistry at 184.9, 228.8, and 253.7 nm.* Little if any $C_4H$ or $C_2H$ radicals are formed at 228.8 nm or above, since no $C_4HD$ or $C_2HD$ products are formed in the photolysis of $C_4H_2$ + $D_2$ mixtures (see Table III).

The transition that occurs at 184.9 and 228.8 nm is probably $^1\Delta_u \leftarrow {}^1\Sigma_g^+$ and that at 253.7 nm is $^1\Sigma_u \rightarrow {}^1\Sigma_g^+$.[18] At 184.9 and 228.8 nm, process 6, $C_4H_2 \rightarrow C_4H + H$, is energetically possible. However, the radical process is found to be less than 0.1, and the excited-state reactions predominate at these wavelengths. Pontrelli[7] found $C_2H_2$ in the photolysis of $C_4H_2$ at 253.7 nm. This finding is in disagreement with our results and is energetically not possible (see Table IV). It is possible that $C_2H_2$ was formed at 184.9 nm which was transmitted through glass walls.

The effective wavelength of solar radiation in Titan's atmosphere to induce the photochemical reaction in diacetylene depends on altitude. In the mesosphere the vacuum-UV radiation is almost as effective as the near-UV radiation, because the absorption coefficient of diacetylene in the vacuum-UV is almost 100 times larger than that in near-UV, although the intensity of solar radiation in the vacuum-UV is 100–1000 times weaker than that in the UV. However, in the stratosphere the near-UV radiation becomes more important because the vacuum-UV radiation is absorbed mainly by $CH_4$ and $C_2H_2$ at higher altitude. Thus, photodecomposition studies of $C_4H_2$ over a wide wavelength region are needed.

The photochemistry of $C_4H_2$ in Titan's stratosphere is probably dominated by the reactions involving the excited-state $C_4H_2^{**}$ which is not quenched by $N_2$. The products of the excited-state reactions have not been studied. It is most likely, however, that various polyacetylenes are efficiently formed by reactions 15–17 followed by $C_4H_2^{**} + C_8H_2 \rightarrow C_{12}H_2 + H_2$, etc., and may lead to the stratospheric haze layer on Titan as suggested by Allen et al.[1]

*Acknowledgment.* We thank the reviewer for numerous constructive comments. H. Okabe thanks Dr. L. Stief for his hospitality during his stay at NASA/GSFC. This research was supported by the NASA Planetary Atmospheres Program.

**Registry No.** $C_4H_2$, 460-12-8; $C_2H_2$, 74-86-2; $C_2HD$, 2210-34-6; $C_4HD$, 74488-01-0; deuterium, 7782-39-0; nitrogen, 7727-37-9.

# Photochemistry in a Heterogeneous System: Chlorophyll-Sensitized Reduction of *p*-Dinitrobenzene by Hydrazobenzene

**G. R. Seely* and G. A. Haggy**

*Battelle-Kettering Laboratory, Yellow Springs, Ohio 45387* *(Received: June 25, 1986)*

The photoreduction of *p*-dinitrobenzene, sensitized by aqueous suspensions of chlorophyll *a* with other amphiphiles adsorbed onto polyethylene–tetradecane particles, differs in some respects from the photoreduction in solution. The reaction proceeds in two stages. The products of the first stage, *N*-(*p*-nitrophenyl)hydroxylamine and azobenzene, are separated into the aqueous and hydrocarbon particle phases, respectively. The nature of the second stage of reaction is uncertain, but observations are best explained by a reduction of *N*-(*p*-nitrophenyl)hydroxylamine to 4,4′-dinitrohydrazobenzene. The quantum yield of photoreduction to the hydroxylamine does not seem to correlate at all with the quantum yield of fluorescence of the sensitizing particles. This and the relative magnitudes of the yields suggest that the principal photochemical reaction is reduction of dinitrobenzene not by the excited singlet state of chlorophyll or by the triplet state formed directly by intersystem crossing but by high-energy ion pair states or perhaps triplets formed from them by decay. Absorption spectrometry in the heterogeneous system is complicated by superposition of the so-called sieve effect on the path-length enhancement effect of the highly scattering system. The role of the interface between the particle and aqueous phases on the course of the reaction is discussed.

## Introduction

Heterogeneous systems such as micelles, liposomes, and electrode surfaces offer some advantages for photochemistry over homogeneous systems. The one perhaps most often discussed is the possibility of separating products into different phases. Others might be stabilization of ground or excited electronic states and reaction products and promotion of interaction between reagents or products.

The interactions of chlorophyll *a* (Chl) with other amphiphilic substances, when adsorbed to particles of polyethylene swollen with hydrocarbon diluents, have been described.[1-3] It was noted that Chl existed in monomeric or oligomeric associated forms only when another amphiphile was present which could ligate the Mg; otherwise it was largely in the microcrystalline hydrate form absorbing at 742 nm.[1,2,4] In the presence of a ligating amphiphile, Chl is fluorescent at room temperature and below, and resolution of absorption and fluorescence spectra into Gaussian components reveals that associated as well as monomeric species of Chl fluoresce.[2] The temperature dependence of the distribution of fluorescence intensity among these components indicates a degree of transfer and equilibration of energy among the different species.[5]

The swollen particle system was developed specifically in the hope that the viscous nature of the particle substratum would preserve singlet excited states, by retarding bimolecular processes that lead to their quenching. The persistence of fluorescence, with quantum yields of several percent, at fairly high densities of Chl at the particle surface confirms that this is so.[6] It might therefore be expected that photochemical reactions of the Chl excited singlet state could be observed in the particulate system if oxidants and reductants are added. In fact, a large variety of photochemical reactions have been observed with the particulate systems, among them several reactions of Chl and pheophytin that have no reported counterparts in homogeneous and other heterogeneous systems. As a start toward unraveling the rich photochemistry of the

(1) Seely, G. R.; Rutkoski, A. M.; Kusumoto, Y.; Senthilathipan, V.; Shaw, E. R. *Photochem. Photobiol.* **1982**, *36*, 633.
(2) Kusumoto, Y.; Seely, G. R.; Senthilathipan, V. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1598.
(3) Kusumoto, Y.; Senthilathipan, V.; Seely, G. R. *Photochem. Photobiol.* **1983**, *37*, 571.
(4) Jacobs, E. E.; Vatter, A. E.; Holt, A. S. *Arch. Biochem. Biophys.* **1954**, *53*, 228.
(5) Senthilathipan, V.; Seely, G. R.; Kusumoto, Y., unpublished observation.
(6) Seely, G. R.; Senthilathipan, V. *J. Phys. Chem.* **1983**, *87*, 373.

0022-3654/87/2091-0440$01.50/0 

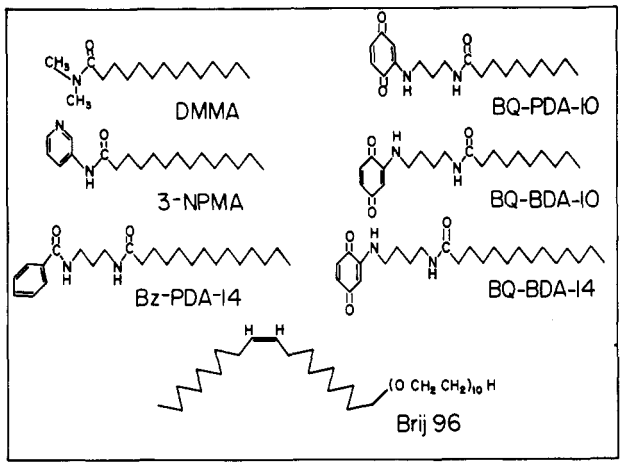


**Figure 1.** Structures of amphiphiles mentioned in text and abbreviations for them. In DMMA, Bz-PDA-14, and the three oxidizing amphiphiles on the right, it is the aliphatic amide carbonyl that ligates the Mg of Chl; in 3-NPMA it is the pyridine N, and in Brij, the ether.

heterogeneous system we are investigating the photosensitized reduction of a series of aromatic nitro compounds.

The aim of this investigation is to define the energetic limitations of photochemical reactions sensitized by Chl in the heterogeneous system and incidentally the identities of excited states responsible. Aromatic nitro compounds are appropriate for this, because although the usual products of their reduction are the four-electron reduced phenylhydroxylamines, the rate is controlled mainly by the potential for one-electron reduction to the nitro radical anion. These potentials span the range of interest to Chl photochemistry and in the past have correlated rather well with reactivities of triplet and singlet states of molecules like Chl.[7-11] There is also much known about the direct photoreduction and the electrochemical reduction of nitro compounds that relates to their sensitized reduction.

In this paper we describe photoreactions of the easily reduced compound, *p*-dinitrobenzene (DNB); in another the relation between redox potential and rate of reduction of a series of nitro compounds will be treated. Since it is important to us which excited states of Chl are effectual in the reactions, preparations were employed in which Chl was associated with a variety of ligating amphiphiles. Some of these ligating amphiphiles also contained an oxidizing group that could accept an electron from photoexcited Chl as a primary photochemical process. As reducing agent we used hydrazobenzene, which can reduce the oxidized Chl cation radical efficiently but not the singlet or triplet excited state.[12] Hydrazobenzene is recognized as an efficient donor to photosystem 2 of photosynthesis.[13]

## Experimental Section

*Materials.* Figure 1 shows structures and abbreviations for the amphiphiles adsorbed with Chl on particles for the present photoreactions. *N,N*-Dimethylmyristamide (DMMA) from Sigma Chemical Co. was recrystallized from aqueous methanol. Brij 96 (oleyl poly(oxyethylene), also from Sigma, is a weak ether ligand for the Mg of Chl and was used as received. The preparation of *N*-(3-pyridyl)myristamide (3-NPMA) has been described.[2]

The preparation of the oxidizing amphiphile BQ-PDA-10 is typical. Methyl decanoate (10.7 $cm^3$, 0.05 mol) was reacted with 1,3-diaminopropane (8.35 $cm^3$, 0.10 mol) in heptane (10 $cm^3$) at 60 °C under $N_2$ for 24 h. On cooling, solid products were collected with the aid of 100 $cm^3$ of heptane. The monoamide was separated from the diamide with hot acetonitrile, in which the latter is less soluble. The recovered monoamide (6.22 g, 55% yield) gave a satisfactory IR spectrum. Benzoquinone (0.722 g, 6.68 mmol) was added to monoamide (0.665 g, 3.16 mmol) in 100 $cm^3$ of dimethylformamide. After 20 min, water (100 $cm^3$) was added to the reddish brown solution and crude product was collected. Recrystallization from toluene–chloroform, extraction with dimethylformamide, and washing with 1:1 aqueous propanol gave 0.363 g of reddish crystals: mp 216 °C. The IR spectrum in KBr had strong bands at 3350, 3290, 2960, 2880, 1670, 1595, 1575, 1525, 1490, and 1320 $cm^{-1}$. UV spectrum: 342 nm (15 670 $M^{-1}$ $cm^{-1}$) in methanol and a broad, weak absorption at 490 nm.

The amphiphiles BQ-BDA-10 and BQ-BDA-14 were prepared similarly. The nonoxidizing amphiphile Bz-PDA-14 was prepared by reaction of benzoyl chloride with the monomyristamide of diaminopropane and recrystallized from ammoniacal aqueous alcohol: UV 226 nm (5950 $M^{-1}$ $cm^{-1}$); IR 3330, 3090, 2930, 2860, 1660, 1570, 695 $cm^{-1}$ in KBr.

Chlorophyll *a* was purified by chromatography on sugar with hexane–ether development. Hydrazobenzene was recrystallized from hexane–toluene. 1,4-Dinitrobenzene was recrystallized from methanol.

*N*-(*p*-Nitrophenyl)hydroxylamine (NPHA) was prepared from DNB by reduction with ascorbic acid, following the procedure of Kuhn and Weygand,[14] and recrystallized from benzene: mp 107–108 °C (lit. 107 °C), satisfactory IR; UV 363 nm in methanol, 12 100 $M^{-1}$ $cm^{-1}$; compare for *p*-nitroaniline 369 nm in methanol, 15 300 $M^{-1}$ $cm^{-1}$. *p*-Nitronitrosobenzene was prepared from NPHA by $FeCl_3$ oxidation[15] and recrystallized from 95% ethanol: mp 120–121 °C (lit. 119 °C); IR in KBr satisfactory for dimer; UV 282 nm in methanol, 9400 $M^{-1}$ $cm^{-1}$ (lit. 282.5 nm, 8170 $M^{-1}$ $cm^{-1}$ in dimethylformamide[16]). *p*-Nitronitrosobenzene is reduced to NPHA by hydrazobenzene in methanol over the course of a few minutes. Reaction of *p*-nitronitrosobenzene with NPHA in methanol produced 4,4′-dinitroazoxybenzene: UV 345 nm (lit. 342 nm[17]). 4,4′-Dinitroazobenzene was prepared by peroxide oxidation of *p*-nitroaniline.[18]

Swollen polyethylene particles were prepared as before[1,2] by dissolving 10 g of polymer (cleaned by extraction with 1-propanol) in 100 $cm^3$ of purified tetradecane at 87 °C and cooling with stirring. The collected particles were washed by suspending in 50 $cm^3$ of methanol and vacuum dried at room temperature; 46.1 g of waxy particles was recovered.

Chl and the soluble amphiphiles DMMA, 3-NPMA, Brij 96, and Bz-PDA-14 could be, and usually were, adsorbed to particles out of aqueous methanol.[1] The three oxidizing amphiphiles in Figure 1 are not very soluble in methanol or any solvent tested at room temperature and could not be successfully applied this way. They were better applied to particles by slow evaporation of a solution in warm methanol. (More recently, we have found that evaporation of a solution in 1,2-dichloroethane–ethanol is more effective in achieving ligation of BQ-PDA-10 to Chl.)

These oxidizing amphiphiles are liable not to be monomolecularly dispersed on polyethylene particles. For example BQ-BDA-10, applied to particles from methanol but without Chl, had a peak at 415 nm and a broad band around 340 nm, instead of the expected narrow band near 342 nm.

Table I summarizes the properties of the particle preparations used in this investigation. Some preparations contain only nonoxidizing amphiphiles, some only oxidizing ones, and some both. The last were prepared in order to investigate possible effects of energy transfer from fluorescent chlorophyll species to quenched species on the fluorescence and photochemical quantum yields. Particles to which a second amphiphile was added are indicated

(7) Seely, G. R. *J. Phys. Chem.* **1969**, *73*, 117.
(8) Seely, G. R. *J. Phys. Chem.* **1969**, *73*, 125.
(9) Connolly, J. S.; Gorman, D. S.; Seely, G. R. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 649.
(10) Andreeva, N. E.; Barashkov, B. I.; Zakharova, G. V.; Shubin, V. V.; Chibisov, A. K. *Biofizika* **1978**, *23*, 565.
(11) Droupadi, P. R.; Krishnan, V. *Photochem. Photobiol.* **1984**, *39*, 161.
(12) Seely, G. R. *J. Phys. Chem.* **1965**, *69*, 2633.
(13) Havemann, J.; Duysens, L. N. M.; van der Geest, T. C. M.; van Gorkom, H. J. *Biochim. Biophys. Acta* **1972**, *283*, 316.
(14) Kuhn, R.; Weygand, F. *Chem. Ber.* **1936**, *69*, 1973.
(15) Gamba, A.; Bellobono, I. R. *Gazz. Chim. Ital.* **1972**, *102*, 445.
(16) Barzaghi, M.; Gamba, A.; Morosi, G. *Chim. Ind. (Milan)* **1975**, *57*, 274.
(17) Gore, P. H.; Wheeler, O. H. *J. Am. Chem. Soc.* **1956**, *78*, 2160.
(18) Mehta, S. M.; Vakilwala, M. V. *J. Am. Chem. Soc.* **1952**, *74*, 563.

**TABLE I: Constitution and Fluorescence Yield of Particle Preparations**

| prep[a] | $10^3$[Chl]p,[b] $m$ | amphiphile | $10^3$[amphiphile]p,[b] $m$ | $\Phi_f$[c] |
|---|---|---|---|---|
| I | 0.91 | DMMA + | 4.0 | 0.139 |
| | | BQ-PDA-10 | 1.2 | |
| II | 1.03 | DMMA | 4.0 | 0.118 |
| IIa | 1.03 | DMMA + | 4.0 | 0.031 |
| | | BQ-PDA-10 | 5.0 | |
| IIIa | 0.76 | DMMA | 9.0 | 0.042 |
| IIIb | 0.74 | DMMA + | 4.0 | 0.029 |
| | | BQ-PDA-10 | 7.1 | |
| IV | 0.44 | BQ-PDA-10 | 6.6 | nd |
| V | 1.12 | Bz-PDA-14 | 5.3 | 0.024 |
| VI | 0.74 | BQ-PDA-14 | 7.0 | 0.019 |
| VII | nd | Brij 96 | nd | ~0.10 |
| VIIa | nd | Brij 96 + | nd | 0.024 |
| | | BQ-BDA-10 | 4.0 | |
| VIII | 1.47 | 3-NPMA | 2.8 | nd |

[a] The significance of letter subscripts is explained in the text. [b] Chl and amphiphile concentrations are expressed as $\mu$mol $g^{-1}$ particles, or mmolal. [c] Apparent fluorescence quantum yields, as explained in the text, measured with 430-nm excitation preferentially, for which reabsorption is less important. nd indicates not determined.

by letter subscripts in Table I. For example, particles II were prepared by adsorption of Chl and DMMA from aqueous methanol; later, BQ-PDA-10 was added by evaporation of methanol solution (IIa). Particles III were prepared by adsorption of Chl and DMMA (4 $\mu$mol/g). To half of the particles was added DMMA (5 $\mu$mol/g) by evaporation from methanol (IIIa); to the other half was added BQ-PDA-10 (IIIb).

Particle preparations were characterized by absorption and fluorescence spectra and fluorescence quantum yields. For this purpose, the particles were suspended at typically 4% concentration in a paste composed of Ficoll, glycerol, and cellulose (Sigmacell) in the ratio 12:25:6. Absorption spectra of a layer of suspension in a 1-mm demountable quartz cell were recorded by a Cary 2200 spectrophotometer. Fluorescence of the same sample was measured with the apparatus described[2] but with a cooled Hamamatsu R928 photomultiplier as detector. Quantum yields were determined by integration of the spectrum, correction for variation of sensitivity with wavelength, and comparison with a layer of Kodak white reflectance coating ($BaSO_4$) as a standard scattering sample. The quantum yields in Table I are what we prefer to call "apparent quantum yields"; they are ratios of integrated fluorescence to the differences between back-scattered exciting light without and with absorbing substance present. Intuition suggests and calculations which will be presented elsewhere demonstrate that apparent yields do not differ a great deal from true quantum yields and therefore may be used as valid measures of relative fluorescence intensity. It will be observed that in every case addition of a quenching amphiphile such as BQ-PDA-10 diminishes the fluorescence yield of the particles.

Fluorescence lifetimes for some of the preparations were measured on the apparatus at the Solar Energy Research Institute, Golden, CO, through the courtesy of Dr. John S. Connolly and his colleagues. These measurements incidentally confirmed the relative magnitudes of quantum yields measured by our apparatus.

*Photoreactions.* To conduct photoreactions, the particles, with oxidants and reductants, were suspended in an aqueous medium thickened with guar gum (2%). The suspension contained typically 10% particles and in addition about 5% cellulose (Sigmacell, 20 $\mu$m), the purposes of which were to facilitate blending and to increase uniformity of light scattering and absorption. The guar solution also contained Hepes (*N*-(2-hydroxyethyl)piperazine-*N*'-2-ethanesulfonic acid)–KOH buffer, 0.1 M, pH 7.0, and $NaN_3$ ($4 \times 10^{-3}$ M) as preservative. Hydrazobenzene was added in solid form to the weighed particles and distributed upon application of a stock solution ($10^{-2}$ M) of DNB in methanol. Methanol was removed in a stream of $N_2$ and cellulose was added, followed by the guar solution. After the suspension was blended in a mortar, it was weighed into a special cell, in which the sample was

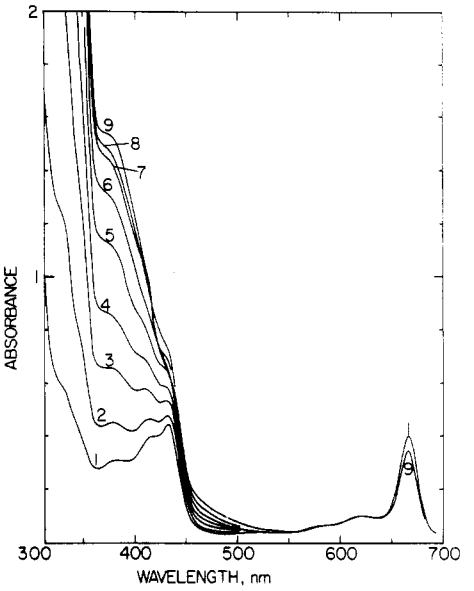


**Figure 2.** Photoreduction of *p*-dinitrobenzene ($2.0 \times 10^{-4}$ M) by hydrazobenzene ($2.4 \times 10^{-3}$ M) sensitized by ethyl chlorophyllide in 1-pentanol. Spectra recorded after (1) 0, (2) 20, (3) 50, (4) 80, (5) 110, (6) 160, (7) 240, (8) 400, and (9) 7575 s irradiation at 670 nm. The reaction was conducted in a quartz cuvette of 0.5-cm path length under $N_2$.

equilibrated with a stream of research grade $N_2$ for at least an hour and then compressed between two quartz plates to a layer a little less than 0.1 cm thick. The sample was exposed to light through a 670-nm interference filter for intervals, and a succession of spectra were recorded on a Cary 2200 spectrophotometer. The optical density range of the highly scattering samples was about 1.9–4 as perceived by the instrument, but quite satisfactory spectra were nevertheless obtained.

Quantum yields were calculated from the estimated rate of absorption of light by the sample and the estimated rate of conversion of DNB to NPHA. The former was estimated from the intensity of light incident on the sample (about 24 W $m^{-2}$) and the absorbance at 670 nm measured on transmitted light by the Cary 2200. Because of the properties of light transport in scattering systems, this procedure overestimates somewhat the fraction of incident light that is absorbed. The rate of conversion of DNB to NPHA was estimated from changes in the absorption spectrum, as will be described. In consideration of the many possible sources of systematic error, the quantum yields so calculated are probably correct within a factor of 2. Reproducibility and precision are much better, however, and comparisons of quantum yields are probably valid within ±10%.

For comparison with the heterogeneous system we also conducted reactions in a homogeneous system. To find a single solvent that would imitate the environment of a hydrocarbon–water interface is of course not possible; we settled on 1-pentanol, whose hydrocarbon and hydroxyl functions at least combine those of the water and tetradecane phases. Pentanol was purified by warming with $NaBH_4$, neutralizing with oxalic acid, and distilling, at first as an azeotrope with added water. Homogeneous photochemical reactions were performed in 0.5-cm-thick cuvettes in an apparatus previously described,[19] with ethyl chlorophyllide as sensitizer under 670-nm excitation.

## Results

The course of the photosensitized reduction of DNB in a homogeneous system is shown in Figure 2. The absorption band of one product, azobenzene, rises at the left margin, and the other product, NPHA, appears as a shoulder near 370 nm. The relative increases are consistent with the stoichiometric 2:1 ratio of products. There is no further change on prolonged irradiation

(19) Seely, G. R. *Photochem. Photobiol.* **1977**, *26*, 115.

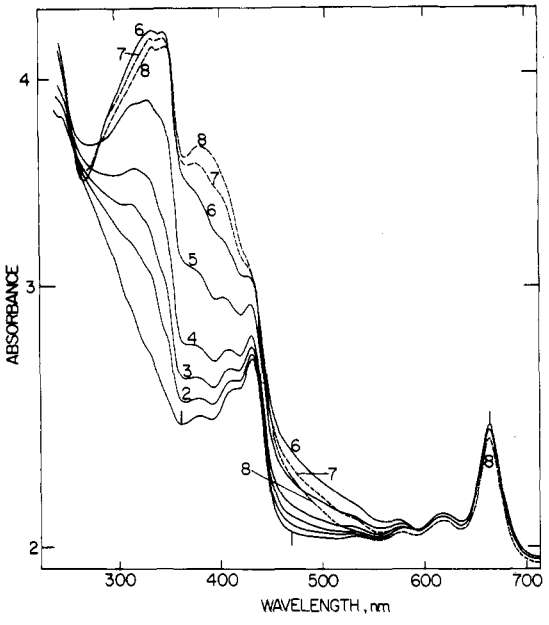


**Figure 3.** Photoreduction of *p*-dinitrobenzene by hydrazobenzene, sensitized by particle preparation IIIa; see Tables I and II for composition and concentrations. Solid traces (first stage of reaction): spectra after (1) 0, (2) 25, (3) 50, (4) 100, (5) 250, and (6) 500 s total time of irradiation at 670 nm. Dashed traces (second stage of reaction): spectra after a total of (7) 2150 and (8) 3350 s irradiation. Reaction was conducted in the compression cell with a geometrical optical path of 0.069 cm.

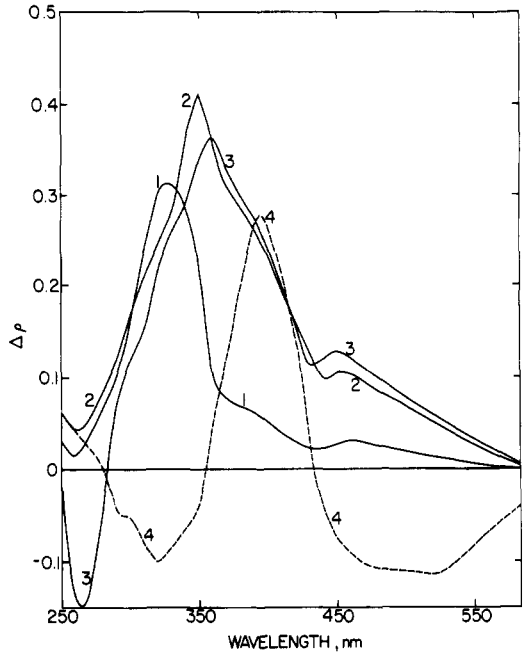


**Figure 4.** Absorbance difference ($\Delta\rho$) spectra for intervals in the reaction of Figure 3. Solid traces: (1) 0–25 s, (2) 100–250 s, (3) 250–500 s. Dashed trace: (4) 500–3350 s. The wave at 445 nm in (2) and (3) may be a small shift in the position of the Chl Soret band.

(to 2 h), except for a gradual attrition of chlorophyllide. The quantum yield for NPHA production is 0.058 initially and decreases gradually as the reaction progresses. The aspect is typical of a triplet Chl-sensitized reaction and resembles our earlier results with pyrochlorophyll.[7,20]

The course of a typical particle-sensitized, heterogeneous-phase reaction exhibits some striking differences (Figure 3). First, the relative increase of absorption in the near-UV and visible regions, even to 600 nm, is greater. Second, the wavelength of greatest absorbance increase is about 350 nm, whereas 320 nm is more appropriate for azobenzene, as in Figure 2. Third, the reaction proceeds in two stages. During the first, absorbance increases in the entire 300–600-nm region; this stage is complete in 500 s. During the second, absorbance increases in the near-UV but decreases below 350 nm and above 450 nm. A distinct band builds up at 380 nm. When the sample is left standing for several hours, absorbance decreases in the near-UV region and may increase somewhat in the visible and middle-UV regions.

Difference spectra (Figure 4) reveal somewhat more about these complex spectral changes. During the first 25 s of reaction, the difference peak is near the normal position for azobenzene, and absorbance increase in the 370–600-nm region is relatively small. But by 100 s the difference peak has shifted to 350 nm, and thereafter the difference spectrum takes the form shown for the 100–250-s interval, with a peak at 350 nm, shoulders at 320 and 380 nm, and a substantial absorption tail extending to 600 nm. The absorbance increase at 380 nm, relative to 350 and 320 nm, increases with the extent of reaction and with the initial concentration of DNB. During the last 10% or so of the first stage, a trough develops in the difference spectrum at 265 nm (also seen in Figure 3), and in compensation there is an increase around 380 nm. This is at least in part a dark reaction, and it requires hydrazobenzene, because it failed to appear in a sample that became deficient in that reductant.

During the second stage of reaction, a positive difference band at 395 nm is superimposed on a general decrease in the 280–600-nm region.

Several samples were extracted with methanol after the reaction and chromatographed on alumina, diethyl(aminoethyl)cellulose, or Sephadex LH-20 with appropriate eluents. Azobenzene was always recovered, followed by hydrazobenzene and a yellow material identified by spectrum and cochromatography as NPHA, not *p*-nitroaniline. Sometimes at least one other yellow or orange band was seen, which had a spectrum similar to that of azobenzene. No substance was detected that could account for the large visible absorption increase in the first stage of reaction or the near-UV band that develops during the second stage of the reaction.

Some controls were performed. Without a reductant, Chl does not react with DNB to give a permanent product. Without DNB, the only significant change on irradiating a sample with hydrazobenzene is a limited oxidation to azobenzene (i.e., 0.07 AU at 320 nm) by residual $O_2$ during the first light period only. When particle preparation IIa was irradiated with hydrazobenzene and azobenzene present but not DNB, a small decrease in the 360–400-nm region, perhaps of BQ-PDA-10, was followed by partial conversion of Chl to pheophytin and slow oxidative loss of Chl as already described.[21] This control also permitted an estimate of the effective molar absorptivity of azobenzene in particle preparations. Its value, which did not exceed 6400 $M^{-1}$ $cm^{-1}$ at 320 nm, is only one-third of a representative solution value and as will be shown is typical of azobenzene absorptivities measured under these reaction conditions. In contrast to this, the absorbance increase in the blue region in Figure 3 is about 10 times as great as might be expected for the azobenzene ($n,\pi$) band alone.

Some photochemical experiments with expected reduction products of DNB helped explain the differences between the homogeneous and heterogeneous phase reactions of Figures 2 and 3. NPHA, in a reaction mixture with particle preparation IIIa but without hydrazobenzene, showed a band at 359 nm which on irradiation for 2 h at 670 nm diminished to leave a band with substructure similar to that of an azobenzene derivative. This reaction is shown in Figure 5. If hydrazobenzene is included, the initial spectrum reproduces the essential features of the 500-s spectrum in Figure 3, including the tail into the visible region; note that a certain amount of azobenzene (334-nm peak in Figure 5) inevitably accompanies hydrazobenzene. Under 670-nm irradiation, the second stage of the reaction of Figure 3 is closely reproduced, only now it is complete in 2500 s. The further changes

(20) Seely, G. R. *J. Phys. Chem.* **1971**, *75*, 1667.

(21) Seely, G. R.; Senthilathipan, V. *Photochem. Photobiol.* **1985**, *41*, 371.

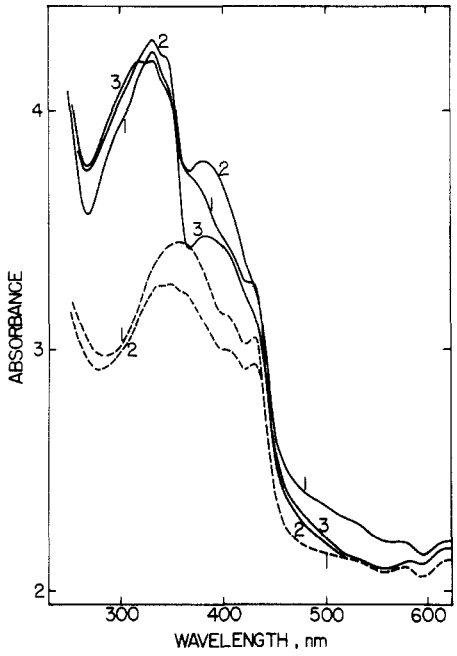


**Figure 5.** Photoreactions of *N*-(*p*-nitrophenyl)hydroxylamine, sensitized by particle preparation IIIa, with and without hydrazobenzene present. Dashed traces: NPHA (1.28 m*m*), without hydrazobenzene, before (1) and after (2) a total of 7000 s irradiation at 670 nm. Solid traces: NPHA with 6.1 m*m* hydrazobenzene, before (1) and after 2500 s (2) and 5100 s (3) total irradiation. The mixture contains adventitious azobenzene (structure in the 320–350-nm region).

that appear on continued irradiation may be a photoreaction in this case, because there had been no change in the visible and near-UV region on standing in the dark for a similar period. However, similar changes did occur in other samples on long standing in the dark.

A probable intermediate in DNB reduction is *p*-nitronitrosobenzene. Reduction of this substance by hydrazobenzene in the dark may be responsible for the development of a trough at 265 nm in the difference spectrum toward the end of the first stage of the reaction and the accompanying absorbance increase in the near-UV and visible regions. Another possible reduction product is 4,4′-dinitroazoxybenzene. Although this substance underwent some kind of photosensitized reduction, it did not appear to be related to any stage in the reduction of DNB.

The difference between the first stage of the reaction in Figure 3 and that in Figure 2 resides mainly in the location of the products NPHA and azobenzene within the reaction mixture. In Figure 6 are compared the spectra of these products, in ordinary solution and in the reaction mixture, complete except for adsorbed Chl and other amphiphiles. NPHA dissolves in water and in the guar phase of the reaction mixture. Its spectra under both conditions are similar; only the apparent molar absorptivity is increased by about 30% in the reaction mixture, owing to the increased path length of scattered light through the sample. The band extending into the visible spectral region in both spectra is due to a small amount of NPHA anion present at neutral pH. Azobenzene is soluble in tetradecane at this concentration and is therefore concentrated in the particles. Compared to its spectrum in hydrocarbon solution, the measured spectrum in the reaction mixture has a much foreshortened ultraviolet band and a visible band enhanced by a factor of about 3.5. Azobenzene spectra were recorded for a number of concentrations in the reaction mixture. The apparent molal absorptivity at 320 nm descended from an enhanced 35 500 $m^{-1}$ $cm^{-1}$ at 1.28 × $10^{-4}$ *m* to 11 400 at 6.24 × $10^{-4}$ *m*, 7000 at 1.215 × $10^{-3}$ *m* (Figure 6b) and 4000 at 2.49 × $10^{-3}$ *m*. In contrast, Beer's law is nearly obeyed for the visible band, and the apparent molal absorptivity is around 1400 $m^{-1}$ $cm^{-1}$, compared with 380 $m^{-1}$ $cm^{-1}$ in tetradecane solution. These dramatic changes are presumably due to a kind of "sieve effect" superimposed on path-length enhancement due to scattering.

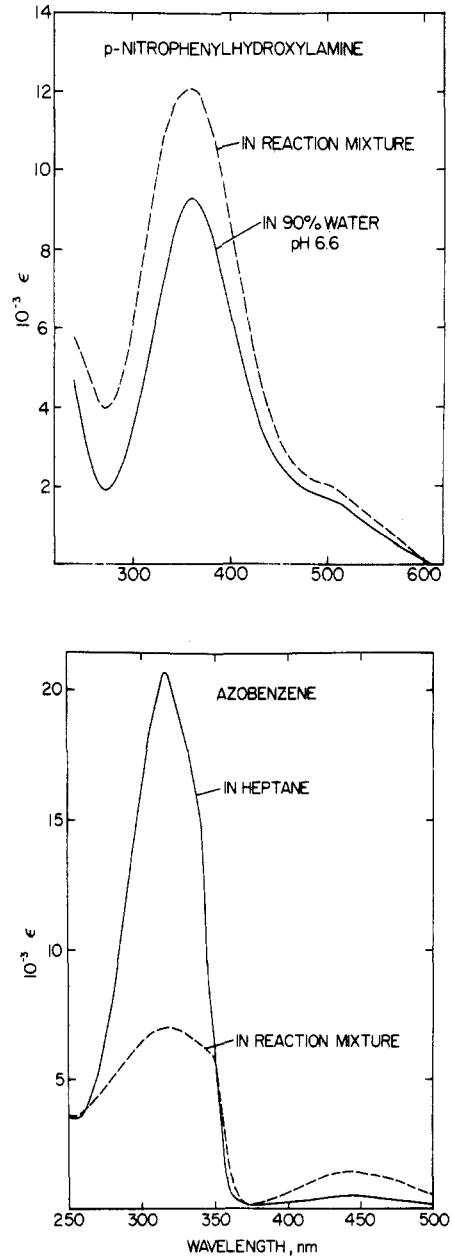


**Figure 6.** (a) Spectrum of NPHA in neutral aqueous solution, and the difference spectrum from background in a reaction mixture with polyethylene–tetradecane particles without Chl, at 1.09 × $10^{-3}$ *m*. In both spectra the peak is at 359 nm. The enhanced absorptivity of the latter spectrum is attributed to increased optical path length in the scattering medium, as described and illustrated by Butler.[28] Spectra were recorded in a 0.1-cm cuvette and in a 0.105-cm layer in a demountable cell, respectively. (b) Spectrum of azobenzene in heptane (the spectrum in tetradecane is similar), and the difference spectrum from background in reaction mixture without Chl, at 1.22 × $10^{3}$ *m*. The visible part of the spectrum is intensified by path-length increase, while the UV band is diminished by the "sieve effect" by Duysens,[30] because azobenzene is confined to the particles. It is not excluded, however, that there may also be a real redistribution of azobenzene absorptivity incident to the state of association with the polyethylene particles.

The consequence of the above is that absorption changes in the UV reflect more closely changes in the NPHA concentration than the azobenzene concentration.

*Quantum Yields.* The reaction coordinate chosen for estimation of DNB loss was the sum of absorbance changes at 265, 320, 350, and 380 nm, normalized by its maximum value at the end of the first stage. The last two wavelengths largely represent NPHA increase, the middle two represent azobenzene increase, and the first two make some allowance for the rise and fall of nitro-nitrosobenzene, which absorbs in this region. The use of four wavelengths instead of one reflects the belief that integrated

**TABLE II: Quantum Yields for Photoreduction of p-Dinitrobenzene by Hydrazobenzene, Sensitized by Chlorophyll Adsorbed to Polyethylene–Tetradecane Particles[a]**

| prep | amphiphile | $10^3$[DNB] | $10^3$[HAB] | $10^2\Phi$(I) | $10^2\Phi$(II)[b] |
|---|---|---|---|---|---|
| I | DMMA + BQ-PDA-10 | 1.49 | 16.6 | 6.6 | 0.52 |
| II | DMMA | 1.54 | 9.8 | 5.0 | 0.79 |
| IIa | DMMA + BQ-PDA-10 | 1.34 | 10.7 | 7.0 | 0.65 |
| IIa | DMMA + BQ-PDA-10 | 3.09 | 13.9 | 7.8 | ng (1000 s) |
| IIIa | DMMA | 1.52 | 13.0 | 8.5 | 0.44 |
| IIIb | DMMA + BQ-PDA-10 | 1.48 | 3.7 | 6.9 | nh |
| IIIb | DMMA + BQ-PDA-10 | 1.46 | 6.5 | 7.3 | 0.35 |
| IIIb | DMMA + BQ-PDA-10 | 1.50 | 12.0 | 8.5 | 0.42 |
| IIIb | DMMA + BQ-PDA-10 | 1.47 | 23.4 | 7.0 | 0.32 |
| IIIb | DMMA + BQ-PDA-10 | 1.48 | 48.1 | 6.2 | 0.39 |
| IIIb | DMMA + BQ-PDA-10 | 3.03 | 12.3 | 6.5 | ng (500 s) |
| IV | BQ-PDA-10 | 1.58 | 16.8 | 5.0 | 0.46 |
| V | Bz-PDA-14 | 0.36 | 7.1 | 3.7 | nc |
| V | Bz-PDA-14 | 0.73 | 7.0 | 5.2 | nc |
| V | Bz-PDA-14 | 1.30 | 7.0 | 6.5 | nc |
| V | Bz-PDA-14 | 2.93 | 6.6 | 8.5 | nc |
| VI | BQ-BDA-14 | 1.48 | 9.1 | 1.6 | nc |
| VI | BQ-BDA-14 | 2.95 | 9.3 | 1.65 | nc |
| VII | Brij 96 | 1.50 | 7.1 | 6.3 | ng (250 s) |
| VIIa | Brij 96 + BQ-PDA-10 | 1.50 | 7.3 | 3.7 | nc |
| VIII | 3-NPMA | 1.26 | 6.1 | 1.25 | 0.113 |
| | | $10^3$[NPMA] | | | |
| IIIa | DMMA | 1.28 | 6.1 | | 0.95 |
| VI | BQ-BDA-14 | 1.28 | 9.0 | | 0.39 |

[a] Listed are the particle preparation numbers from Table I, the amphiphiles they contain in addition to Chl, the concentrations of DNB (or NPHA) and hydrazobenzene (HAB) in mmolal units, based on total sample mixture weight, and the quantum yields for the two stages of the reaction, calculated as described in the text. [b] Where no number is given, the following excuses apply: ng, no evidence of a second stage reaction during the time indicated beyond the end of the first stage; nh, hydrzobenzene apparently insufficient to complete the first stage, much less the second; nc, the reaction was not continued beyond the end of the first stage.

absorbance increase is a better measure of reaction progress than the change at any one wavelength. This choice of reaction coordinate at least gives uniformly well-behaved saturation curves for product increase. Quantum yields for DNB reduction calculated from this reaction coordinate are listed in Table II. These quantum yields are usually about 10% higher than those calculated from the absorbance change at 350 nm alone. The quantum yield falls monotonically but not steadily as the reaction progresses, which may be partly an optical effect but also suggests some kind of product inhibition. Quantum yields listed are for 5% reduction, which requires at most only a short extrapolation in plots of yield vs. reaction coordinate.

In addition to the particle constituents, the initial concentrations of DNB and hydrazobenzene were varied. The quantum yield is independent of hydrazobenzene concentration with particle preparation IIIb. There is a weak dependence on initial DNB concentration in reactions sensitized by preparation V, but it is less than a proportionality.

The second stage of photoreduction is characterized by continued absorbance increase in the near-UV region (350–440 nm) and decrease in the visible (450–600 nm). A convenient reaction coordinate is the algebraic difference between absorbance changes at 395 and 520 nm. Plots of this quantity against time from the end of the first stage of reaction are nearly zero order in remaining starting material (NPHA) and permit calculation of the quantum yields listed for this stage in Table II. Data are not available for all the reactions for the reasons noted, but those that are indicate quantum yields lower than those for the first stage by factors of about 10 or 20, depending on the sample. Also included are yields for two reactions in which the starting material was NPHA; these are about twice as high as yields in corresponding reactions that started with DNB. The second stage of reduction appears to be suppressed by high concentrations of azobenzene, perhaps because azobenzene can reoxidize a reduction product of NPHA.

## Discussion

*Relation to Fluorescence Yield.* Taking the data of Tables I and II as a whole, we see no discernible correlation of reaction quantum yields with fluorescence quantum yields of the sensitizing particles. This is true especially for the closely related particle preparations II and IIa and preparations IIIa and IIIb. This result is in contrast to our previously reported results with a macroscopically homogeneous model system in which pyrochlorophyll, bound to poly(4-vinylpyridine) in nitromethane, sensitized the photoreduction of DNB by hydrazobenzene with a quantum yield that was directly proportional to the fluorescence quantum yield.[20] Fluorescence in that system was subject to concentration quenching, and the yield of the sensitizing triplet state decreased in parallel with fluorescence. Furthermore, the yield of DNB reduction in the present system is usually greater than the fluorescence yield, whereas in the previous model system it was just about 0.4 times as much. These results suggest that the processes of fluorescence and of photochemical sensitization are not closely connected mechanistically. A closer examination of the fluorescence properties of the sensitizing particles supports this suggestion.

The absorption band peak (666–667 nm) and bandwidths of preparations with only Chl and DMMA suggested a substantially associated state of Chl, but the fluorescence band peak (667–668 nm) indicated predominance of the monomeric component. This accords with previous observations.[1] Addition of an oxidizing amphiphile, as in preparations IIa and IIIb, changes the absorption spectrum little but the red band becomes narrower, indicating an increase in monomeric Chl. The intensity of the fluorescence is reduced without change in the band position. Sterically encumbered amphiphiles such as BQ-PDA-10 do not compete well with DMMA as ligands for Chl, but the few that are ligated with Chl act as electron-transfer energy traps. Fluorescence lifetime measurements support this idea. Most (92%) of the weak fluorescence of preparation IIa had a 5.8-ns (±2%) lifetime, representative of monomeric Chl ligated with DMMA, while the rest had an average lifetime of 2.3 ns (±30%). The former therefore represents a small subset, about 10%, of monomeric Chl located beyond transferring distance to a quenching trap. This small subset cannot reasonably be held responsible for the reaction quantum yields reported in Table II, especially if the reaction is initiated by triplet-state Chl, produced from the singlet in competition with fluorescence.

The position of the fluorescence band of preparation VI with BQ-BDA-14, 676 nm, bears the normal Stokes shift relation to the position of the absorption band, 671 nm. The weak fluorescence of this sample may therefore belong to a subset of Chl ligated with BQ-BDA-14 in a conformation in which quenching by electron transfer cannot occur rapidly. A similar effect of conformation has been proposed for a covalently linked porphyrin–quinone system.[22]

Particles were prepared with Brij surfactant, because the poly(oxyethylene) group is a weak ligand for Chl with which an oxidizing amphiphile might successfully compete. It apparently does so since the fluorescence peak shifts from 666.5 nm with Brij alone to 674.5 nm when BQ-PDA-10 is added, and fluorescence intensity is reduced. The quantum yield of sensitized reduction also decreases, but not as much.

The slowest reductions were sensitized with preparation VIII, containing 3-NPMA, and in which Chl is ligated by pyridine.

(22) Siemiarczuk, A.; McIntosh, A. R.; Ho, T.-F.; Stillman, M. J.; Roach, K. J.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 7224.

Absorption spectral resolutions for this sample have been tabulated[2] and show that about one-third of the Chl is in monomeric form. The fluorescence yield was not measured, but by comparison with other samples, it would have been fairly large, and about one-third of it would be from the monomeric component. Because of observed strong fluorescence of most preparations with 3-NPMA,[2] we had expected that of all preparations, this one would be most prone to sensitize via the triplet state.

The reduction of DNB per se provides no clue as to which excited or high-energy states of Chl are responsible for sensitization, because all conceivable states would be capable of it. The high quantum yield of reduction tends to discount direct reaction of DNB with the Chl excited singlet state or the triplet state formed from it by intersystem crossing. In the case of particles with Chl and DMMA only, the easiest explanation is that a [$Chl^{\bullet+}Chl^{\bullet-}$] ion pair formed from associated Chls is responsible, but there is as yet no direct evidence for the existence of such a species. When an oxidizing amphiphile is present also or alone, ion pairs such as [$Chl^{\bullet+}$--$BQ^{\bullet-}$] should contribute. It is also possible that either type of ion pair might decay into a triplet Chl state, which would then be produced in spite of singlet excited-state quenching. However, this does not occur in most other model systems or in solution. The sensitized reduction of other nitroaromatic compounds provides better energetic criteria and will be presented in due course.

*Second Stage of Photoreduction.* Previous accounts of the photoreduction of DNB do not lead one to anticipate that the reaction would go beyond the NPHA stage. But in the heterogeneous system it does, producing a band around 380 nm (Figures 3 and 5) and a peak in the difference spectrum at 395 nm (Figure 4). NPHA is reduced electrochemically in aqueous ethanol to *p*-phenylenediamine, through the bis(hydroxylamine) and certain other compounds, none of which accounts for the 380-nm band.[23] Alternatively, azobenzene derivatives might be formed through condensation. For example, in a photochemical system, where electrons become available one at a time instead of all at once as at an electrode, the reduction of NPHA might hesitate at the (*p*-nitrosophenyl)hydroxylamine stage. This should condense with the remaining NPHA to form 4-nitro-4′-(hydroxylamino)azoxybenzene, which would be further reduced to the azo dye *N*-(((*p*-nitrophenyl)azo)phenyl)hydroxylamine. The latter should absorb around 450 nm[24] and thus not account for the observed band either.

The position of the band rather suggests the nitro hydrazo chromophore, from among those accessible to the system (cf. (*p*-nitrophenyl)hydrazine, 380 nm in methanol). Experiment has established the following features of the reaction: the starting material is NPHA; hydrazobenzene is required; azobenzene is not produced in conspicuous amounts; the product disappears slowly in the dark and has not been recovered by methanol extraction after the reaction; in the absence of hydrazobenzene, Chl slowly converts NPHA into a substance having a spectrum with azobenzene-like structure. Although the products of these reactions have not been isolated sufficiently for identification, there are substantial reasons to conclude that the product of reaction without hydrazobenzene is 4,4′-dinitroazobenzene (DNAB) and the product with hydrazobenzene is the corresponding 4,4′-dinitrohydrazobenzene (DNHAB).

DNAB has been reported as an unexpected product of reduction of DNB by NaHS[25] and by alkaline glucose.[26] It is formally a product of dehydration of NPHA and therefore needs no net redox reaction for its formation. Its spectrum in methanol resembles that of azobenzene but the peak is at 330 nm and the vibrational structure is slightly different. The vibrational structure of the product emerging from photosensitized reaction of NPHA (Figure 5) resembles that of authentic DNAB on particles, though a certain identification cannot be made.

Reduction of DNAB by $H_3PO_3$ and diphenyl diselenide,[27] 2,3-dimercaptopropanol, or dithiothreitol in 95% ethanol at 32 °C gave *p*-nitroaniline (374 nm in ethanol) as the final product. However, especially with the last, the reaction went in two stages. At first, there was an isosbestic point at 346 nm and a peak in the difference spectrum at 382 nm. After subtraction of the estimated residual DNAB spectrum, a product band at 380 nm remained. Later, the crossover point slides to shorter wavelengths as the *p*-nitroaniline band builds up. On exposure to air before reduction was complete, the reaction partially reversed with increase of DNAB bands. Presumably the 380-nm band belongs to DNHAB, which is easily reduced further to *p*-nitroaniline. Among the fractions recovered by chromatography of products of DNB photoreduction are some with a spectrum very much like that of DNAB, presumably formed by the air oxidation of DNHAB.

The following sequence can account for the formation of DNAB and DNHAB photochemically. One-electron reduction of NPHA by photoexcited Chl or an ion pair formed from it is followed by protonation and dehydration to form the radical $O_2NC_6H_4NH^{\bullet}$. These radicals dimerize, but in the absence of hydrazobenzene the product is oxidized to DNAB by $Chl^{\bullet+}$. In the presence of hydrazobenzene, $Chl^{\bullet+}$ is reduced and DNHAB remains. Azobenzene is also produced but in an amount equivalent to half the NPHA consumed, so its appearance in the spectrum is more than compensated by disappearance of NPHA. The potential for one-electron reduction of NPHA is such (cathodic wave at −1.26 V (SCE) in acetonitrile, irreversible) that the reaction should only be accessible to the Chl singlet excited state and certain high-energy ion pairs, which would account for its absence in homogeneous-phase, triplet-excited photochemistry.

*Separation of Products.* Interpretation of the spectral changes of Figure 3 became possible only when it was recognized that the disparate spectral behavior of NPHA and azobenzene was owing to solution of the former in the aqueous suspending medium and concentration of the latter in the polyethylene–tetradecane particles. The fact that spectral behavior is so different demonstrates clearly that the products are separated into different phases and that one of the advantages of using a heterogeneous system has been realized.

There are two distinct effects of heterogeneity at work on these spectra. The first is an increase in absorbance due to increase in path length through the sample by scattering. This enhancement applies to substances dissolved in the suspending phase or adsorbed to the major scattering material (cellulose in this case) and can be calculated from equations given by Butler[28] or directly from Kubelka's[29] equation for transmission of light through a scattering medium. Calculated enhancement factors ($\beta$) are more strongly dependent on the "scattering power" (to use Butler's phrase) of the sample than on the absorbance; factors of 20 or so were found in Butler's thick and highly scattering samples, but much smaller values would be appropriate for our thinner and less highly scattering mixtures. Empirically $\beta$ is determined from spectra such as those of Figure 6.

If, however, an absorbing substance is not distributed uniformly in a mixture but is confined to a minor scattering particle component and the sample is not extremely thick, a limitation on absorbance may be imposed by the "sieve effect" in the sense described by Duysens.[30] This effect is not considered in Kubelka's equations or in Butler's application of them. The addition of cellulose mitigates the "sieve effect" by increasing the "scattering power", but even so, a residual influence may have to be taken into account with strongly absorbing products such as azobenzene.

The subject requires a more detailed treatment than is possible here, but the form of the effect may be sketched, with some simplifications. Straightforward application of Duysens's equation

(23) Darchen, A. *C.R. Acad. Sci., Paris, Ser. C* **1971**, *272*, 2193.
(24) Brode, W. R.; Seldin, I. L.; Spoerri, P. E.; Wyman, G. M. *J. Am. Chem. Soc.* **1955**, *77*, 2762.
(25) Hodgson, H. H.; Ward, E. R. *J. Chem. Soc.* **1948**, 2017.
(26) Antener, I. *Helv. Chim. Acta* **1938**, *21*, 812; *Chem. Abstr.* **1938**, *32*, 7024.
(27) Günther, W. H. H. *J. Org. Chem.* **1966**, *31*, 1202.
(28) Butler, W. L. *J. Opt. Soc. Am.* **1962**, *52*, 292.
(29) Kubelka, P. *J. Opt. Soc. Am.* **1948**, *38*, 448.
(30) Duysens, L. N. M. *Biochim. Biophys. Acta* **1956**, *19*, 1.

for absorbance ($\rho$), but with enhancement of the path length, gives in our terms eq 1, where $x$ is the geometrical cell thickness, $d$ is

$$\rho = (\beta x/d) \ln (1 - v_p(1 - \exp(-\epsilon c d))) \quad (1)$$

the effective diameter of the absorbing particle, $v_p$ is the volume fraction of absorbing particles, and $\epsilon$ and $c$ are the absorptivity and concentration of absorbing substance within the particle. When $\epsilon$ and $c$ are small, the absorbance reduces to $\rho_0$ (eq 2); i.e.,

$$\rho_0 = \epsilon(v_p c)(\beta x) \quad (2)$$

the absorbance shares the path enhancement $\beta$ for substances in solution. The quantity $(v_p c)$ is of course the nominal concentration of absorber, as in Table II. At high values of absorptivity and concentration, the absorbance approaches a limit $\rho_\infty$ (eq 3). For

$$\rho_\infty = -(\beta x/d) \ln (1 - v_p) \quad (3)$$

example, if $\beta = 3$, $x = 0.1$ cm, $d = 30$ $\mu$m, and $v_p = 0.1$, $\rho_\infty$ is about 4.6 on a decadic extinction scale. Differentiation of eq 1 gives

$$d\rho/d(v_p c) = (\epsilon\beta x/v_p)(1 - (1 - v_p) \exp(\rho d/\beta x)) \quad (4)$$

which relates the marginal absorbance change with concentration to the *total* absorbance ($\rho$) of the particles, including that due to Chl and other amphiphiles, at the wavelength in question.

As an alternative to the above explanation, we have considered that the distortion of the azobenzene spectrum might be due to its crystallization or some kind of association within the particle or at its surface. Opposed to this explanation are the facts that azobenzene is soluble in tetradecane at the concentrations produced and that eq 1-4 can account for its appearance in a semiquantitative way. Because there are still some problems in a fully quantitative application of the sieve effect to this case, the possibility of distortion through association cannot be rejected totally, but the conclusion that azobenzene is concentrated in the particles while NPHA passes to the suspending medium is unchanged.

*Influence of the Surface.* An unusual and perhaps unexpected feature of this system is that a complex and lively photochemistry is supported in a two-liquid-phase system among reagents, none of which (Chl, amphiphile, hydrazobenzene, or DNB) is more than sparingly soluble in either of the phases. The implication is that the reagents are concentrated in a surface layer surrounding the core of the swollen polyethylene particles and that static photochemical processes, i.e., between preformed associations of molecules, dominate. The volume of the surface layer, and consequently the concentrations of reagents within it, can be estimated, at least within an order of magnitude. With the assumption of a thickness of 50 Å (roughly twice the length of a Chl molecule) and a specific surface area of 2 $m^2$ $g^{-1}$,[6] the specific volume of the surface layer would be about $10^{-2}$ $cm^3$ $g^{-1}$. Since particles make up about 10% of a reaction mixture, if all reagents were concentrated in this layer their concentrations would be typically 0.3-3 *m* DNB, 10 *m* (!) hydrazobenzene, 0.1 *m* Chl, and 0.5 *m* ligating amphiphile. Although such high local concentrations of DNB and hydrazobenzene would not be realized because of crystallization of the excess, it is easy to understand why there should be little or no effect of formal concentration on the rates even of singlet-state photoreactions. The products, however, are soluble in tetradecane and water, respectively, and separate by partition into those phases.

In summary, the interface between the viscous hydrocarbon particles and the aqueous phase, or the polar organic surface layer, affects the reaction in the following ways:

1. The association of Chl with ligating amphiphiles is promoted, which keeps the pigment in photochemically active forms.
2. Electron-transfer states, or ion pairs, are probably stabilized, although there is not yet direct evidence to support this.
3. Redox reagents are concentrated at the interface, where they can react quickly with whatever high-energy states are available.
4. Products depart the interface for the particle interior or aqueous medium phase, in which they are soluble. If this separation occurs at the stage of one-electron reduced or oxidized radicals, back-reaction of these primary products may be retarded.

*Acknowledgment.* This work was supported in part by the U.S. Department of Energy, Division of Chemical Sciences, under Grant No. DE-FG02-84ER13187. Fluorescence lifetimes were measured at the Solar Energy Research Institute, Golden, CO, in collaboration with Dr. John S. Connolly. This is Contribution No. 908 from the Battelle-Kettering Laboratory.

**Registry No.** DMMA, 3015-65-4; 3-NPMA, 84081-60-7; Bz-PDA-14, 105457-93-0; BQ-PDA-10, 105457-94-1; BQ-BDA-10, 105457-95-2; BQ-BDA-14, 105457-96-3; Brij 96, 9004-98-2; chlorophyll *a*, 479-61-8; *p*-dinitrobenzene, 100-25-4; hydrazobenzene, 122-66-7; polyethylene, 9002-88-4; tetradecane, 629-59-4; *N*-(*p*-nitrophenyl)hydroxylamine, 16169-16-7; azobenzene, 103-33-3; ethyl chlorophyllide a, 14444-88-3.

# Cesium-133 NMR Study of the Kinetics of $Cs^+$ Ion Complexation by 1,10-Diaza-18-crown-6 and Cryptand C221 in Some Nonaqueous Solutions

**Mojtaba Shamsipur[1] and Alexander I. Popov***

*Department of Chemistry, Michigan State University, East Lansing, Michigan 48824*
*(Received: July 25, 1986)*

The kinetics of complexation of the $Cs^+$ ion with ligands 1,10-diaza-18-crown-6 (C22) and cryptand C221 were studied in nitromethane, acetonitrile, methanol, and dimethylformamide solutions by cesium-133 NMR line-shape analysis at various temperatures. While the exchange of the cesium ion between the solvated and complexed sites proceeds via a dissociative mechanism for the $Cs^+$·C221 cryptate in all solvents used, a bimolecular exchange mechanism predominates for the $Cs^+$·C22 complex in nitromethane. The exchange reaction rates and the activation parameters $E_a$, $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger$ for the exchange have been determined. For the $Cs^+$·C221 systems there is a correlation between the solvating abilities of the solvents as expressed by the Gutmann donor numbers and the logarithm of the dissociation rates as well as the $E_a$ and $\Delta G^\ddagger$.

## Introduction

Substitution of two oxygen atoms by two nitrogens in the 18-crown-6 macrocyclic ring significantly decreases the stability of the $Na^+$ and $Cs^+$ complexes.[2] For example, 1,10-diaza-18-crown-6 (C22) forms a rather weak complex with cesium ion, even in solvents of low solvating ability such as nitromethane[3] (log $K_f$ in NM = 2.79). The resulting complexes in various nonaqueous solvents show a decrease of about 2 orders of magnitude in $K_f$

(1) On leave from the Department of Chemistry, Razi University, Bakhtaran, Iran.

(2) Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 600.
(3) Shamsipur, M.; Popov, A. I. *Inorg. Chim. Acta* **1980**, *43*, 243.

0022-3654/87/2091-0447$01.50/0 