Photochemistry of Diacetylene

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Absorption coefficients of C_4H_2 have been measured in the 183-260-nm wavelength region. The photochemistry of diacetylene has been studied at 147.0, 184.9, 228.8, and 253.7 nm. The primary dissociative processes at 147 nm, deduced from the photolysis of C_4H_2 and D_2 mixtures, are, in order of decreasing importance, $C_4H_2 + h\nu \rightarrow C_4H + H$, $C_4H_2 + h\nu \rightarrow C_2H_2$ + C₂, and C₄H₂ + $h\nu \rightarrow 2C_2H$ with quantum yields of 0.2, 0.1, and 0.03, respectively. In addition, the quantum yields of products and of reactant disappearance were measured in neat C_4H_2 and C_4H_2 and N_2 mixtures. It is concluded that (1) reactions involving metastable excited states, $C_4H_2^{**} + C_4H_2 \rightarrow C_8H_2 + H_2$, are the main disappearance processes at three other wavelengths and (2) the $C_4H_2^{**}$ states are stable toward collisions with N₂. The excited-state reactions may be the predominant photochemical processes of C_4H_2 in Titan's stratosphere.

Introduction

Titan, a satellite of Saturn, has a unique atmosphere consisting of a mixture of various hydrocarbons and cyanogen compounds. Voyager 1 and 2 flights have provided infrared and ultraviolet spectral data which have established that the main constituent is nitrogen and the minor constituents are CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , CH_3C_2H , C_3H_8 , C_4H_2 , HCN, HC₃N, C_2N_2 , CH_3D , CO, and CO_2 .¹ It is believed that the present complex composition is the result of an atmospheric evolution by photochemical processes starting with a few simple parent molecules.¹

One of the many interesting and complicated chemical problems posed by the composition and structure of Titan's atmosphere is that of the mechanism by which a haze is formed. A mechanism of haze formation was first proposed by Danielson et al.² and is often referred to as Danielson dust. Allen et al.¹ have proposed a photochemical mechanism by which polyacetylenes are formed and condense to produce the obscuring haze. Specifically, these authors propose a stepwise increase in polyacetylene chain length beginning with the well-established C_2H_2 photolysis by Okabe³ and also Laufer and Bass⁴ to produce diacetylene (C_4H_2).

$$C_2H_2 + h\nu \to C_2H + H \quad (<225 \text{ nm})$$
 (1)

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \tag{2}$$

Allen et al.¹ then proposed an analogous increase in chain length

$$C_2H + C_4H_2 \rightarrow C_6H_2 + H \tag{3}$$

$$C_4H + C_4H_2 \rightarrow C_8H_2 + H \tag{4}$$

$$C_2H + C_2H_2 \rightarrow C_2H_2 + H \tag{5}$$

Polyacetylenes larger than C_8H_2 are removed from the system by condensation leading to the haze formation.

There are few photochemical studies of diacetylene. Callomon and Ramsay⁵ studied the flash photolysis of C_4H_2 in which transient species were detected by a rapid optical absorption technique. The xenon flash lamp used was a quartz tube which presumably transmitted to a lower wavelength limit of at least 185 nm. At helium pressures that precluded thermal heating, these authors report observing only C3. In contrast, Dismuke, Graham, and Weltner⁶ used a flowing C_4H_2 and rare gas mixture which was exposed to 121.6-nm radiation and was deposited on a window at 4 K for optical and ESR observation. The observed free radicals were C_4H , C_2H , CH_3 , H, C_4H_3 , and C_4 .

A gas-phase photolysis of C_4H_2 at 253.7 nm using a product analysis method has been reported by Pontrelli.⁷ In his brief report, the only gas-phase products found were acetylene and a small amount of triacetylene (C_3H_2) . The indication of an absence of free radical formation was supported by C_4H_2 experiments with NO added which resulted in no change in the yield of C_2H_2 . The heats of formation of C_4H_2 , C_2H_2 , and C_2 have been tabulated.^{8,9}

The photochemistry of diacetylene in the weak structured region of absorption (180-260 nm) may be different from that in the strong diffuse region below 180 nm.¹⁰ In analogy to acetylene photochemistry,^{3,10,11} it is expected that the excited-state mechanism predominates in the long-wavelength region and radical process may be important in the short-wavelength region. The purpose of this work is to compare the primary process in the two regions, namely, at 147.0, 184.9, 228.8, and 253.7 nm.

The primary free radical process is obtained by a radical scavenger technique using D₂, followed by product analysis of C₂HD and C₄HD. These analyses are then used to evaluate the quantum yields for the radical primary process. The ratio $D_2 \mbox{ to } C_4 H_2$ is 1000, which should be sufficiently large to scavenge almost all C_4H and C_2H , since the analogous ratio of rate constants for C_2H + H_2 to $C_2H + C_2H_2$ is about 130.¹¹ Information concerning the extent of polymerization and quenching is also required, particularly in the presence of a large quantity of nitrogen to simulate the photochemistry in Titan's atmosphere. In addition, since there is no adequate quantitative absorption coefficient data available between 183 and 260 nm, an absorption spectrum is provided to facilitate photochemical interpretation.

Experimental Section

Light Sources. A Hg resonance lamp was made by distilling a small quantity of Hg into a Pyrex body and adding 2 Torr of

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Ar. The lamp window was 1/2-in.-diameter Suprasil attached to the Pyrex body with a graded seal. Interference filters (Acton Research Corp.) were used to isolate the 184.9- and 253.7-nm lines. The 147-nm lamp, containing 1 Torr of Xe and Ti getter, was provided with a MgF₂ window attached to the Pyrex body by epoxy cement, as described by Gorden et al.¹² Both resonance lamps (mercury and xenon) were powered by a 2450-MHz microwave generator (Raytheon). The emission spectrum of the Xe lamp showed only two lines, 147 and 129.6 nm, the latter being 2% of the former. An outer Pyrex jacket was removed from a commercial cadmium lamp so that the 228.8-nm line could be transmitted. The emission spectrum showed three weak lines other than the 228.8-nm line. These weak lines, however, contributed less than 10% to the product yield, since absorption coefficients at these lines are small.

Absorption Coefficients of C_4H_2 . Absorption coefficients were obtained with a 0.3-m monochromator (McPherson Co.) fitted with a sodium salicylate coated window and a photomultiplier electrometer assembly. The signal was recorded on a strip chart recorder. A 10 cm path length stainless steel cell was fitted with 1-in. Suprasil windows. A single beam was used to obtain the absorption coefficients of C_4H_2 between 183 and 260 nm. The continuum background light source was a high-pressure xenon lamp. A large amount of scattered light of wavelengths above 300 nm was found in the 183-260-nm region. The scattered light intensity was measured by placing a Pyrex plate at the exit slit, while scanning the 183-260-nm region, and that amount was subtracted from the incident light intensity.

Apparatus and Materials. A grease- and mercury-free glass vacuum system was used in this work. The pressure up to 1 Torr was measured by a diaphragm gauge (Baratron). The reaction vessel was a 400-cm³ spherical Pyrex bulb fitted with either a Suprasil or MgF₂ window attached by epoxy cement. A right angle trap, maintained at -195 °C, was used to collect photolysis products and remaining C₄H₂ prior to analysis by a mass spectrometer. The latter was calibrated daily with synthetic mixtures of gases whose quantities approximated those obtained in a given experiment. Diacetylene was photolyzed in three ways: (1) in a large excess of deuterium, (2) in a large excess of nitrogen, and (3) neat. Blank experiments were run to determine the efficiency of separating condensables, C_4H_2 and C_2H_2 , from a large excess of deuterium or nitrogen. After passage through a trap at -195 °C, the condensable gases obtained from mixtures of 80 mTorr of C₄H₂, 2 mTorr of C₂H₂, and 100 Torr of N₂ (typical reaction mixtures after photolysis was completed) prepared in a 400-cm³ vessel were analyzed by a mass spectrometer. The original amount of C_4H_2 was recovered within 2% accuracy, while that of much smaller C_2H_2 was found within 10%. All condensable gases were purified by low-temperature distillation. Noncondensable gases were passed through traps at -195 °C prior to use. Diacetylene was prepared as described by Okabe¹⁰ in an earlier paper. The only impurity observed by mass spectrometry was a peak at mass 86 attributed to CH₂CClCCH by Georgieff and Richard.¹³ The impurity found in the present work was about 1% or less after low-temperature distillation prior to each experiment.

The following are additional gases used along with their stated purities: acetylene, 99.6% (min); ethylene, 99.5%; xenon, 99.995%; phosgene, 99.0%; nitrogen, 99.999%; deuterium, 99.65% D; and argon, 99.999%. All condensables were subjected to low-temperature distillation, and noncondensable gases passed through cold traps prior to use.

Results

UV Absorption Spectrum of Diacetylene. There appear to be no quantitative absorption coefficients available for diacetylene in the 183-260-nm region. There have been several spectroscopic studies¹⁴⁻¹⁸ in which the primary purpose is to identify structure

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Figure 1. Absorption coefficient k (atm⁻¹ cm⁻¹, base e) vs. wavelength (nm) in the 183-260-nm region. Resolution is 0.1-nm fwhm. The threshold wavelengths for the production of three primary processes are indicated at 202, 205, and 235 nm respectively for $C_4H_2 \rightarrow 2C_2H$, $C_4H_2 \rightarrow C_2H_2 + C_2$, and $C_4H_2 \rightarrow C_4H + H$ (see Table IV).

TABLE I: Absorption Coefficients (k, Base e) of Molecules Used in Quantum Yield Calculations

	$k, atm^{-1} cm^{-1}$				
	147 nm	185 nm	229 nm	254 nm	
C ₄ H ₂	838 ^b	11.2ª	39ª	1.3ª	
C_2H_4	350 ^b	8.2 ^b	nd¢	\mathbf{nd}^{c}	
COCl ₂	nd¢	62.1 ^b	3.2ª	1.97ª	

^aValues obtained in this work. ^bValues taken from earlier work by Okabe (ref 10 and 11). ^cNot determined.

and determine electronic states. Figure 1 is a plot of the spectrum obtained in this work with a resolution of 0.1-nm fwhm and data points taken at 0.05-nm intervals. The error limit of the coefficient measurements is 10%. The band positions of the C₄H₂ absorption spectrum shown in Figure 1 agree well with those in ref 14–18, while the relative band intensities are in fair agreement. Haink and Jungen¹⁸ obtained the absorption spectrum of C₄H₂ between 200 and 280 nm and assigned them to the vibrational progressions of two forbidden overlapping electronic transitions, i.e., ${}^{1}\Sigma_{g}{}^{-1}\Sigma_{g}{}^{+}$ and ${}^{1}\Delta_{u}{}^{-1}\Sigma_{g}{}^{+}$. Okabe¹⁰ has obtained the absorption coefficients of C₄H₂ between 120 and 180 nm. This wavelength region contains several Rydberg series with large absorption coefficients; viz., at 147.0 nm the coefficient is 838 atm⁻¹ cm⁻¹.

Reaction Products and Polymer Formation. Acetylene was the only gaseous product detected in this work as indicated by mass spectrometry. The lamp intensity decreased with exposure, as a colorless deposit was formed on the window. The intensity was restored by the removal of the deposit which was presumably polyacetylenes. The entire cell was cleaned with nitric acid when the intensity decreased to $^2/_3$. No gaseous products were produced by extended photolysis (3 h) of the evacuated reaction cell containing wall deposits produced by several photolyses. The C₄H₂ conversions in these experiments were about 6–8%. Quantum yields measured at larger conversions were not reproducible.

Actinometry. The absorption coefficients of C_4H_2 , C_2H_4 , and $COCl_2$ at 147, 185, 229, and 254 nm, measured by Okabe^{10,11} and in this work, are shown in Table I. The quantum yields of noncondensable products H_2 and CO from C_2H_4 and $COCl_2$ photolysis, respectively, at 147, 185, 229, and 254 nm have been obtained.^{19,20} The CO quantum yield of unity from $COCl_2$ photolysis at 185 nm was found in this work in comparison with the H_2 yield of 0.42 from C_2H_4 photolysis. The absorption coefficients denoted by superscript "a" in Table I were obtained in this work using three resonance lamps.

Photolysis of Diacetylene. C_4H_2 was photolyzed at four wavelengths, viz., 147.0, 184.9, 228.8, and 253.7 nm. The pho-

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TABLE II: Quantum Yields in the Photolysis of Neat C_4H_2 and C_4H_2 and N_2 Mixtures

	neat $C_4H_2^a$		C_4H_2 and N_2 mixtures ^b	
λ, nm	$\Phi(C_2H_2)$	$\Phi(-C_4H_2)^c$	$\Phi(C_2H_2)$	$\Phi(-C_4H_2)^c$
147.0	0.10 ± 0.05	2 ± 0.5		
184.9	0.05 ± 0.02	2 ± 0.5	0.03 ± 0.01	2.0 ± 0.5
228.8	<0.003	2 ± 0.5	<0.003	2.0 ± 0.5
253.7	<0.005	2 ± 0.5	<0.005	2.0 ± 0.5

^a Pressure of C_4H_2 is 80 mTorr. ^b 80 mTorr of C_4H_2 and 2000-fold nitrogen. ^cQuantum yield of disappearance of diacetylene.

TABLE III: Quantum Yields in the Photolysis of C_4H_2 and D_2 $Mixtures^{\alpha}$

λ, nm	$\Phi(C_2H_2)$	$\Phi(C_2HD)$	$\Phi(C_4HD)$	$\Phi(-C_4H_2)$
147.0	0.10 ± 0.05	0.07 ± 0.02	0.20 ± 0.05	2 ± 0.5
184.9	0.06 ± 0.03	0.02 ± 0.01	(<0.08) ^b	2 ± 0.5
228.8	<0.003	<0.001	(<0.06) ^b	2 ± 0.5
253.7	<0.004	<0.004	(<0.09) ^b	2 ± 0.5

^aAll mixtures contain 1000-fold D_2 excess in 80 mTorr of C_4H_2 . ^bThese values are calculated estimates of possible minimum observable values. Mass 51 from C_4H_2 was too large for analysis of relatively small mass 51 from C_4HD . True values are very likely smaller than that calculated.

tolyses were conducted (1) in the presence of a large excess of deuterium, (2) in large excess of nitrogen, and (3) neat. In all cases the pressure of C₄H₂ was maintained at 80 mTorr. At appreciably higher pressures the C_4H_2 sample polymerizes rapidly, and at lower pressures the reaction time becomes excessively long with the increased possibility of unwanted side reactions. Table II contains the quantum yields for the production of C_2H_2 and the decrease of C_4H_2 [(i.e., $\Phi(-C_4H_2)$] for photodecomposition of 80 mTorr of diacetylene in the absence of an added gas (neat). The $\Phi(C_2H_2)$ values at 228.8 and 253.7 nm are presented as maximum because of a large contribution to m/e 26 from C₄H₂ fragmentation which obscures the yield of C_2H_2 . Table II also shows $\Phi(C_2H_2)$ and $\Phi(-C_4H_2)$ obtained with up to 2000-fold excess of nitrogen added to 80 mTorr of C₄H₂. The acetylene quantum yield values at 228.8 and 253.7 nm are also presented as upper limits because of the small amounts produced.

The results of photolyses of mixtures of C_4H_2 and a 1000-fold excess of D_2 are given in Table III. As in the previous table, the acetylene (C_2H_2 and C_2HD) yields are presented as upper limits at 228.8 and 253.7 nm because of large contributions to m/e 26 and 27 from the fragmentation of C_4H_2 and other impurity hydrocarbons. The fourth column labeled $\Phi(C_4HD)$ contains three values bearing the superscript "b". These are calculated minimum observable values assuming C_4HD is present. A direct mass spectrometer measurement of C_4H_2 at mass 51 was not possible due to a large isotope peak of C_4H_2 at mass 51. The latter totally obscured the observation of C_4HD , except in the 147.0-nm photolysis where a relatively large quantity of the isomer was produced.

Discussion

Table II and III show that the quantum yield of C_4H_2 disappearance is, within a large error limit of 0.5, independent of wavelengths used in this study. The added N₂ or D₂ does not change the quantum yield of C_4H_2 disappearance. Table III shows that the quantum yields of C_2H_2 , C_2HD , and C_4HD production are significant only at 147.0 nm. At 184.9 nm the yields of C_2H_2 , C_2HD , and C_4HD become small, and at two longer wavelengths the yields become zero within the experimental error limit. Since $\Phi(-C_4H_2)$ is 2 at all wavelengths, the excited-state reaction with C_4H_2 must become more important at longer wavelengths where fewer radicals are formed. Table IV contains the threshold wavelengths below which the indicated process is possible, based mainly on standard heats of formation data. While all three processes listed in Table IV are energetically possible at 147 and 184.9 nm, the quantum yield of combined radical (C_4H , C_2H) and molecular (C_2H_2) processes is mush less than unity.

TABLE IV: Photodissociation Energetics

process	ΔH° , kcal/mol	threshold λ , nm
$C_4H_2 \rightarrow C_2H_2 + C_2$	140	205
$C_4H_2 \rightarrow 2C_2H$	141ª	202
$C_4H_2 \rightarrow C_4H + H$	120-123	235

 ${}^{a}\Delta H_{f}^{\circ}$ (C₂H) = 127 kcal/mol (Okabe, H.; Dibeler, V. H. J. Chem. Phys. **1973**, 59, 2430). ^bObtained from high-temperature thermal decomposition of diacetylene (Frank, P.; Just, Th. Combust. Flame **1980**, 38, 231).

The photochemistry of C_4H_2 is discussed at 147 nm and at longer wavelengths.

Photochemistry at 147.0 nm. The substantial amounts of C_2H_2 , C_2HD , and C_4HD formed at 147.0 nm in the photolysis of C_4H_2 and D_2 mixtures indicate that three primary processes are important

$$C_4H_2 + h\nu \rightarrow C_4H + H \qquad \Phi_p = 0.2 \tag{6}$$

$$C_4H_2 + h\nu \rightarrow C_2H_2 + C_2 \qquad \Phi_p = 0.1$$
 (7)

$$C_4H_2 + h\nu \rightarrow C_2H + C_2H \qquad \Phi_p = 0.07 \qquad (8)$$

followed by

$$C_4H + D_2 \rightarrow C_4HD + D \tag{9}$$

$$C_2H + D_2 \rightarrow C_2HD + D \tag{10}$$

where Φ_p signifies the quantum yield of radical or molecular product. On the other hand, the primary quantum yield of each process is 0.2, 0.1, and 0.03 for processes 6, 7, and 8, respectively, since process 8 gives two C₂H radicals per one photon absorbed.

Process 6 is several times more important than (8), in accordance with $D_0(H-C_4H) < D_0(HC_2-C_2H)$. The C_2H_2 must arise mainly from a molecular elimination process, (7), since the yield of C_2H_2 is invariant (= 0.1), when large amounts of D_2 are added, indicating that C_4H and C_2H radicals do not form C_2H_2 , when they react with C_4H_2 (see Tables II and III). For process 7 to occur, the simultaneous H atom shift to the neighboring C atoms and cyclic configuration of the excited molecule may be required, before the excited molecule dissociates into C_2H_2 and C_2 . In the absence of D_2 , the secondary reactions may be

$$C_2H + C_4H_2 \rightarrow C_6H_2 + H \tag{3}$$

$$C_4H + C_4H_2 \rightarrow C_8H_2 + H \tag{4}$$

$$H + C_4 H_2 \rightarrow C_4 H_3 \tag{11}$$

$$C_4H_3 + H \rightarrow C_4H_2 + H_2 \tag{12}$$

in analogy to

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \tag{2}$$

From processes 6, 8, 3, 4, 11, and 12, the overall process may be written as

$$2C_4H_2 + h\nu \rightarrow C_8H_2 + H_2 \tag{13}$$

$$3C_4H_2 + h\nu \rightarrow 2C_6H_2 + H_2 \tag{14}$$

That is, for each photon absorbed, approximately two diacetylene molecules disappear. The C₂ radicals formed in reaction 7 may further react with C₄H₂. Although little is known about the reaction, one possible product is C₆H₂ which is suggested by Pontrelli.⁷

Since the total primary yield Φ for processes 6–8 is 0.33, the remaining 0.67 must be the yield of the excited state. The overall yield of C₄H₂ disappearance of 2 at all wavelengths studied can be explained by reactions 13 and 14 and the following excited-state reactions

$$C_4H_2 + h\nu \rightarrow C_4H_2^* \tag{15}$$

$$C_4 H_2^* \to C_4 H_2^{**}$$
 (16)

$$C_4H_2^{**} + C_4H_2 \rightarrow C_8H_2 + H_2$$
 (17)

where $C_4H_2^*$ signifies initially formed singlet state and $C_4H_2^{**}$

is a metastable state such as ${}^{3}\Delta_{u}$ at 3.21 eV²⁰ with a long lifetime and stability toward collisions with N₂ or D₂.

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, $C_{4}H_{2} \rightarrow C_{4}H + H$, is energetically possible. However, the radical process is found to be less than 0.1, and the excited-state reactions predominate at these wavelengths. Pontrelli⁷ found $C_{2}H_{2}$ in the photolysis of $C_{4}H_{2}$ at 253.7 nm. This finding is in disagreement with our results and is energetically not possible (see Table IV). It is possible that $C_{2}H_{2}$ 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 N₂. 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

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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

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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

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