Picosecond Flash Photolysis Studies on Phenothiazine in Organic and Micellar Solution

H. N. Ghosh, A. V. Sapre,* D. K. Palit, and J. P. Mittal

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400-085, India

Received: October 2, 1996[⊗]

Picosecond laser flash photolysis studies are carried out on phenothiazine (PTH) in cyclohexane, alcoholic solvents such as methanol and decanol, and aqueous micellar solutions like Triton X-100, Brij-58, and sodium dodecyl sulfate (SDS) on excitation at different wavelengths, *viz.*, 266 and 355 nm. In cyclohexane solution, $S_1 \rightarrow S_n$ transient absorption has been characterized and the intersystem crossing process has been studied. In alcoholic and micellar media, transient absorptions due to PTH cation radical and solvated electron (e_s^-) have also been observed along with the absorption of singlet and triplet states of PTH. Quantum yields of the different transient species in different solvents have been determined using both 266 and 355 nm excitation. Dependence of the yields of photoionization and singlet excited state on light intensity has also been investigated at these two excitation wavelengths. It is observed that the photoionization of PTH in methanol at 355 nm is a stepwise biphotoionic process. In aqueous SDS micellar medium, the photoionization is found to be monophotonic at 266 nm, but both mono- and biphotonic processes seem to operate at 355 nm. Direct evidence of the involvement of the S_1 state of PTH in the biphotonic processes is presented.

Introduction

Phenothiazine (PTH) is a biologically important molecule and has long been used as a probe to study photoionization behavior in micellar media, with light of moderate energy (λ = 347, 351, and 355 nm).[1−4] Although solvated electron yields in methanolic PTH solutions have been found to depend linearly on laser intensity, biphotonic ionization of PTH has also been reported in reverse micellar media.[4,5] The photophysics of PTH is not well studied in neat solvents except for some reports on the triplet state of PTH in organic solvents.[6−8] It is not clear whether biphotonic ionization proceeds via the singlet or triplet state. Excited states of PTH and its derivatives are known to transfer an electron to certain bromides.[7b] Recently, Smith and Grant McGimpsey[6] have studied one- and two-color laser photochemistry of PTH in acetonitrile and reported photoionization *via* the singlet manifold yielding the cation radical, PTH•+, in competition with intersystem crossing (ISC) and bond cleavage. The mechanism for photoionization of phenothiazine derivatives, promazine and chlorpromazine, has been studied as a function of solvent and excitation condition by Garcia *et al.*[9] They observed that the predominant mechanism for single-wavelength-induced photoionization (λ_{ex} = 355 nm) in alcohol is via the singlet manifold with the S_1 state being excited to the ionizing state. In cyclohexane, homolytic bond cleavage was observed to give neutral radical (PT•) in competition with ISC. Participation of the upper triplet state was also postulated by the authors.[6] The optical absorption characteristics of the first excited singlet state (S_1) of PTH are not reported in the literature. In the present study the temporal behavior of the S_1 state of PTH is investigated in neat organic solvents following photoexcitation at 355 nm. Picosecond transient absorption and nanosecond time-resolved fluorescence measurements have been undertaken for this purpose. For comparison, studies on micellar solutions of PTH have also been carried out. Experiments have also been carried out using 266 nm laser pulses for excitation to see the effect of excess energy on the photolytic behavior in methanol and aqueous micellar solutions.

Experimental Section

PTH (Fluka Purris) was used after purification by repeated crystallization from methanol. Triton X-100 [(CH₃)₃CCH₂C-(CH₃)₂C₆H₄(OCH₂CH₂)ₓOH] (x = 9.5−10.5, Sigma), Brij-58 [C₁₆H₃₃(OCH₂CH₂)₂₀OH] (Sigma), and sodium dodecyl sulfate (SDS) [CH₃(CH₂)₁₁OSO₃Na] (Fluka) were used as received. All the solvents were of spectroscopic grade and were used without further purification. In all the micellar solutions the concentration of the surfactant was kept well above the cmc (typically $\sim 10^{-2}$ mol·dm^{-3}). These solutions were at their natural pH values (5.6−8) at ambient temperature ($\sim$25 °C). All the experimental solutions were purged with high-purity (99.99%) N_2 before doing experiments.

A Shimadzu UV−vis spectrophotometer (model 160A) was used for the ground state optical absorption measurements. Steady-state fluorescence studies were carried out with a Hitachi model F-4010 spectrofluorimeter. Fluorescence lifetimes were measured using a nanosecond time-correlated single-photon-counting spectrometer (Model 199, Edinburgh Instrument, U.K.).[10] Picosecond laser flash photolysis experiments were carried out using a pump−probe spectrometer, described elsewhere.[11−13] Briefly, the third (355 nm, 5 mJ, 35 ps) and fourth (266 nm, 1.5 mJ, 35 ps) harmonic output from an active-passively mode locked Nd:YAG laser was used for excitation of the sample. The transients so produced were detected by their optical absorption using a white light continuum (400−950 nm) produced by focusing the residual 1064 nm fundamental light of the Nd:YAG laser onto a quartz cell of 10 cm path length containing a H₂O−D₂O mixture (50:50 by volume). Solutions were flowed through a 1 cm cuvette so that a fresh solution was exposed to the excitation laser pulses. The delay between the pump and probe pulses was adjusted by a 1 m long delay rail. The probe beam was bifurcated by a beam splitter (50:50) to generate a reference and an analyzing beam, which were then dispersed through a spectrograph and recorded using a dual diode array based optical multichannel analyzer system, and the signals were processed on a personal computer. Transient absorption studies above 50 ns were carried out using the same picosecond Nd:YAG laser as an excitation source and a tungsten lamp as an analyzing light source, Bausch and Lomb
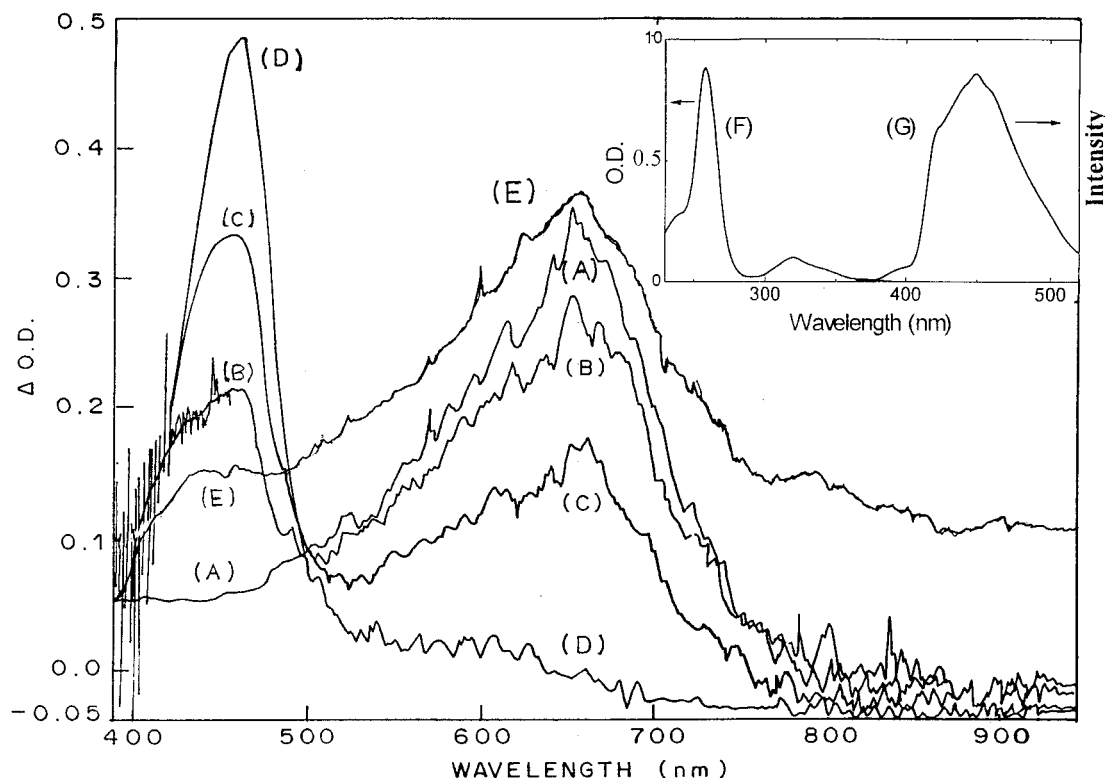

Figure 1. Transient absorption spectra obtained on excitation of PTH in cyclohexane: (A) 0 ps, (B) 200 ps, (C) 525 ps, and (D) 3.2 ns after 355 nm laser excitation pulse; (E) 0 ps after 266 nm laser excitation pulse. Inset: (E) optical absorption spectrum and (G) fluorescence spectrum (λ_{max} = 355 nm) of PTH in cyclohexane.

TABLE 1: Fluorescence Quantum Yields and Lifetimes of the S_1 State of PTH in Different Solvents and Micellar Solutions As Determined by Fluorescence Lifetime and Transient Absorption Measurement

solvent	$\phi_f{}^a$	τ_f	$\tau_a{}^b$
cyclohexane	0.006	0.74	0.75
methanol	0.008	0.91	0.92
decanol	0.011	1.08	1.10
Tx-100/water	0.010	1.12	1.14
Brij-58/water	0.011	1.13	1.14
SDS/water	0.009	1.01	1.01

^{a} ϕ_f is the fluorescence lifetime (error limit ±0.05 ns). ^{b} τ_a is the lifetime of the S_1 state measured by transient absorption technique (error limit ±0.03 ns).

monochromator, photomultiplier (Hamamatsu, R-928), and digital oscilloscope (Tektronix, TDS-500, 500 MHz). Although excitation was carried out by 35 ps laser pulses, the overall time resolution of detection system was ~15 ns. Quantum yields were estimated by knowing the laser light intensity from T−T absorption of benzophenone at 530 nm, taking the molar extinction coefficient (ϵ) for the triplet to be 6.5×10^3 dm^3 mol^{-1} cm^{-1}.[14]

Results and Discussion

1. Fluorescence Studies on PTH in Solutions. Solution of PTH in cyclohexane shows absorption maxima at 254 and 316 nm and a weak fluorescence with λ_{max} at 446 nm (Figure 1, inset). The energy of the 0−0 band for the $S_0 \rightarrow S_1$ absorption of PTH in cyclohexane is estimated to be 3.14 eV (395 nm) from the intersection of the excitation and emission spectra. The fluorescence quantum yields (ϕ_f) are estimated using anthracene in cyclohexane as standard and are given in Table 1. The fluorescence lifetimes (τ_f) measured by the time-correlated single-photon-counting technique at λ_{ex} = 355 nm are given in Table 1. These τ_f values range from 0.74 ns in

cyclohexane to 1.08 ns in decanol. The decay curves fit to single exponential with χ^2 values better than 1.1. These τ_f values are shorter than 1.5 ns reported earlier.[16] Rizikov *et al.*[8] obtained a fluorescence lifetime of ~2.3 ns in glassy isopentane matrices. It can be seen from Table 1 that both ϕ_f and τ_f values are smaller in cyclohexane than those in methanol and other media used. Our fluorescence quantum yield values match well with those reported by Saucin *et al.*[17]
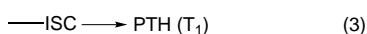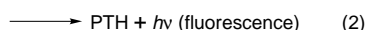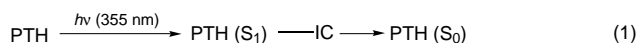
2. Transient Absorption Studies. *(a) In Cyclohexane. (i) Studies on the Picosecond Time Scale.* Since PTH is used as a probe to study photoionization behavior in micellar and microheterogeneous media, it is of interest to compare the photoionization vs photoexcitation behavior of PTH in different solvents. Laser flash photolysis studies are carried out on PTH by excitation with 266 and 355 nm laser pulses, in the picosecond time domain for this purpose. The shorter wavelength absorption band (254 nm) is attributed to $\pi^* \leftarrow \pi$ (^{1}b) transition, whereas the longer wavelength band (316 nm) belongs to ^1L_a and ^1L_b transitions.[18] These two states are designated as S_2 and S_1 respectively in the present work. On irradiation at 355 nm, it is assumed that the lowest excited singlet state (S_1) of PTH is formed, while irradiation at 266 nm produces the upper excited singlet state (S_2) of PTH as these excitations are carried out in two different excitation bands of PTH. PTH in cyclohexane, when excited by 355 nm laser pulses, produces a broad transient absorption having λ_{max} at *ca.* 650 nm at 0 ps delay. This absorption then decays by first-order kinetics and has a lifetime (τ_a) of 0.75 ns. The transient absorption spectra at different delay times are shown in Figure 1. The lifetime values determined from transient absorption (τ_a) and fluorescence studies (τ_f) match well (Table 1). Hence, the transient absorption maximum at *ca.* 650 nm is attributed to the $S_1 \rightarrow S_n$ transition of PTH. Recently Garcia *et al.*[7] have also seen $S_1 \rightarrow S_n$ transient absorption of substituted PTH, e.g., chlorpromazine (λ_{max} = 680 nm). It is seen from Figure 1 that transient

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TABLE 2: Quantum Yields of Excited Species in Various Solvents and Micellar Solutions Produced on Excitation of PTH by 355 and 266 nm Laser Pulses[a]

solvent	$\epsilon(S_1) \times 10^{-13}$ $(dm^3\ mol^{-1}\ cm^{-1})$	$f(S_1)$	$\phi(T_1)$	$\phi(e_s^0)$	$\phi_{PT^\bullet}$
cyclohexane	9.6	0.8	0.64 (0.41)		0.12 (0.18)
methanol	6.7	0.8	0.44 (0.33)	0.1 (0.12)	0.05 (0.10)
decanol	7.4		0.45		
Tx-100	7.5		0.38	0.22	
Brij-58	7.7		0.36	0.25	
SDS	6.3	0.9	0.34 (0.30)	0.32 (0.35)	

[a] Relative errors ± 0.05 in ϕ. Values in parentheses are for 266 nm excitation. $f(S_1) = \phi(S_1)_{266nm\ exc.}/\phi(S_1)_{355nm\ exc.}$.

absorption at 650 nm decays with a concomitant increase in another absorption peak at 460 nm due to the triplet state of PTH.[4] An isosbestic point is seen at 500 nm. Interestingly $S_1 \rightarrow S_n$ transitions have lower energy ($\sim$1.94 eV, λ_{max} = 650 nm) compared to the $T_1 \rightarrow T_n$ transition ($\sim$2.7 eV, λ_{max} = 460 nm). Assuming excitation to singlet state is the only process due to absorption of 355 nm light, the molar extinction coefficient of the PTH singlet state is estimated to be $\sim$9.6 $\times$ 10^3 dm^3 mol^{-1} cm^{-1} (Table 2). Since the molar extinction coefficient of the PTH triplet in cyclohexane is known[6] (ϵ_T = 2.06 $\times$ 10^4 dm^3 mol^{-1} cm^{-1} at 460 nm), from the OD at 460 nm at 5 ns delay, the triplet yield has been estimated to be 0.64. It is clear that only about 64% of singlets undergo ISC to triplets. A small fraction undergoes radiative transition (ϕ_f = 0.006) (Table 2 and reaction 2). PTH is also known to undergo photodissociation giving PT$^\bullet$ radicals and H atom radicals (reaction 4).[6,19]

$$PTH \xrightarrow{h\nu\ (355\ nm)} PTH\ (S_1) \longrightarrow IC \longrightarrow PTH\ (S_0) \quad (1)$$

$$\longrightarrow PTH + h\nu\ (\text{fluorescence}) \quad (2)$$

$$\longrightarrow ISC \longrightarrow PTH\ (T_1) \quad (3)$$

$$\longrightarrow PT^\bullet + H^\bullet \quad (4)$$

Smith and McGimpsy[6] have put forth two different mechanisms giving neutral PT$^\bullet$ radicals:

(1) monophotonic homolytic cleavage of PTH* (reaction 4);

(2) thermal or photolytic deprotonation of radical ion PTH$^{\bullet+}$ (reaction 5).

$$PTH^+ \rightarrow PT^\bullet + H^\bullet \quad (5)$$

In cyclohexane no absorption at 520 nm due to the cation radical of PTH is seen. Hence, the possibility of reaction 5 in cyclohexane can be excluded, but reaction 4 having a quantum yield of 0.11 is a likely process.[6] Reaction 4 competes with ISC, reducing triplet yields. Another reaction (reaction 6) giving PT$^\bullet$ radicals has been proposed by Iwaoka *et al.*[19] in the presence of O$_2$.

$$PTH + O_2 \xrightarrow{h\nu} PT^\bullet + HO_2^\bullet \quad (6)$$
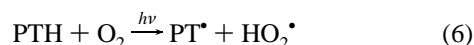
The authors find the quantum yields of PT$^\bullet$ to be 0.007 for the above reaction and conclude from the flash photolysis studies that PT$^\bullet$ arises from the triplet state of PTH. Smith and McGimpsy[6] concluded that generation of PT$^\bullet$ in cyclohexane takes place by homolytic cleavage of the N–H bond in the S$_1$ state. Since the energy of the exciting photon of 355 nm and also that of the S$_1$ state is higher than the N–H bond dissociation energy (3.47 eV), photodissociation of the NH bond is energetically possible. Assuming PT$^\bullet$ arises from a higher vibrationally excited singlet state (S$_1$), it can be said that a fraction [$\phi(S_1) - \phi_T - \phi_{PT^\bullet} - \phi_f$ = 1 − 0.65 − 0.11 − 0.006 = 0.24] of the excited PTH molecules decay by internal conversion (IC).
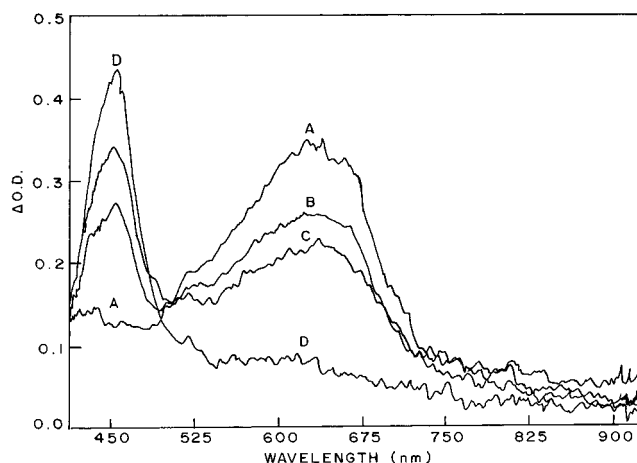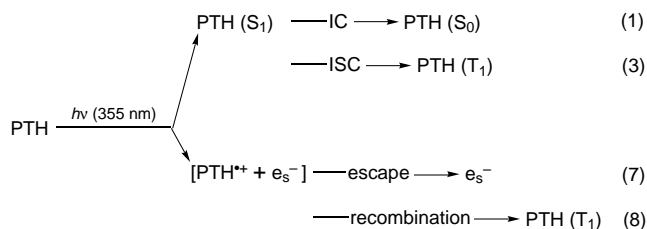

Figure 2. Transient absorption spectra obtained on excitation of PTH in methanol by 355 nm laser light: (A) 0 ps, (B) 330 ps, (C) 730 ps, and (D) 4 ns after the laser pulse.

When PTH was excited to the S$_2$ state on excitation with 266 nm laser pulses, it was seen that the extent of S$_1 \rightarrow S_n$ absorption decreases by 20%. The spectrum at 0 ps is also somewhat broader than one obtained by 355 nm excitation. Further, only about 50% of the S$_1$ state undergo ISC. This figure is lower than that for 355 nm excitation. Probable reasons could be

(1) S$_2$ partly undergoes ISC to T$_2$ which undergoes IC to T$_1$;

(2) S$_2$ undergoes IC to S$_1$, which is responsible for observed S$_1 \rightarrow S_n$ absorption;

(3) Excitation to S$_2$ (with higher vibronic energy) leads to higher yields of reaction 4. It is found that the singlet absorption spectrum at 0 ps delay is broader for 266 nm excitation (Δfwhm $\cong$ 220 nm) (Figure 1E) compared to that at 355 nm excitation (Δfwhm $\cong$ 140 nm) (Figure 1A). This is attributed to the vibrationally hot molecules in S$_1$ state produced by 266 nm excitation.

(ii) Studies on the Nanosecond Time Scale. Nanosecond experiments have also been carried out using 266 and 355 nm laser pulses for excitation, and the transient absorptions due to ^{3}PTH* at 460 nm and PT$^\bullet$ at 380 nm have been observed. It is seen that on 266 nm excitation the yield of PT$^\bullet$ radical improves but the triplet yield decreases as compared to 355 nm excitation (Table 2). At the photon fluxes used, multiphotonic processes seem to make negligible contribution (see section 3, Laser Intensity Effects). This observation clearly shows that on excitation to S$_2$ state the yield of homolytic cleavage (reaction 4) is higher.

(b) In Alcoholic Solvents. Methanol can be considered as a representative polar and protic solvent. On excitation with 355 nm pulses, a transient absorption with λ_{max} at 650 nm appears at 0 ps delay (Figure 2). At the same delay time a small hump at 520 nm corresponding to the cation radical of PTH[4] is also seen. Thus, both ionization and excitation processes (reactions 1 and 7) occur simultaneously in methanol.

$$\text{PTH} \xrightarrow{h\nu \text{ (355 nm)}} \begin{cases} \text{PTH (S}_1) \begin{cases} \text{—IC} \longrightarrow \text{PTH (S}_0) & (1) \\ \text{—ISC} \longrightarrow \text{PTH (T}_1) & (3) \end{cases} \\ \\ [\text{PTH}^{\bullet+} + e_s^-] \begin{cases} \text{—escape} \longrightarrow e_s^- & (7) \\ \text{—recombination} \longrightarrow \text{PTH (T}_1) & (8) \end{cases} \end{cases}$$

Transient absorptions at both the wavelengths 650 and 520 nm decrease, and absorption due to the PTH triplet[4] at 460 nm rises. Since the electron solvation in methanol is faster (solvation time $\sim$ 10 ps[20]) than the duration of excitation pulse (fwmh = 35 ps), the geminate recombination between solvated electron and its sibling hole (PTH$^{\bullet+}$) in the solvent cage should be over within the pulse duration, and the spectrum recorded at 4 ns delay should give the yield of separated ion pair. At a 4 ns time delay there should not be any absorption left due to the singlet state ($\tau_{S1} = 0.92$ ns in methanol). The absorption at 650 nm does not decay to the base line but reaches a plateau at about 4 ns. The residual broad absorption band with $\lambda_{max} \sim$ 630 nm can be attributed to the optical absorption of solvated electron (e_s^-) in methanol.[20] Since $\epsilon_{\text{PTH}^{\bullet+}}$ (9×10^3 dm^3 mol^{-1} cm^{-1} at 520 nm) is smaller and the PTH triplet ($\epsilon_T = 2.06 \times 10^4$ dm^3 mol^{-1} cm^{-1} at 460 nm) has a stronger absorption, the absorption due to PTH$^{\bullet+}$ appears only as a shoulder. The e_s^- peak at 630 nm is also small as the photoionization yield in methanol is low. The 650 nm peak is attributed to the singlet–singlet (S$_1 \rightarrow$ S$_n$) absorption of PTH by comparison with the results in cyclohexane and τ_f value in methanol. From its first-order decay, a lifetime of 0.92 ns has been estimated after correction for e_s^- absorption. For determining the extinction coefficient (ϵ) of S$_1$ state in methanol, lowest light intensity was used where the photoionization yield could be neglected and it was assumed that all photons absorbed led to the S$_1$* state. From the OD measured at 650 nm at 0 ps delay in methanol, ϵ was obtained to be 6.7×10^3 dm^3 mol^{-1} cm^{-1}, which is $\sim$30% less than that in cyclohexane. The electron yield is estimated from the known ϵ_{630nm} for e_s^- in methanol (1.47×10^4 dm^3 mol^{-1} cm^{-1}) to be 0.1 at the moderate laser light intensity used in our experimental conditions. The yield of PTH$^{\bullet+}$ could not be estimated due to the overlapping absorption of cation radical and S$_1$, but the former is longer lived. Direct excitation to PTH(T$_1$) can be neglected. From the known value of ϵ_T at 460 nm (2.7×10^4 dm^3 mol^{-1} cm^{-1}),[4] the triplet yield is estimated to be 0.45, which is somewhat lower than the reported value of 0.54.[1,4] It has been found that the decomposition reaction (reaction 4) is a minor channel ($\phi = 0.05$) in methanol, although the reported value is still lower ($\phi = 0.002$).[17] Hence, it is concluded that the extent of IC is more in methanol. Due to strong H-bonding interaction between PTH and methanol,[18] a faster IC is expected.

On 266 nm excitation to the S$_2$ state of PTH in methanol, it was found that the OD due to S$_1 \rightarrow$ S$_n$ decreases by $\sim$20% as compared to 355 nm excitation. Similar behavior was seen in cyclohexane solvent explained in an earlier section. Solvated electron yields increase on 266 nm excitation as compared to 355 nm excitation.

In decanol, a viscous protic polar solvent ($\eta > 10$ cP), on excitation at 355 nm, transient absorption due to a singlet of PTH at 650 nm is seen at a delay time of 0 ps. Its lifetime is determined to be $\sim$1.1 ns. This matches well with the fluorescence lifetime (Table 1) studies. No transient absorption due to cation radical or e_s^- could be seen. The yield of escaped ions is too low for the moderately polar liquid n-decanol (dielectric constant, $D = 10.2$). Triplet yield following decay
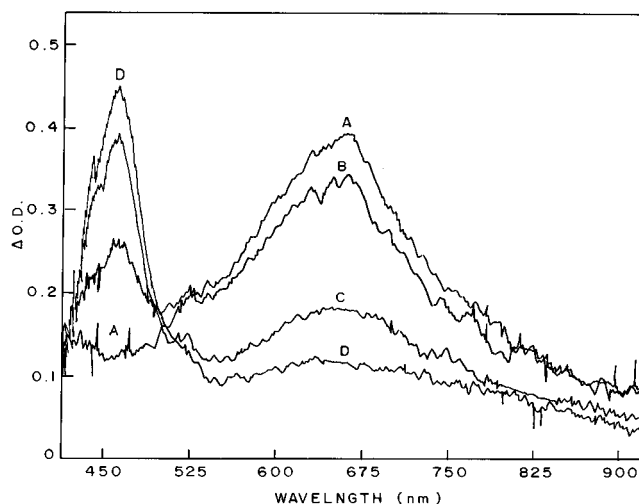

Figure 3. Transient absorption spectra obtained on excitation of PTH in Triton X-100 micellar solution by 355 nm laser light: (A) 0 ps, (B) 400 ps, (C) 1.8 ns, and (D) 6 ns after the laser pulse.
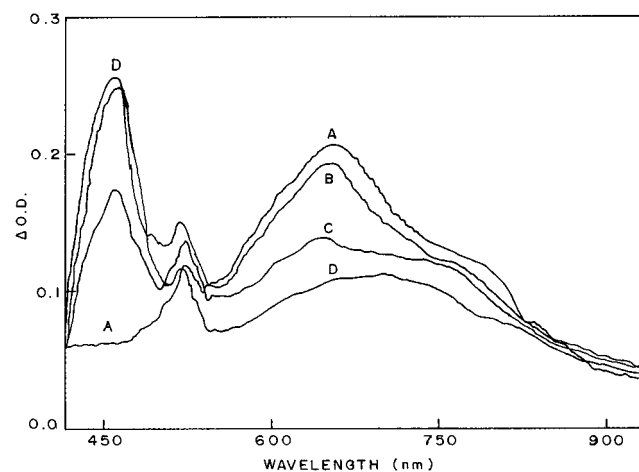

Figure 4. Transient absorption spectra obtained on excitation of PTH in SDS micellar solution by 355 nm laser light: (A) 0 ps, (B) 850 ps (C) 3.2 ns and (D) 6. ns after the laser pulse.

of singlet is estimated to be 0.6. The extent of ISC in decanol is comparable to that in cyclohexane probably due to the low polarity of decanol.

(c) In Aqueous Micellar Solutions. Nonionic and anionic micelles are being used as excellent media for charge separation on photoionization.[21] PTH solubilized in nonionic Tx-100 and anionic SDS micelles is excited by 355 nm laser pulses, and the results are shown in Figures 3 and 4 respectively. In SDS micelles both the photoexcitation and photoionization processes (reaction 1 and 7) are clearly seen at 0 ps delay. Transient absorptions due to the cation radical (PTH$^{\bullet+}$), and e_{aq}^- absorption at 520 and 720 nm respectively are seen due to photoionization (Figure 4). However, the 650 nm peak due to the singlet state of PTH is also quite strong. As the time delay increases, absorption due to the singlet state decreases. However, at 6 ns delay transient absorption peaks due to the separated ion pairs, PTH$^{\bullet+}$ and e_{aq}^-, is clearly seen. The triplet state of PTH grows at the expense of the singlet state *via* ISC. The yields of e_{aq}^- and singlet and triplet states are estimated and given in Table 2. Similar results are obtained for PTH in Tx-100 (Figure 3) and Brij-58. As compared to methanol, the ionization yields are more in the micellar solutions studied and singlet yields are correspondingly less. The e_s^- yields in Tx-100 and Brij-58 are estimated from OD at 630 nm at 6 ns delay when the singlet state has decayed ($\epsilon_{es^-} = 1.47 \times 10^4$ dm^3 mol^{-1} cm^{-1}

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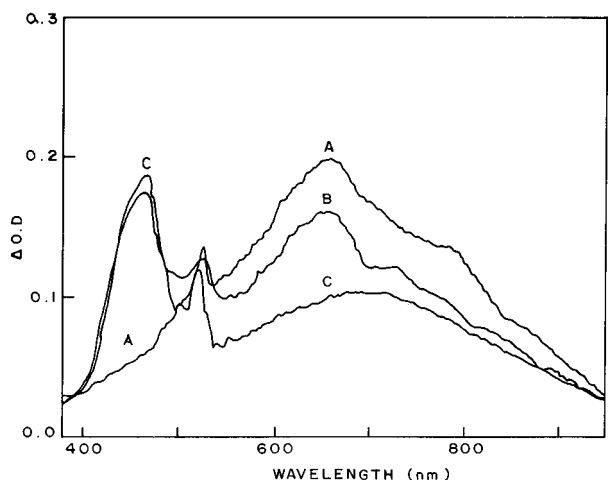*J. Phys. Chem. B, Vol. 101, No. 13, 1997* **2319**

Figure 5. Transient absorption spectra obtained on excitation of PTH in SDS micellar solution by 266 nm laser light: (A) 0 ps, (B) 1.32 ns, and (C) 6. ns after the laser pulse.

Figure 6. $\log(OD_0)$ vs $\log(I_t)$ (relative laser intensity) for electron yields on PTH: (A) 266 nm excitation ($\lambda = 720$ nm) and (B) 355 nm excitation ($\lambda = 720$ nm) in SDS micellar solution; (C) 355 nm excitation ($\lambda = 630$ nm) in methanol solution.

SCHEME 1: Biphotonic Ionization in Methanol at 355 nm Excitation

SCHEME 2: Monophotonic Ionization in SDS Micellar Solution at 266 nm Excitation

SCHEME 3: Mixed Mono- and Biphotonic Ionization in SDS Micellar Solution at 355 nm Excitation

in methanol) (Table 2). No distinction was made between the two sites of electron solvation in nonionic micelles studied earlier[3] as at the time scale of study both sites are not fully developed. It has been observed that electron yield is more in ionic micelles (SDS) as compared to nonionic micelles (Tx-100 and Brij-58) (Table 2). This is due to the negative charge of the Stern layer of the ionic micelles which repels the electron out of the micellar phase to water. ϕ_T values are estimated to be 0.34, 0.38, and 0.36 respectively for SDS, Tx-100, and Brij-58, assuming ϵ_T at 460 nm to be 2.2×10^4 dm^3 mol^{-1} cm^{-1}.[1] These ϕ_T values are close to the triplet yields in SDS solutions (0.3) as reported by Alkaitis *et al.*[1]

3. Laser Intensity Effects. The mechanism of photoionization of PTH is controversial and not yet clear. On the basis of linear dependence of e_s^- yields on laser intensity (I_t), Alkaitis *et al.*[1] have shown that the ionization is monophotonic in SDS micelles. Both biphotoionic and monophotonic ionization of PTH in solution phase has been reported in literature.[22−25] Smith and McGimpsy[6] have recently found that the ionization of PTH in acetonitrile proceeds by a stepwise biphotonic mechanism *via* singlet manifold. Photoionization of chlorpromazine and promazine were found to be monophotoionic in solution phase by Navaratnam *et al.*[26] However, Buetner *et al.*[27] observed that photoionization of chlorpromazine is a stepwise biphotoionic process. Recently, Garcia *et al.*[9] have also found that singlet state of promazine and chlorpromazine is involved in the ionization process in methanol and aqueous solutions. To gain further insight into the problem, laser intensity effects have been studied in methanol and micellar media by monitoring $S_1 \rightarrow S_n$ absorption at 650 nm and e_s^- absorption at 630 or 720 nm. It is seen that the quantitative criterion given by Lasisch *et al.*[28] for saturation is satisfied (eq 9)

$$\sigma(I_t) < 1 \tag{9}$$

where σ is the absorption cross section of PTH at the wavelength of photolysis and I_t is the photon flux in photons/cm^2. Typical values of $\sigma(I_t)$ range from 0.05 to 0.16 for 266 and 355 nm excitations used in the present work. For estimation of singlet yields the contributions of e_s^- were subtracted (taken at 4 ns). In an effort to determine whether the observed photoionization processes is monophotonic or stepwise biphotonic, we have measured $[e_s^-]$ as a function of light intensity. For this purpose PTH solubilized in SDS micellar solutions was excited by 266 and 355 nm laser pulses of different intensities, and OD of e_{aq}^-
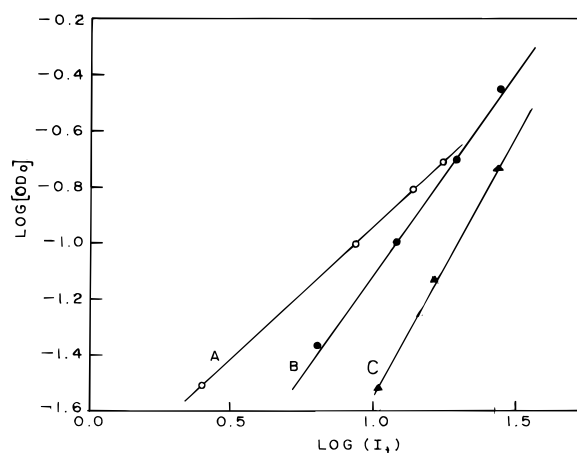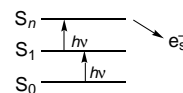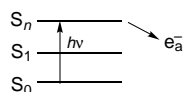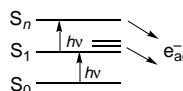
at 720 nm at 6 ns delay (OD_0) was monitored where the contribution from the singlet state was negligible. For methanol solution OD_0 was determined taking the absorbance of e_s^- at 630 nm at 6 ns delay. At moderate laser intensities, the initial absorbance of a transient chemical species can be described as a function of laser intensity as given by eq 10

$$OD_0 = kI_t^n \tag{10}$$

where OD_0 is the optical density of e_{aq}^- at 720 nm at 6 ns, I_t is the laser intensity, n is an integer, and k is a constant encompassing the specified experimental condition. The value of n can be determined from the logarithmic plot of eq 10.

$$\log[OD_0] = \log k + n \log(I_t) \tag{11}$$

Figure 6 presents the plot of $\log[OD_0]$ vs $\log(I_t)$ for PTH in SDS micellar solution. For experiments with 355 nm excitation, the slope is determined to be 1.48 (Figure 6B) and for excitation at 266 nm yields a slope of 0.95 (Figure 6A). Hence, it can be concluded that the photoionization of PTH by 266 nm light (S_2) proceeds *via* a monophotonic ionization processes, while that at 355 nm occurs through a complex process involving both mono- and biphotonic routes. The various processes are explained in Schemes 1−3.

The results for methanol are shown in Table 3. It is found that as the laser intensity at 355 nm increases, the yield of singlet

TABLE 3: Effect of Laser Intensity on the Yields of PTH Singlet and Solvated Electron Yields Observed on Excitation of PTH in Methanol by 355 nm Laser Light[a]

I (photons/cm^3) $\times 10^{-16}$	$\phi(S_1)$	$\phi(e_s^-)$
0.51	1.0	
1.22	0.72	0.07
1.84	0.70	0.1
2.1	0.62	0.14
2.6	0.46	0.18

[a] Relative errors $\pm 10\%$ in ϕ.

decreases and the e_s^- yields improve. These results clearly show that the electrons are generated at the expense of the singlet of PTH in methanol. The intensity dependence for e_s^- absorption in methanol is also incorporated in Figure 6C, and from its slope ($\sim$1.7) it is concluded that the photoionization of PTH in methanol proceeds by a biphotonic mechanism.

To know whether the photon energy used for excitation (355 nm = 3.49 eV) is sufficient to ionize the PTH molecule in alcoholic and micellar solution, the ionization potential of molecules in liquid phase (IP$_1$) can be calculated using the following equation[15]

$$IP_1 = IP_g + P + V \qquad (12)$$

where IP$_g$ is the gas phase ionization potential of the molecule, P is the polarization energy of the positive ion, and V is the ground-state conduction band potential in liquid. For PTH the ionization potential (I_D) is known to be 6.96 eV[29] in nonpolar solvents. Since the contribution of P and V are negligible in nonpolar media, I_D is equated to IP$_g$. Hence, using eq 12, IP$_1$ is calculated to be 3.96 eV ($\sim$315 nm) in methanol and 3.56 eV ($\sim$351 nm) in micellar solutions used. Thus, it is estimated that ionization potential is lowered by 3 eV in methanol and 3.4 eV in aqueous micellar solution of SDS. The above calculations indicate that monophotonic ionization of PTH is not possible by 355 nm (3.49 eV) excitation in methanolic solutions.

From the above arguments, it is clearly seen that photolysis by 266 nm pulses (4.66 eV) supports monophotonic ionization both in methanol and micellar media (Scheme 2), but for 355 nm excitation ionization proceeds through stepwise biphotonic processes in methanol as observed (Scheme 1). For SDS, the photoionization seems to proceed via mixed mono- and biphotonic (Scheme 3) processes.

Conclusion

Picosecond laser flash photolysis of phenothiazine is carried out in cyclohexane, methanol, decanol, and aqueous micellar solutions like Triton X-100, Brij-58, and SDS on excitation by 355 nm pulses. In cyclohexane S$_1$ → S$_n$ absorption of PTH and ISC to the triplet state has been investigated on the picosecond time scale. In alcoholic and micellar solutions besides singlet and triplet states, radical cation and solvated electrons are also observed. The quantum yields of the transient species have been determined. It has been observed that electron yield is higher in micellar solutions than in alcoholic solvents,

and correspondingly the singlet and triplet yields are lower in micellar solution. To see the effect of excess energy on the photolytic behavior of PTH in the above solvents used, experiments have also been carried out on excitation by 266 nm laser light. Yields of the excited species were determined and compared with those obtained on 355 nm excitation results. Intensity dependence experiments have been carried out both in methanol and SDS micellar solution using both 266 and 355 nm laser pulses for excitation. It has been observed that ionization is monophotonic at 266 nm excitation and stepwise biphotonic processes occur at 355 nm excitation for PTH in methanolic and SDS micellar solution.

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