Steady-State and Time-Resolved Studies on Photoinduced Interaction of Phenothiazine and 10-Methylphenothiazine with Chloroalkanes

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Received: August 11, 1997; In Final Form: March 17, 1998

Phenothiazine and 10-methylphenothiazine have been found to form weak complexes with the chloroalkanes, such as CCl_4 and $CHCl_3$, both in the ground and excited singlet states as investigated by spectrophotometric and fluorimetric techniques. Steady-state and time-resolved fluorescence quenching experiments indicate that the strength of interaction of the excited singlet (S_1) state of the phenothiazines with the chloroalkanes increases as the reduction potentials of the latter become less negative or the oxidation potentials of the phenothiazines become less positive. These results indicate that the electron-transfer or charge-transfer type of interaction is operative in these systems. In less polar solvents, such as cyclohexane and ethyl acetate, weak exciplex formation between the S_1 state of the phenothiazines and the chloroalkanes has been observed, whereas in a more polar solvent, such as acetonitrile, direct electron transfer takes place from the S_1 state of the phenothiazines to the chloroalkanes, leading to dissociation of the C−X bond of chloroalkanes. Picosecond flash photolysis studies carried out on these systems showed the presence of the cation radical of the phenothiazines and support the photoinduced charge separation and other processes proposed.

1. Introduction

Phenothiazine (PTH) and its derivatives are an important class of molecules having a variety of applications.[1−4] Use of phenothiazines and related compounds as dyes, antioxidants, and pharmaceuticals is well-known. The physiological activity of the phenothiazines and related compounds is mainly related to their neuroleptic properties.[4] Phenothiazine derivatives are often used as tranquilizers. Drugs containing the phenothiazine moiety, however, frequently give severe side effects, which are often attributed to their redox reactions. Studies on the chemical oxidation of phenothiazines have long attracted much attention.[5] Formation and reactions of the different oxidative intermediates, namely, the cation radical ($PTH^{\bullet+}$) and the neutral ($PT^{\bullet}$) radicals of the phenothiazines, have been investigated for the past three decades.[5] Studies on the photooxidation of the phenothiazines are being pursued since the late 1970s.[6] The possibility of photoionization of phenothiazines with light of moderate energies (λ = 347, 351, and 355 nm)[7] has made this molecule an excellent probe to study the photoionization behavior and related phenomena, such as electron solvation in organic, aqueous, and micellar media. The photochemical and photophysical behavior of the phenothiazines has been a subject of some recent studies,[8−10] including the picosecond laser flash photolysis work on PTH in different organic and micellar media from our laboratory.[11] Since the hydrogen atom attached to the nitrogen heteroatom in PTH is labile and often participates in the deprotonation reaction following the oxidation of PTH, a comparison between the photochemistry of PTH and 10-methyl phenothiazine, MPTH, and its implication are worth investigating.[11]

During our investigations on the photophysical properties of phenothiazines in different solvents we observed that their behavior in chloroalkane solvents is quite different from that in other solvents. It appeared that the phenothiazines undergo some specific interactions with chloroalkanes. In the present study we have investigated in detail the interactions of both the ground and excited singlet (S_1) states of PTH and MPTH with chloroalkanes using spectrophotometric and steady-state and time-resolved fluorimetric techniques. Since both PTH and MPTH are strong electron donors due to their low oxidation potentials ($E_{1/2}$ = +0.59 V for PTH and +0.73 V for MPTH in acetonitrile vs SCE[12]) and since the chloroalkanes are known to be good electron acceptors, a charge-transfer (CT) and/or electron-transfer (ET) type of interaction between the phenothiazines and the chloroalkanes seems to be operative in the present systems. Picosecond transient absorption studies have also been carried out to confirm the possibility of photoinduced charge separation (CS) and electron-transfer (ET) reaction.

2. Experimental Section

PTH (Fluka) and MPTH (Acros Organics) were purified by repeated crystallization from methanol. All the solvents used were of spectroscopic grade from Spectrochem India and were used without further purification.

Ground-state absorption measurements were carried out using a Shimadzu model 160A UV−vis spectrophotometer. Steady-state fluorescence measurements were carried out using a Hitachi model 4010F spectrofluorimeter.

Time-resolved fluorescence measurements were carried out using a nanosecond time-correlated single-photon-counting spectrometer (Edinburgh Instruments, U.K., model 199), which has been described in detail elsewhere.[13] Observed fluorescence decay curves were analyzed using a reconvolution program which uses an iterative nonlinear least-squares fitting method. The instrument response function used in the reconvolution procedure was obtained by substituting the sample cell with a scatterer. All the observed decay curves were fitted to a monoexponential function as

$$I(t) = B \exp(-t/\tau) \quad (1)$$

S1089-5639(97)02614-5 CCC: $15.00
Published on Web 06/18/1998

TABLE 1: Ground-State Absorption and Fluorescence Characteristics of PTH and MPTH in Different Solvents

solute	solvent (ϵ_s)	λ_{abs}^{max} (nm)	fwhm[a] (cm^{-1})	ϵ_{abs}^{max} (dm^3 mol^{-1} cm^{-1})	λ_{fl}^{max} (nm)	Φ_{fl}	τ_{fl} (ns)
PTH	CH (2.02)	316	4500	4.7×10^3	433	0.006	0.82
	EA (6.03)	317	4844	4.9×10^3	444	0.009	1.19
	AN (37.5)	316	4900	4.4×10^3	447	0.010	1.15
	CCl_4 (2.30)	320	5860	5.3×10^3			
	$CHCl_3$ (4.81)	318	5080	4.5×10^3			
MPTH	CH	310	4210	5.6×10^3	441	0.014	1.61
	EA	309	4350	5.4×10^3	447	0.016	1.91
	AN	308	4440	5.2×10^3	449	0.018	2.0
	CCl_4	315	5240	6.6×10^3			
	$CHCl_3$	312	4650	5.6×10^3			

[a] Full width half-maximum for the longest wavelength absorption band.

where τ is the fluorescence lifetime of the sample and B is the preexponential factor.

Picosecond laser flash photolysis experiments were carried out using a pump−probe spectrometer, described elsewhere.[14,15] Briefly, the third-harmonic output (355 nm, 5 mJ, 35 ps) of an active−passive mode-locked Nd:YAG laser (Continuum, USA, model 501-C-10) was used for the excitation of the samples. The transients produced in the irradiated samples were detected by their optical absorption. A white light continuum (∼400 to 950 nm) produced by focusing the residual fundamental (1064 nm) of the Nd:YAG laser onto a 10 cm length quartz cell containing a 50:50 (v/v) H_2O-D_2O mixture was used as the monitoring light source. The probe light was passed through a variable optical delay line (1 m long) and then split into two parts using a 50:50 beam splitter. One part of the monitoring light was used as the reference beam, and the other was used as the analyzing beam (passing through the irradiated sample). Both the reference and the analyzing beams were dispersed through a spectrograph and monitored using a dual diode array based optical multichannel analyzer, which is interfaced to a personal computer to process the data. For all the measurements the sample solutions were deoxygenated by continuously bubbling high-purity nitrogen (Iolar grade from Industrial Oxygen Co. Ltd., India) through the solutions. The solutions were flowed through a 2 mm × 10 mm quartz cell during all the measurements. The excitation and the analyzing beams (2 mm diameter at the overlapping region) were close to a collinear geometry within the sample cell, and thus the effective sample thickness was about 2 mm.

3. Results and Discussion

3.1. Ground-State Interactions of PTH and MPTH with Chloroalkanes. Ground-state optical absorption spectra of PTH and MPTH are found to shift significantly to longer wavelengths and become broader (see Table 1 for fwhm values) in CCl_4 and $CHCl_3$ as compared to those solvents of varying polarity such as cyclohexane (CH), ethyl acetate (EA), and acetonitrile (AN) (see Figure 1). The molar extinction coefficients of PTH and MPTH in the above chloroalkanes also increase substantially (see Table 1). These observations clearly indicate the formation of ground-state complexes between phenothiozines and chloroalkanes. In dichloromethane (CH_2Cl_2) the absorption spectral studies do not indicate any complex formation. On the addition of chloroalkanes to the solution of phenothiazines in solvents such as CH, EA, and AN the absorption spectra of phenothiazines become broader, absorption maxima get red shifted, and optical density (OD) increases. Assuming the formation of a 1:1 complex, the OD changes at λ_{abs}^{max} were fitted to Benesi−Hildebrand relation,[16] (eq 2) modified for the overlapping absorption of free donor (PTH/MPTH) and complex at the monitoring wavelength.

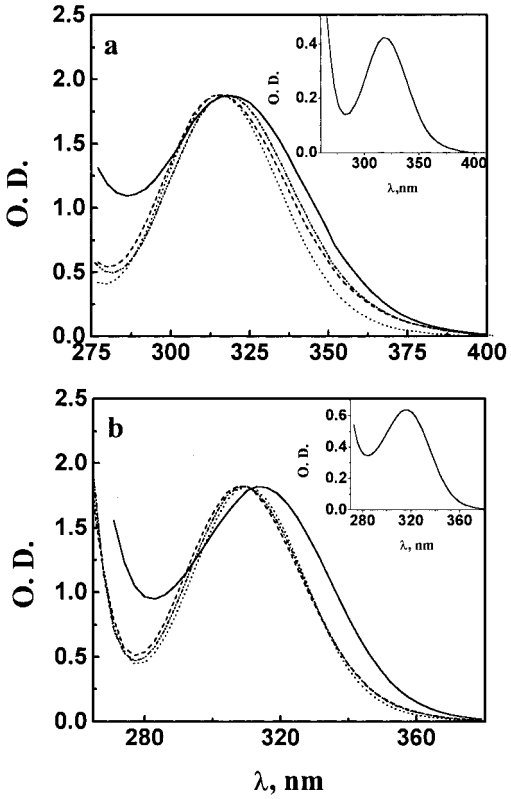


Figure 1. Ground-state absorption spectra of (a) PTH and (b) MPTH in CH (···), EA (- ·· -), AN (- - -), and CCl_4 (—). Inset: Absorption spectra of the ground-state (PTH···CCl_4) complex as obtained by subtracting the normalized absorption spectra of PTH in CH from that in CCl_4.

$$\frac{1}{\Delta OD(\lambda)} = \frac{1}{K_G C_D^0 \epsilon'(\lambda)}\left(\frac{1}{C_A}\right) + \frac{1}{C_D^0 \epsilon'(\lambda)} \qquad (2)$$

where $\Delta OD(\lambda) = \{OD(\lambda) - OD_0(\lambda)\}$, $OD(\lambda)$ and $OD_0(\lambda)$ are the observed absorbances at wavelength λ in the presence and absence of chloroalkanes, respectively, C_A is the concentration of CCl_4, C_D^0 is the total concentration of the donor, K_G is the equilibrium constant for the ground-state complex formation, $\epsilon'(\lambda) = \{\epsilon_{DA}(\lambda) - \epsilon_D(\lambda)\}$, and $\epsilon_{DA}(\lambda)$ and $\epsilon_D(\lambda)\}$ are the molar extinction coefficients of the complex and the free donor at wavelength λ. From the slopes and intercepts of $1/\Delta OD(\lambda)$ vs $1/C_A$ plots K_G and $\epsilon_{DA}(\lambda)$ were extracted and are listed in Table 2. Tables 1 and 2 show that the extinction coefficients for the complexes are only slightly higher than those of the donor. Thus, the absorbance changes at the λ_{abs}^{max} of the phenothiazines are

TABLE 2: Equilibrium Constant and the Absorption Characteristics of the Ground-State Complexes between Phenothiazines and CCl_4

donor	solvent	K_G (mol^{-1} dm^{-3})	λ_{com}^{max} (nm)	ϵ_{com}^{max} (dm^3 $mol^{-1}cm^{-1}$)
PTH	CH	1.430	318	5000
	EA	0.320	320	5695
	AN	0.122	320	5212
MPTH	CH	0.252	315	6243
	EA	0.043	318	8972
	AN	0.045	318	10 456

small in the presence of the chloroalkanes, but are distinctly evident. Since with $CHCl_3$ the absorbance changes at the λ_{abs}^{max} are not substantial for both PTH and MPTH in any of the above three solvents, eq 2 could not be used to obtain K_G and $\epsilon_{DA}(\lambda)$ for these complexes. From the K_G values it is evident that as the oxidation potential of the phenothiazines decreases, i.e., as the donor ability increases, the extent of complex formation increases, which indicates that the interactions between phenothiazines and chloroalkanes are of charge-transfer (CT) type.

The K_G value is the highest in nonpolar CH and decreases with the solvent polarity (see Table 1). This is contrary to the usual concept that a CT complex gets stabilized as the solvent polarity increases. The reason for this unusual trend in K_G in the systems studied is not very clear. It could be related to some structural changes associated with the phenothiazines undergoing complex formation. The phenothiazines are usually nonplanar molecules[17] and are expected to form a stable complex in which the molecular species need to attain near planar geometry.[18] In nonpolar solvents these structural changes could be easier than in polar solvents, because the functional groups of the phenothiazines strongly interact with polar solvents, which will hinder any structural rearrangement of the phenothiazines.

3.2. Interaction of the Excited State (S_1) of PTH and MPTH with Chloroalkanes. It was seen that both CCl_4 and $CHCl_3$ quench the fluorescence of PTH and MPTH by using both steady-state and time-resolved techniques in solvents CH, EA, and AN. In neat CCl_4 or $CHCl_3$ no fluorescence from either PTH or MPTH was seen. Typical steady-state fluorescence quenching results are shown for the PTH/CCl_4 system in CH and AN (Figure 2). In CH concomitant with reduction of fluorescence intensity a new broad emission appears at the longer wavelength side of the spectrum (Figure 2a). This red-shifted emission is also seen in EA. This red-shifted emission in CH and EA is assigned to the exciplex between phenothiazines and chloroalkanes. In polar solvent AN no exciplex emission was seen even at the highest concentration of chloroalkane used.

The fluorescence quenching behavior is usually described by two Stern−Volmer (S−V) relations.

$$\frac{I_0}{I} = 1 + K_{SV}^{SS}[Q] = 1 + k_q^{SS}\tau_0[Q] \quad (3)$$

$$\frac{\tau_0}{\tau} = 1 + K_{SV}^{TR}[Q] = 1 + k_q^{TR}\tau_0[Q] \quad (4)$$

where, I_0 and I are the fluorescence intensities in the absence and presence of the quenchers (Q, chloroalkanes), K_{SV} is the Stern−Volmer constant related to the bimolecular quenching constant, k_q, by $K_{SV} = k_q\tau_0$, and τ_0 and τ are fluorescence lifetimes of the fluorophore, PTH or MPTH, in the absence and presence of the quencher.

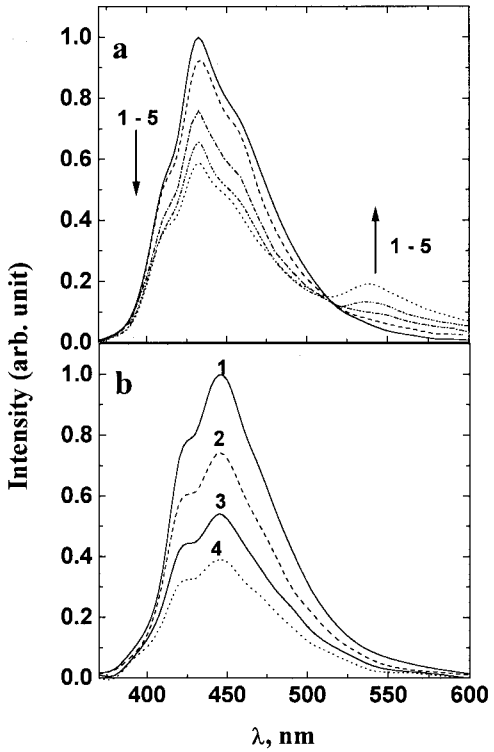


Figure 2. (a) Fluorescence quenching of PTH in CH by different concentrations of CCl_4: (1) 0, (2) 1.39×10^{-4}, (3) 2.74×10^{-4}, (4) 4.04×10^{-4}, and (5) 6.50×10^{-4} mol dm^{-3}. (b) Fluorescence quenching of PTH in AN by different concentrations of CCl_4: (1) 0, (2) 1.39×10^{-4}, (3) 2.74×10^{-4}, and (4) 5.29×10^{-4} mol dm^{-3}.

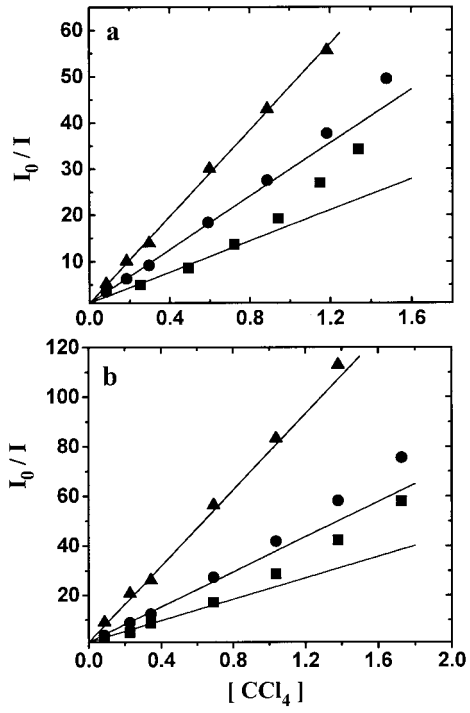


Figure 3. Stern−Volmer plot for the steady-state fluorescence quenching of (a) PTH and (b) MPTH by CCl_4 in different solvents: CH (■), EA (●), and AN (▲). The emission was monitored at λ = 445 nm.

Typical S−V plots for steady-state fluorescence quenching of both PTH and MPTH by CCl_4 are shown in Figure 3. At lower concentrations of the quencher, S−V plots of I_0/I vs [Q] are linear within experimental error, and at higher quencher

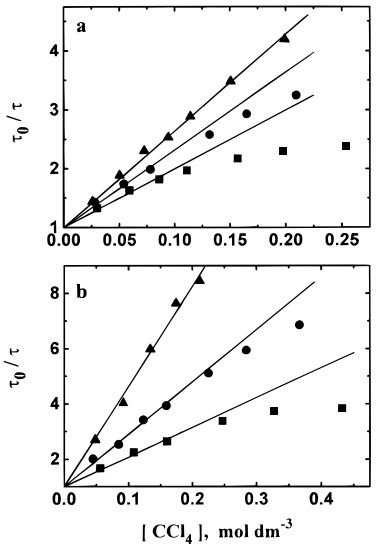


Figure 4. Stern−Volmer plot for the time-resolved fluorescence quenching of (a) PTH and (b) MPTH by CCl_4 in different solvents: CH (■), EA (●), and AN (▲). The emission was monitored at λ = 445 nm.

TABLE 3: Bimolecular Steady-State (SS) and Time-Resolved (TR) Quenching Constants for Phenothiazine−Chloroalkane Systems in Different Solvents

donor	acceptor	solvents	k_q (SS) (dm^3 mol^{-1} s^{-1})	k_q (TR) (dm^3 mol^{-1} s^{-1})
PTH	CCl_4	CH	1.11×10^{10}	
		EA	1.91×10^{10}	
		AN	2.57×10^{10}	2.10×10^{10}
PTH	$CHCl_3$	CH	5.60×10^{8}	
		EA	5.06×10^{8}	
		AN	6.90×10^{8}	6.13×10^{8}
MPTH	CCl_4	CH	1.03×10^{10}	
		EA	1.65×10^{10}	
		AN	2.19×10^{10}	1.90×10^{10}
MPTH	$CHCl_3$	CH	0.97×10^{8}	
		EA	1.73×10^{8}	
		AN	4.16×10^{8}	3.80×10^{8}

concentrations positive deviation from linearity was seen. Deviation from linearity is maximum in nonpolar CH but decreases with increase in solvent polarity. In polar AN solvent the S−V plots are linear within experimental error. The k_q values obtained from the initial slope are listed in Table 3. Since positive deviation is associated with ground-state complex formation, the extent of deviation follows the equilibrium constant values, K_G, and hence is higher in CH and minimum in AN.

The τ_0/τ vs [Q] S−V plots are shown in Figure 4. These S−V plots for CH and EA solvents show a negative deviation from linearity and tend toward a limiting value at higher quencher concentrations. In polar solvent AN, however, the τ_0/τ vs [Q] plots are seen to be linear within experimental error for the entire range of quencher concentrations used. The negative deviation from the linearity in the τ_0/τ vs [Q] plots for less polar solvents such as CH and EA, as expected, is due to exciplex formation between the S_1 state of phenothiazines and chloroalkanes.[19,20] The lack of negative deviation for AN solvent indicates that there is no exciplex formation and the quenching might be due to direct ET from phenothiazines to chloroalkanes.

Scheme 1 shows the processes taking place during the formation and decay of the exciplex. Because of the exciplex formation, the lifetime of the fluorophore (τ) should vary

SCHEME 1

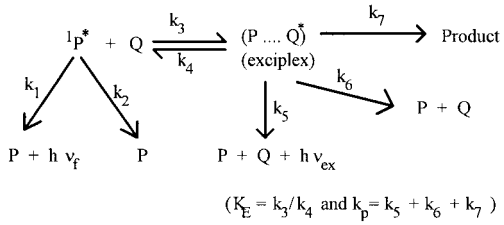


TABLE 4: Formation (K_E) and Decay (k_p) Constants of the Phenothiazine−Chloroalkane Exciplex

system	solvent	K_E (mol^{-1} dm^{-3})	k_p (s^{-1})
PTH/CCl_4	CH	4.5 ± 0.05	$(4.9 \pm 0.1) \times 10^{10}$
	EA	0.3 ± 0.05	$(5.8 \pm 0.1) \times 10^{10}$
PTH/$CHCl_3$	CH	1.4 ± 0.05	$(1.6 \pm 0.1) \times 10^{9}$
	EA	0.1 ± 0.05	$(2.9 \pm 0.1) \times 10^{9}$
MPTH/CCl_4	CH	0.8 ± 0.05	$(6.9 \pm 0.1) \times 10^{9}$
	EA	0.3 ± 0.05	$(5.3 \pm 0.1) \times 10^{9}$
MPTH/$CHCl_3$	CH	0.1 ± 0.05	$(1.6 \pm 0.1) \times 10^{9}$
	EA	0.1 ± 0.05	$(1.5 \pm 0.1) \times 10^{9}$

nonlinearly with quencher concentration ([Q]) following eq 5[19] where K_E and k_p are exciplex formation and decay constants, respectively.

$$(\tau^{-1} - \tau_0^{-1})^{-1} = \{K_E^{-1}(k_p - \tau_0^{-1})^{-1}\}[Q]^{-1} + (k_p - \tau_0^{-1})^{-1} \quad (5)$$

Thus, from the slope and intercept of $(\tau^{-1} - \tau_0^{-1})^{-1}$ vs $[Q]^{-1}$ plot, K_E and k_p have been evaluated as

$$K_E = (\text{Intercept})/(\text{Slope}) \quad (6)$$

$$k_p = \{(\text{Intercept})^{-1} - \tau_0^{-1}\} \quad (7)$$

The values of K_E and k_p thus obtained are listed in Table 4. Comparing K_E for both PTH and MPTH, it is evident that the stronger the donor, the higher the exciplex formation.

3.3. Photoinduced ET from Phenothiazines to Chloroalkanes in Polar Solvent, AN. As we have discussed in section 3.2, there is no indication of exciplex formation between the phenothiazines and the chloroalkanes in polar AN; the fluorescence quenching of phenothiazines by the chloroalkanes in AN is attributed to the direct ET from the excited singlet state (S_1) of the fluorophores to the chloroalkanes. It is further seen that in AN the k_q values obtained from the steady-state (eq 3) and the time-resolved fluorescence quenching experiments (eq 4) agree well with each other within experimental error (Table 3).

The transfer of an electron from an outer sphere homogeneous electron donor (D) to a halogenated acceptor molecule (RX) results in a irreversible dissociative electron transfer (DET) process and is represented by the following reaction:

$$RX + D \rightarrow D^{\bullet+} + R^{\bullet} + X^{-}$$

Several groups[21−24] have studied both homogeneous and heterogeneous reduction of halo-organic compounds leading to DET. Among the different haloalkanes the dissociative electron capture of CCl_4 has been extensively studied. Optical and EPR techniques indicated the formation of the primary $CCl_4^{\bullet-}$ radical anion under radiolysis of neat CCl_4.[25] At room temperature, $CCl_4^{\bullet-}$ dissociates on the subnanosecond time scale to give the $CCl_3^{\bullet}$ radical and the chloride ion Cl^-.[26]

It has been shown by Eberson[22c] that the reduction of alkyl halides by various electron donors could not be accommodated

TABLE 5: Redox Potentials of Donors and Acceptors and Free Energy Values for ET in AN

donor	E_{00}, eV (λ_{00}, nm)	$E^{Ox}_{1/2}$ (V)[a]	acceptor	E(RX/R• + X$^-$) (V)[a]	ΔG^0 (eV)
PTH	3.15	0.59	CCl_4	−0.66	−1.995
	(390)		$CHCl_3$	−1.15	−1.505
MPTH	3.25	0.73	CCl_4		−1.925
	(382)		$CHCl_3$		−1.435

[a] The redox potentials are in AN vs SCE.

properly by the Marcus theory[27] when the standard free energy changes were estimated on the basis of Hush's original E^0 values for reduction of RX.[28] Marcus theory does not consider any dependence of driving force, ΔG^0, on the strength of the C−X bond, which breaks during the DET process. Hence, the calculation of ΔG^0 needs to be modified by incorporation of a bond strength factor. Thus, for the DET mechanism it is more realistic to consider the following half-reaction for the acceptor.

$$RX + e^- \rightarrow R^\bullet + X^-$$

The standard potential for the above half-reaction is calculated from eq 8.[29]

$$E(RX/R^\bullet + X^-) = E(X/X^-) - BDFE(R-X) \qquad (8)$$

where BDFE is the bond dissociation free energy for the C−X bond in the haloalkanes. The value of E(Cl/Cl$^-$) in AN is +1.89 V vs SCE.[30a] The bond dissociation energies after the correction for entropy in the gas phase for the C−Cl bond are 2.55 and 3.04 eV for CCl_4 and $CHCl_3$, respectively.[29,31] Using these values, the E(RX/R• + X$^-$) in AN calculated for CCl_4 and $CHCl_3$ are −0.66 and −1.15 V vs SCE, respectively.

The reactions studied in the present work can be represented by Scheme 2, which incorporates the DET mechanism and the formation of the products via a transition state.[32]

SCHEME 2

$$RX + D^* \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [(R - X\cdots D)^* \rightleftharpoons (R\cdots X^{\delta-}D^{\delta+})^\#] \xrightarrow{k_{ET}} (R^\bullet + X^- + D^{\bullet+}) \xrightarrow{k_{pr}} \text{Product}$$

where the excited donor (D*) and the acceptor (RX) molecules diffuse toward each other to form the encounter complex, (R−X···D)*. The latter subsequently undergoes reorganization to form a TS in which the C−X bond is loose. Depending on the solvent, the TS undergoes either complete ET to give the ion pair state or charge recombination (CR) to give the reactants back. k_d and k_{-d} are the rate constants for diffusing together and apart, respectively, of the reactants, k_{ET} is the activation-controlled ET rate constant, and k_{pr} is the sum of the rate constants for all the processes by which the ion pair state decays.

The free energy change, ΔG^0, for the reactions under consideration is given by[33]

$$\Delta G^0 = E(D/D^{\bullet+}) - E(RX/R^\bullet + X^-) - E_{00} - e^2/\epsilon_s r \quad (9)$$

where E(D/D$^+$) is the oxidation potential of the donor, E_{00} is the excited-state (S_1) energy of the donor, and $e^2/\epsilon_s r$ is the Coulombic energy experienced by the radical ion pair at a transfer distance r in a solvent with the static dielectric constant, ϵ_s. The oxidation potential values for the donors determined by cyclic voltametry are listed in Table 5.[12] E_{00} values for the phenothiazines have been obtained from the crossing points of the normalized fluorescence excitation and the emission spectra and are also given in Table 5. The electron-transfer distance, r is the sum of the radii of donor and acceptor. The radii were calculated from the molecular volumes of the donor and the acceptor using Edward's atomic volume addition method.[34] The average radii of donors (PTH and MPTH) and acceptors (CCl_4 and $CHCl_3$) are 3.3 and 2.6 Å, respectively. Using these values, the Coulombic attraction energy ($e^2/\epsilon_s r$) for the ion pair is estimated to be about 0.065 eV. The ΔG^0 values thus calculated for the ET processes in the systems studied in AN are all negative (Table 5). Hence, the ET processes studied are thermodynamically favorable.

The observed bimolecular quenching rate constant, k_q, is related to the free energy of activation for the ET, ΔG^*_{ET}, by the Eyring equation, (eq 10).

$$k_q = \frac{k_d}{1 + \frac{k_d}{\nu K_d}\exp\left\{\frac{\Delta G^*_{ET}}{RT}\right\}} \qquad (10)$$

where $K_d = k_d/k_{-d}$ is the diffusional equilibrium constant, ν is the frequency factor, R is the universal gas constant, and T is the absolute temperature. The equilibrium constant K_d is usually close to unity for neutral donor−acceptor pairs.[35−38] The value of the bimolecular diffusion-controlled rate constant (k_d) in AN is on the order of $(2-4) \times 10^{10}$ dm^3 mol^{-1} s^{-1}.[39] According to Sutin,[37] the frequency factor ν, which represents the dynamic properties of the solvent rearrangement, can range from 10^{12} to 10^{14} s^{-1}. A value of ν of 10^{11} s^{-1} has been proposed by Rehm and Weller[33] and that of 10^{13} s^{-1} has been proposed by Marcus.[40]

Saveant has shown that even in DET reactions, as proposed by Marcus[27] for homogeneous outer sphere ET reaction, the free energy of activation (ΔG^*_{ET}) and the driving force (ΔG^0) for ET are related through a quadratic relation,[23a] eq 11

$$\Delta G^*_{ET} = \Delta G^*_0\left(1 + \frac{\Delta G^0}{4\Delta G^*_0}\right)^2 \qquad (11)$$

where ΔG^*_0 is the intrinsic free energy barrier, i.e., the activation energy for the ET reaction at $\Delta G^0 = 0$. ΔG^*_0 is related to the total reorganization energy, λ, by eq 12.

$$\Delta G^*_0 = \frac{\lambda}{4} \qquad (12)$$

The total reorganization energy is composed of two contributions, i.e.,

$$\lambda = \lambda_i + \lambda_s \qquad (13)$$

where λ_i and λ_s are the intramolecular and solvent reorganization energies, respectively. Solvent reorganization refers to the effects of orientational changes of the solvent molecules surrounding the reactants during the ET and are calculated from eq 14.

$$\lambda_s = e^2\left\{\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{d}\right\}\left\{\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right\} \qquad (14)$$

where r_D and r_A are the radii of the donor and the acceptor, respectively, and d is the internuclear separation between the two in the encounter complex. In practice, d is taken as the sum of their radii. ϵ_{op} and ϵ_s are the optical and static dielectric constants of the solvent, respectively. With $r_D = 3.3$ Å and $r_A = 2.6$ Å the value of λ_s was estimated to be 1.32 eV in AN.

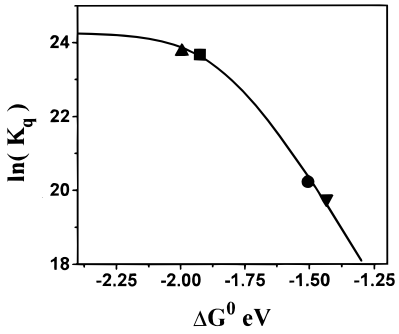


Figure 5. Variation of ln k_q with ΔG^0 in acetonitrile (AN). The experimental points are PTH−CCl_4 (▲), MPTH−CCl_4 (■), PTH−$CHCl_3$ (●), and MPTH−$CHCl_3$ (▼). The solid curve is calculated according to eq 10.

In the systems studied, the variations of k_q with ΔG^0 were correlated according to eq 10 and shown in Figure 5. A fairly good correlation gives the values of k_d, ν, and λ as 3.5×10^{10} dm^3 mol^{-1} s^{-1}, 1.6×10^{13} dm^3 mol^{-1} s^{-1}, and 3.38 eV, respectively.

Knowing the total reorganization energy, λ_i is calculated from eq 13 and equals 2.06 eV. Such a high value for λ_i indicates that the reactants (donor and acceptor) undergo a large structural change during the ET process. This very high value of λ_i is quite expected for the systems studied. There is a large structural change in the acceptor moiety (CCl_4) due to the breaking of the C−X bond during the ET process. Thus the major contribution toward λ_i is due to the C−X bond breaking. However, it has been experimentally observed that the phenothiazines are nonplanar molecules with a dihedral angle between the benzene rings of the phenothiazines of about 145° for PTH and 158° for MPTH.[17] On radical cation formation the molecule adopts almost a planar configuration.[18] Thus the donor phenothiazines should also have some contribution toward λ_i. Kowert[41] has shown that the self-exchange reaction of phenothiazine is associated with an intramolecular reorganization energy of 0.32 eV.

Saveant has considered the intramolecular reorganization energy in haloalkanes (λ_A) in terms of the C−X bond dissociation energy (D_{RX}) as in eq 15

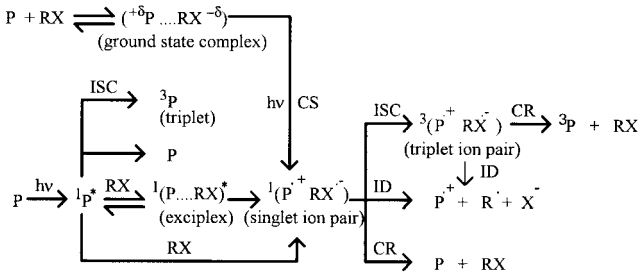
$$\lambda_A = (1 - \gamma)^2 D_{RX} \qquad (15)$$

where γ is a factor introduced to consider the attraction between $R^\bullet$ and X^-. The average value of bond dissociation energy for the acceptors after the correction for the entropy in the gas phase is around 2.8 eV. The λ_A obtained from the total λ after subtracting the solvent and phenothiazine contribution is 1.74 eV. This gives an estimate for γ of 0.203. The γ values reported for the CCl_4 and $CHCl_3$ in the gas phase are 0.31 and 0.23, respectively.[31a] Our correlated value of γ is lower than the reported gas-phase value. This is quite expected because in liquid phase the attraction between the products decreases due to the presence of the surrounding polar medium.

3.4. Picosecond Laser Flash Photolysis Studies. The rationale behind these experiments can be understood following the mechanistic Scheme 3, proposed for the systems investigated.

On photoexcitation the free phenothiazine molecules produce the S_1 state ($^1P^*$), which can effectively produce the singlet ion pair state (SIPS), $^1(P^{\bullet+}\cdots RX^{\bullet-})$, during the interaction with the chloroalkanes (RX) depending on the solvent polarity either via the formation of the intermediate exciplex $^1(P\cdots RX)^*$ or by direct ET during the encounter. The SIPS can also be produced

SCHEME 3



by an instantaneous charge separation (CS) on photoexcitation of the phenothiazine−chloroalkane ground-state complex, $(^{+\delta}P\cdots RX^{-\delta})$. The SIPS thus produced can undergo a number of possible reactions. An intersystem crossing process (ISC) leads to the triplet ion pair state, $^3(P^{\bullet+}\cdots RX^{\bullet-})$, which eventually can undergo charge recombination (CR) to produce the triplet state of the phenothiazines. Depending on the solvent polarity, the SIPS can undergo CR to give the reactants (P + RX) back or ion dissociation (ID), in which the breaking of the C−X bond occurs, to produce the solvent-separated ions ($P^{\bullet+}$ and X^-) and haloalkyl radical ($R^\bullet$). The ID process can also take place from the triplet ion pair state. In high-polarity solvents such as AN the SIPS can be very short-lived due to the instantaneous dissociation of the C−X bond (DET, section 3.3), and in that case ISC and CR from the SIPS would be very unlikely and the most dominating channel would be the ID from SIPS.

Picosecond laser flash photolysis experiments were carried out using 355 nm pulses to confirm various possible steps involved in Scheme 3. In one set of experiments the concentration of the chloroalkanes was kept reasonably high (∼0.4 mol dm^{-3}) to assure an appreciable amount (∼40%) of ground-state complexation. In the second set of experiments the concentration of the chloroalkanes was kept reasonably low (∼0.025 mol dm^{-3}) to assure minimum contribution from the ground-state complexation (∼3%). The results of these experiments are discussed below. In these experiments the laser intensity was deliberately kept low enough (∼3 mJ) to avoid direct photoionization of the phenothiazines by bi- or multiphotonic processes in typical polar solvents like AN.

3.4.1. Picosecond Laser Flash Photolysis with Higher Concentration of the Chloroalkanes. Photoexcitation of the phenothiazine solutions in all the solvents used (CH, EA, and AN) with 35 ps, 355 nm laser pulses gives a broad transient absorption band at ∼640 nm due to the $S_1 \rightarrow S_n$ transition of phenothiazine.[11] As the time delay between the pump and analyzing beams increases, the absorbance at 640 nm decreases and concomitantly an absorption peak at 460 nm increases. The absorption peak at 460 nm is attributed to the $T_1 \rightarrow T_n$ absorption and is produced via the ISC process from the S_1 state.[11] Lifetimes measured from the decay of the transient absorption at 640 nm agree well with those obtained from fluorescence lifetime measurements. In the presence of a high concentration (∼0.4 mol dm^{-3}) of CCl_4 or $CHCl_3$ the picosecond laser flash photolysis of PTH or MPTH in the above three solvents, besides the absorption peak due to the S_1 state at 640 nm, gives one more transient absorption peak at about 525 nm due to the phenothiazine cation radicals ($PTH^{\bullet+}$ or $MPTH^{\bullet+}$) even at the zero delay between the pump and the analyzing beam. It is seen that as the concentration of the chloroalkane is increased, the 525 nm absorption at zero delay gradually increases (Figure 6a). Because of the overlap of the absorption bands for cation radical and $S_1 \rightarrow S_n$ transition, the actual absorbance due to cation radical at zero delay was obtained by

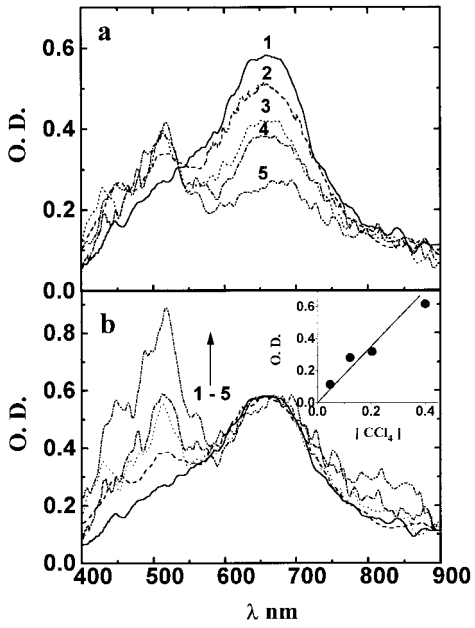


Figure 6. (a) Transient absorption spectra as obtained in the picosecond laser flash photolysis of the MPTH−CCl_4 system in AN at zero delay between the pump and the analyzing beams at different concentrations of CCl_4: (1) 0, (2) 0.047, (3) 0.119, (4) 0.203, and (5) 0.398 mol dm^{-3}. (b) Transient absorption spectra in part a normalized for the 640 nm band. The concentrations of CCl_4 for spectra 1, 2, 3, 4, and 5 are similar to those in part a. Inset: Plot of corrected absorption signal of MPTH cation vs the concentration of CCl_4.

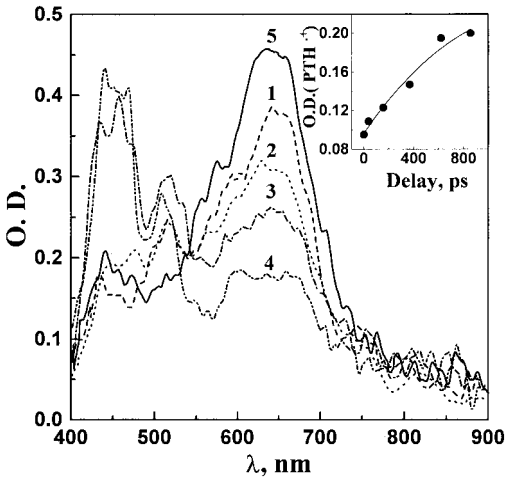


Figure 7. Picosecond transient absorption spectra obtained for the PTH−CCl_4 ($[CCl_4]$ = 0.026 mol dm^{-3}) system in AN at different time delay between the pump and the analyzing beams: (1) 0, (2) 158, (3) 620, and (4) 858 ps. Spectrum 5 is the transient absorption spectrum obtained at 0 ps for only PTH in AN. Inset: Plot of the corrected absorption signal of PTH cation vs delay between the pump and the analyzing beam.

subtracting the normalized (at 640 nm) zero delay transient absorption spectra obtained with the phenothiazines in the respective solvents in the absence of any quencher. Figure 6b shows the transient absorption spectra normalized at 640 nm for the MPTH−CCl_4 system in AN for different concentrations of CCl_4. The inset of Figure 6b shows the plot of the corrected absorbances due to the cation radical obtained by the above method vs the concentration of the CCl_4 used, which shows that within experimental error the cation radical signal at zero delay varies linearly with the concentration of the CCl_4 used and passes through the origin at zero concentration of the chloroalkane. Thus, it is evident that the cation radicals have been produced due to the instantaneous charge separation (CS) in the photoexcited phenothiazine−chloroalkane ground-state complexes to produce the SIPS.

The addition of chloroalkanes also reduced the triplet yield of phenothiazines. The decrease in yield of the triplet may be due to various reasons. Firstly concentration of the S_1 state produced on flash photolysis decreases due to removal of a fraction of the ground-state free phenothiazines by complex formation. Also, apart from the ISC process, which produces the triplet state directly, the S_1 state finds another competitive decay route via quenching by the chloroalkanes. However, CR (see Scheme 3) in the triplet ion pair state is a new route in the presence of the chloroalkanes to generate the triplet. So the total yield of the triplet is governed by all these processes. It is also seen that in the presence of the chloroalkanes the phenothiazine triplet yield is more in less polar solvent (like CH) than in a more polar solvent, like AN. Since in a polar solvent the SIPS can undergo preferentially the ID process, the lower triplet yield in such a solvent in comparison to that in a nonpolar solvent indicates that depending on the solvent polarity a portion of the phenothiazine triplet may also be generated from the SIPS via the ISC process followed by CR in the latter state.

To understand the above processes we also carried out a picosecond laser flash photolysis experiment on the phenothiazines in neat CCl_4. In this solvent the S_1 state of the phenothiazines is almost instantaneously quenched, as indicated by the transient absorption spectra at zero delay showing no absorption at 640 nm. Thus, if the triplet state of the phenothiazines was being produced only from the ISC process in the free S_1 state, no triplet absorption in neat CCl_4 is expected. However, formation of the triplet state, although with low yield, due to laser flash photolysis of the phenothiazines in neat CCl_4 confirms that the triplet has been produced from the SIPS via the ISC and CR processes. CCl_4, being a nonpolar solvent (ϵ_s = 2.24), favors the CR process as compared to the ID process. The low triplet yield in neat CCl_4 indicates that the SIPS mostly undergoes direct CR to give the reactants back. It was also qualitatively seen that the cation radical yield derived from the optical absorbance at 525 nm increases from nonpolar CH to polar AN through EA. This shows that the SIPS does not undergo the ID process in low-polarity solvents, increasing the possibility of exciplex formation as compared to polar AN solvent.

3.4.2. Picosecond Laser Flash Photolysis with Lower Concentration of the Chloroalkanes. In laser flash photolysis of the phenothiazines with lower concentrations of the quenchers (<0.05 M), where the effect of the ground-state complex formation can be neglected, it is observed that, besides the strong 640 nm band due to the $S_1 \rightarrow S_n$ absorption, a small absorption signal corresponding to the cation radicals of the phenothiazines was also seen at 525 nm at zero delay. As the delay between the pump and the analyzing beams is increased, the absorption peak due to the S_1 states of the phenothiazines (640 nm) reduces gradually. At the same time two absorption bands, one at 460 nm corresponding to the triplet state of the phenothiazines and the other at 525 nm corresponding to the cation radical of the phenothiazine, are seen to increase gradually, although the increase in the latter is not appreciable, as shown in Figure 7 for the PTH−CCl_4 system in AN. However, due to strong overlap between the absorption bands of the singlet, triplet, and cation radical of the phenothiazines, neither meaningful kinetic data nor quantitative information about the different reaction pathways could be extracted. To nullify the overlapping effect of the $S_1 \rightarrow S_n$ absorption band, we subtracted the normalized (at 640 nm) transient absorption spectra at zero delay as obtained

from the excitation of the phenothiazine solutions alone in respective solvents from the transient absorption spectra obtained in the presence of the chloroalkanes. The resultant transient absorption spectra thus obtained at different delays clearly indicate that the absorption band due to the cation radicals (525 nm) gradually increases with the delay between the pump and probe beams. The inset of Figure 7 shows the plot of the transient absorbance at 525 nm for the PTH−CCl_4 system in AN as obtained following the correction for the $S_1 \rightarrow S_n$ absorption vs the time delay between the pump and analyzing beams. Although the increase of the cation signal with time delay is evident from this plot, we could not perform any meaningful kinetic analysis on these data because of the large overlapping of the $T_1 \rightarrow T_n$ and cation absorption bands. It is, however, qualitatively evident that the cation radical signal increases with time and this increase is related to the quenching of the S_1 state of the phenothiazines by the chloroalkanes, resulting in the ion pair state $^1(P^{\bullet+}\cdots Q^{\bullet-})$, either by direct ET during encounter or via the exciplex formation as shown in Scheme 3.

In picosecond laser flash photolysis experiments it is seen that the behavior of PTH and MPTH is qualitatively very similar. The presence or absence of the labile hydrogen at the 10th position of the phenothiazine moiety, thus, does not affect the photoinduced CS and ET reactions. The difference in the reactivity of PTH and MPTH with the chloroalkanes in their ground and excited states is only due to the differences in their oxidation potentials. Present results suggest a CT/ET type of donor−acceptor interactions between the phenothiazines and the chloroalkanes.

4. Conclusion

Phenothiazines are seen to form weak ground-state complexes with the chloroalkanes. The excited singlet states (S_1) of the phenothiazines are also seen to interact with the chloroalkanes either via the exciplex formation or via the DET processes depending on the solvent polarity. A modified Marcus theory applicable for DET processes was applied for the above system studied. Picosecond laser flash photolysis experiments indicate that the cation radicals of the phenothiazines are produced both by the interaction of the S_1 states of the phenothiazines with the chloroalkanes and by the instantaneous CS in the photoexcited ground-state complexes. A detailed photochemical kinetic scheme is proposed to explain the observed results for the phenothiazine−chloroalkane systems. Both PTH and MPTH are seen to behave similarly except in the strength of their interaction, and the latter is seen to be related to the oxidation potentials of these compounds directly.

Acknowledgment. We are very thankful to one of the reviewers for valuable suggestions regarding the DET mechanism and its energetics.

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$$E^{\mathrm{SCE,AN}}_{\mathrm{Cl/Cl^-}} = E^{\mathrm{SHE,aq.}}_{\mathrm{Cl/Cl^-}} + \Delta E^{\mathrm{AN}}_{\mathrm{SHE\rightarrow SCE}} - \Delta G^0_{\mathrm{tr}}(\mathrm{Cl^-})$$

where $\Delta E^{\mathrm{AN}}_{\mathrm{SHE\rightarrow SCE}}$ is the potential shift when passing from the SHE in AN to aqueous SCE (−0.255 V) and $\Delta G^0_{\mathrm{tr}}(\mathrm{Cl})^-$ is the standard free energy of transfer of Cl^- ion from water to AN (0.43 eV[30c]). Thus the value of $E^{\mathrm{SCE,AN}}_{\mathrm{Cl/Cl^-}}$ is estimated to be 1.89 V. (b) Thornton, A. T.; Laurence, G. S. *J. Chem. Soc., Dalton Trans*. **1973**, 1632. (c) Cox, B. G.; Hedwig, G. R.; Parker, A. J.; Watts, D. W. *Aust. J. Chem*. **1974**, *27*, 477.

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