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Change in Reaction Mechanism with Driving Force in Photoinduced Dissociative Electron Transfer (PDET) Reaction − A Subpicosecond Transient Absorption Study

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Electron-transfer reactions that are dissociative in nature can proceed via two mechanisms, stepwise and concerted. In this work, the mechanism of photoinduced dissociative electron transfer between carbon tetrachloride and four phenothiazine derivatives has been investigated by subpicosecond transient absorption study. Clear evidence was obtained for the stepwise mechanism for the reaction between phenothiazine and carbon tetrachloride, whereas for the other three derivatives concerted reaction is seen to be operative. The mechanism of the dissociative electron-transfer reaction has been correlated with the driving force of the reactions studied. A crossover of reaction mechanism from concerted to stepwise was observed with the increase in the reducing power of the phenothiazine donor, i.e., with the increase in the driving force of the reaction. It was also shown that changes in solvent polarity can trigger the crossover of the reaction mechanism. The change in the reaction mechanism with the driving force of the reaction has been explained by potential energy surfaces involved in the two different mechanisms.

1. Introduction

The main aim of studying the dynamics of photoinduced electron transfer (PET) reactions is to improve the efficiency of the charge separation (CS) process by minimizing the effects of back electron transfer (BET), an energy wasting process. The BET process reduces the net electron transfer (ET) yield. Among several possible ways to prevent BET, dissociative electron transfer (DET) reactions, i.e., ET reactions associated with bond breaking, are certainly attractive. Thus, if a donor or an acceptor or both undergo cleavage of any of their bonds immediately following the ET, the BET process could be totally eliminated maximizing the net ET yield.

The occurrence of the thermal and electrochemical DET processes is well documented.[1,2] Saveant and his group have modified the famous Marcus theory of the outer sphere electron transfer for the DET process.[3] The DET process can follow two different mechanisms as shown below.

$$\text{stepwise:}\ \mathrm{D} + \mathrm{RX} \leftrightharpoons [\mathrm{D}^{+} + \mathrm{RX}^{-}] \rightarrow \mathrm{D}^{+} + \mathrm{R}^{\bullet} + \mathrm{X}^{-}$$

$$\text{concerted:}\ \mathrm{D} + \mathrm{RX} \rightarrow D^{+} + \mathrm{R}^{\bullet} + \mathrm{X}^{-}$$

where D and RX are electron donor and electron acceptor, respectively.

However, whether a given DET reaction proceeds by a stepwise or concerted mechanism is an important question in both electrochemical and photochemical processes. Further, by altering conditions, whether a stepwise ET process can be made to follow a concerted path or vice versa is an exciting proposal. In this connection, Saveant and co-workers have carried out several studies regarding such crossover of the mechanism of DET reaction, involving the ground state of the reactants, in electrochemical processes.[4] They have studied DET processes of several aliphatic[2b,3,5] and aromatic halides[2b,6] by electrochemical means and have shown that for aromatic halides the DET process goes through a stepwise mechanism, whereas for simple aliphatic halides a concerted path is followed. For simple aliphatic halides, it is proposed that the LUMO (σ^*) energy is so high that the incoming electron from a donor cannot reside there even temporarily and cleave the carbon−halogen bond concertedly. In the case of aromatic halides, due to the existence of low energy π^* orbital as LUMO, the incoming electron from the donor can be trapped for some time before the rupture of carbon−halogen bond takes place in a successive step. For example, Andrieux et al.[6a] have shown that the DET in halobenzene follows a stepwise mechanism whereas with a simple aliphatic halide, such as CCl_4 [5a] and *n*-butyl halide,[3,5b] the concerted mechanism is followed. There are several studies that show that the electron attachment reaction of aliphatic halides follows a concerted mechanism.[7] The present study will show that even in the case of an alkyl halide, such as CCl_4, the corresponding anion radical exists for a short time and follows a stepwise mechanism rather than a concerted mechanism as observed in the electrochemical experiments. Although several electrochemical studies have been carried out, only a few studies on PDET[8,9] are available. In the latter cases, the mechanism of the DET reactions is determined on the basis of quantum yield measurements.[10] A unit quantum yield in a PDET reaction has been used as an indication of the concerted mechanism, and the reaction with a quantum yield of less than unity is indicative of a two-step process.[10a] Recently Robert et al. has shown that in the case of the PDET reactions, even if the reaction follows the concerted mechanism, the quantum yield need not be unity[11] because of the competition between BET and the bond cleavage process. The result of such a competition depends on the matrix coupling element for different potential energy surfaces involved in the reactions. Very recently it is also shown by Costentin et al.[12] that the quantum yield for the two-step process can also approach unity, and the value need not be smaller than that for

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the concerted mechanism. Thus, proposing the PDET mechanism solely on the basis of the quantum yield measurement may be erroneous.

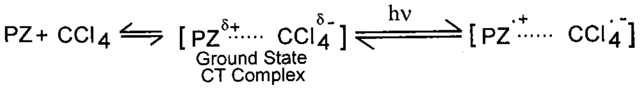
The choice of one mechanism over the other depends on several factors. Among others, it has been shown theoretically[13] and in several electrochemical experiments[14−16] that the stepwise mechanism is favored at higher driving force ($-\Delta G^\circ$) of the reaction. The switchover from stepwise to concerted mechanism could be triggered by decreasing the driving force for the ET reaction, which, for a given family of reactants, can be changed either by changing the standard potential of donor or acceptor or by changing the nature of reaction medium, e.g., by changing the polarity of the medium. In several electrochemical studies, such a switchover in the reaction mechanism has been demonstrated by varying the driving force of the ET reaction.[14a,15b,16] These studies are usually conducted using a cyclic voltametry technique. As the time resolution for these studies is poor ($\lesssim \mu$S), if there is any intermediate that has a still shorter lifetime (e.g., a few ns or ps), the voltammogram may not show any signature for such short-lived intermediate.

Recently, we have studied the ET reactions between phenothiazine (PTH) and chloroalkanes, namely $CHCl_3$ and CCl_4,[17] and have shown that these reactions follow a dissociative mechanism instead of an outer sphere ET mechanism. However, the mechanistic details of the ET reaction could not be resolved due to limited time resolution (~35 ps) of the flash photolysis instrument used. In the present study, we report investigations in subpicosecond time domain on the PDET reaction between PTH and three of its derivatives (PZ), namely promethazine (PMZ), chloropromazine (CPZ), and *N*-methyl-phenothiazine (MPTH) with CCl_4 as acceptor. The aim of the present study is to show how the change in the reducing power of the donor molecule affects the overall mechanism of a PDET reaction and whether the mechanism can be switched over for a given donor−acceptor pair by changing properties of the reaction medium, e.g., polarity. To the best of our knowledge, this is the first report where the change in reducing power of the electron donor causing a crossover from the stepwise to concerted mechanism has been demonstrated in a PDET reaction by directly monitoring the reaction intermediate in real time. For the first time, the existence of CCl_4 radical anion in solution at room temperature has been demonstrated. The present results will also show how the changes in the polarity of the reaction medium can cause a crossover from one mechanism to other in a PDET reaction.

2. Methods and Materials

Ground-state absorption measurements were carried out using a Shimadzu UV−vis spectrometer (model 160A). A home-built subpicosecond transient absorption spectrometer was used to monitor the transients. Briefly, laser pulses of 70 fs duration at 620 nm with 100 pJ energy are generated from an argon-ion-pumped colliding-pulse-mode (CPM) locked dye laser oscillator. These low energy pulses from the CPM dye laser were amplified by a five-stage dye amplifier pumped by a 30 Hz Nd:YAG laser to give about 300 mJ pulses of 300 fs. Pump pulses at 310 nm, generated by passing the fundamental 620 nm pulse through a 0.5 mm BBO crystal, were used for the excitation of the sample. The residual fundamental light was passed through a 1 cm quartz cell containing flowing water to generate a white light continuum in the wavelength range 400−950 nm. The continuum white light was used for probing the transient produced by the pump pulse at different time delays, which is controlled by an optical delay line. The sample was flowed through a 2 mm thick quartz cell. The transient absorption spectra were recorded using the dual diode array based optical multichannel analyzer. Kinetic studies on the transients were done by monitoring the wavelength of interest with an interference filter (bandwidth 10 nm) using two photodiodes coupled with boxcar integrators. One photodiode was used for monitoring the transient absorption from the sample and the other one was used to monitor the continuum probe light. The instrument response, measured from the growth of the $S_1 \rightarrow S_n$ absorption band of 1,4-diphenylbutadiene in cyclohexane solution at 650 nm,[18] is found to be 500 fs.

SCHEME 1



PTH (Fluka) and MPTH (Acros Organics) were purified by repeated crystallization from methanol. CPZ and PMZ hydrochloride (both from Sigma) were used as received. All of the solvents used were spectroscopic grade from Spectrochem, India.

3. Results and Discussion

3.1. Transient Absorption Study. In our previous study,[17] it was found that the addition of chloroalkane, such as CCl_4 and $CHCl_3$, to the PZ solution in acetonitrile (AN) causes a change in the ground state absorption spectra of the PZ due to the formation of charge transfer (CT) complex in the ground state. Fluorescence quenching and picosecond transient absorption studies supported that the changes in the ground state absorption characteristics of PZ on the addition of chloroalkane are due to CT complex formation. It was also shown that if the concentration of chloroalkane is kept sufficiently high, the extent of ground-state complexation will be high and, on photoexcitation by laser light, the CT complex will be excited to give the charge separated species (Scheme 1). To study the dynamics of the charge separation and charge recombination in the excited state of the CT complex, for the present study, we have always used high concentration (~0.5 M) of CCl_4 so that the ground state complex formation will be maximum.

The transient absorption spectra have been recorded for all four PZ in acetonitrile (AN), both in the presence and the absence of CCl_4. Curve A in Figure 1 shows the transient absorption spectra for PTH in AN at zero time delay after the photoexcitation by the 310 nm laser pulse. This spectrum shows a single broad absorption band with maxima at ~650 nm and has been assigned to $S_1 \rightarrow S_n$ absorption of the PTH.[19] Similar observations have been made for the other three PZ. In the presence of high concentration of CCl_4 (~0.5 M), it was seen that the absorption band due to the $S_1 \rightarrow S_n$ transition is drastically reduced and at the same time a new absorption band appears at ~530 nm (spectrum B in Figure 1). The new absorption band is due to the PTH cation radical ($PTH^{\bullet+}$).[17] Similarly, for the other three PZ, the absorption band[17,20] for the respective cation radicals appears at zero time delay in the presence of CCl_4. The appearance of $PZ^{\bullet+}$ immediately after the laser excitation is due to a very fast charge-transfer process that takes place in the photoexcited state of the CT complex formed between PZ and CCl_4 in the ground state (Scheme 1).

Because only one absorption band due to the cation radical, $PZ^{\bullet+}$, is observed in the presence of 0.5 M CCl_4, we have recorded the kinetic trace at 530 nm where the $PZ^{\bullet+}$ has absorption maxima. Figure 2 shows the temporal evolution of the transient produced by laser excitation and monitored at 530 nm in AN for PTH [A] and CPZ [B], both in the presence and the absence of CCl_4. As Figure 1 shows that the S_1 state has

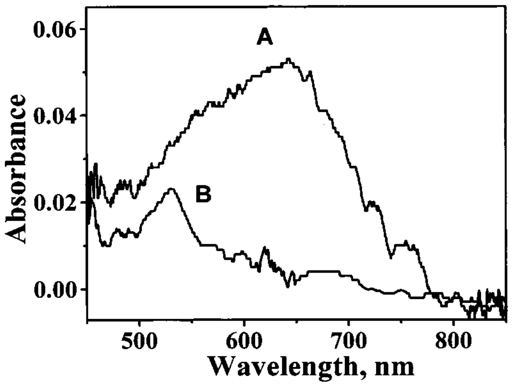


Figure 1. Transient absorption spectra of PTH in acetonitrile in the absence of CCl_4 (A) and in the presence of 0.5 mol dm^{-3} of CCl_4 (B) at zero time delay between the pump and probe pulse. The appearance of 530 nm absorption band in the presence of CCl_4 indicates the formation of PTH cation radical by photoinduced charge-transfer reaction.

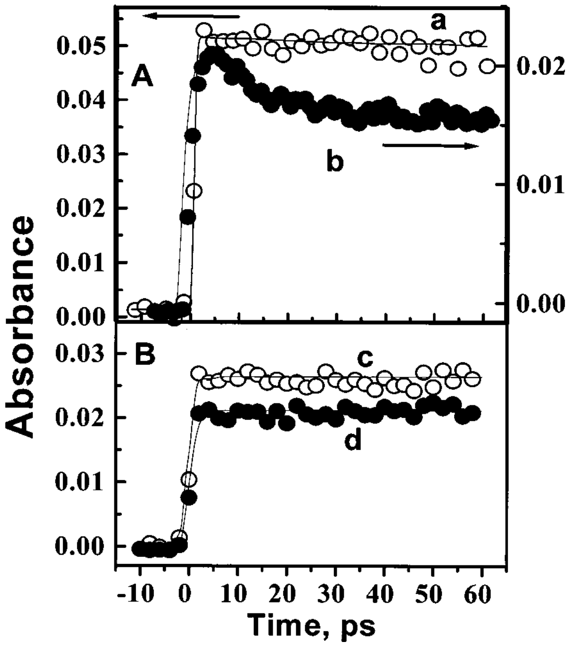


Figure 2. The kinetic traces recorded in acetonitrile at 530 nm for PTH (A) and CPZ (B) in the absence of CCl_4 (○, a,c) and in the presence of 0.5 mol dm^{-3} of CCl_4 (●, b,d). The decay of PTH cation radical absorbance indicates the presence of back electron-transfer process.

some small absorption in the 530 nm, the temporal evolution in the absence of CCl_4 (curve a and c in Figure 2) is due to the S_1 state of PZ only. These kinetic traces do not show any decay even up to 60 ps, which is expected due to the long lifetime of the S_1 state (>1 ns).[17] The decay kinetics is similar in the entire span of the absorption band. All of the other PZ shows similar temporal evolution in the absence of CCl_4. It is evident from Figure 1 that the kinetic traces recorded at 530 nm for all PZ in the presence of 0.5 M CCl_4 are due to the $PZ^{\bullet+}$ only. Temporal characteristics of $PZ^{\bullet+}$ for other pairs, namely PMZ−CCl_4 and MPTH−CCl_4, are very similar to that of the CPZ−CCl_4 pair.

From Figure 2 it is seen that the transient absorption due to $PTH^{\bullet+}$ at 530 nm shows a fast decay (curve b) with a decay time of 8.5 ps. However, for the other three PZ, the transient absorption due to $PZ^{\bullet+}$ (curve d) does not decay at all up to 60 ps. The fast decay of $PTH^{\bullet+}$ can be assigned to the BET process in the contact ion pair (CIP) produced on charge transfer in the excited CT complex. These processes are depicted in Scheme 2. The CIP can decay by two different channels: (i) a BET process, by which the $PZ^{\bullet+}$ combines with its geminate radical anion partner, $CCl_4^{\bullet-}$, and is responsible for the fast decay of $PZ^{\bullet+}$, and (ii) separation of the geminate ions and concomitantly irreversible dissociation of $CCl_4^{\bullet-}$ (see Scheme 2). The former process will result in the decrease in the absorbance due to $PZ^{\bullet+}$. Thus, the decay in the $PTH^{\bullet+}$ absorbance indicates the occurrence of the BET process and also confirms the formations of a CIP state on photoexcitation of the CT complex. Absence of any decay of cation radical for other three PZs indicates the absence of the BET process and hence the absence of CIP formation for these three PZ in AN.

However, there are several other possibilities that can give rise to different kinetic behavior of the photoexcited CT complex. One such possibility is that there could be a difference in the rate for the charge separation process in different CT complexes. Some pairs achieve slow charge separation as compared to others. However, such possibility can be excluded on the basis that, in the presence of CCl_4, all of the four PZ used in the present study show an absorption band due to $PZ^{\bullet+}$ at zero time delay between pump and probe pulse. Thus the formation of the respective cation radical of PZs, immediately after the laser light excitation, indicates that the charge separation in the photoexcited CT complex for all the PZ used is very fast. Another possibility that could make a difference in the kinetics between PTH and other PZ is the reaction of the $PTH^{\bullet+}$ produced in the cage with the dissociation product of the acceptor, CCl_4. The anion radical, $CCl_4^{\bullet-}$, formed following ET, dissociates immediately to $CCl_3^{\bullet}$ radical and Cl^- ion. Because of the electron withdrawing effect of three chlorine atom, the $CCl_3^{\bullet}$ is an electron deficient species and it cannot transfer an electron to $PTH^{\bullet+}$. Similarly, due to unfavorable reduction potential, the reduction of the $PTH^{\bullet+}$ by Cl^- (eq 1) is not energetically possible.

$$PTH^{\bullet+} + Cl^- \rightarrow PTH + Cl \tag{1}$$

The free energy for the above-mentioned electron transfer reaction is given by eq 2.

$$\Delta G^\circ = E(Cl/Cl^-) - E(PTH/PTH^{\bullet+}) \tag{2}$$

where E represents the reduction potential of the respective couples. The values of $E(Cl/Cl^-)$ and $E(PTH/PTH^{\bullet+})$ are 1.89 and 0.59 V,[17] respectively. This gives the ΔG° value as 1.30 eV, which is highly positive, and hence reaction 2 is not energetically favorable. However there is an another possibility of the deprotonation of the $PTH^{\bullet+}$ as it has a labile hydrogen atom attached to the positively charged nitrogen atom. It is reported that the $PTH^{\bullet+}$ undergo the deprotonation to give phenothiazine neutral radical, $PT^{\bullet}$. However, Smith et al.[21] have shown that the process of deprotonation in AN is very slow with decay time ~2.3 μS. Thus, the decay observed for the $PTH^{\bullet+}$ cannot be due to the deprotonation reaction. One more possible way by which the $PTH^{\bullet+}$ can decay is the proton transfer to the caged product Cl^-. The occurrence of the proton transfer can also be excluded from the solvent-dependent kinetic studies. If such reaction is responsible for the difference in the kinetic behavior of the $PZ^{\bullet+}$, then we should expect the same behavior in the other solvent medium, too. We have studied the kinetic bahaviour of PTH and MPTH in other solvents also, where we observed different kinetic behavior as compared to that in AN. Such differences in kinetic behavior observed in

SCHEME 2

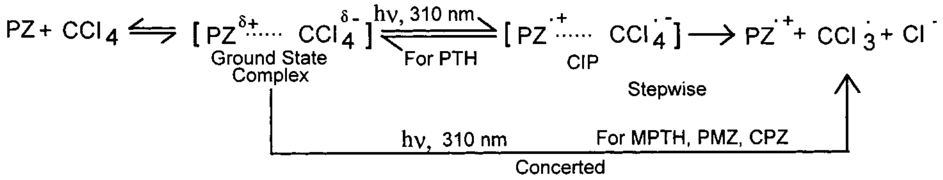


TABLE 1: Redox Potential of PZ and Free Energy of the ET Reaction in AN

donor	E_{00}, eV (λ_{00}, nm)	r (nm)	$E_{1/2}^{\mathrm{PZ}}$ (V)[a]	$-\Delta G°$, (eV)	mechanism
PTH	3.18 (390)	0.344	0.590	2.00	stepwise
MPTH	3.25 (382)	0.355	0.730	1.92	concerted
PMZ	3.32 (374)	0.400	0.865	1.85	concerted
CPZ	3.22 (385)	0.407	0.835	1.78	concerted

[a] vs SCE in acetonitrile.

different solvents confirm that the cage reaction cannot account for the different kinetic behavior seen for PTH and other three PZ in AN.

Thus, in the latter three cases (viz., MPTH, CPZ, and PMZ), the excitation of the ground-state CT complex is followed by immediate dissociation of the C−Cl bond of CCl_4 on ET. Hence, the PDET processes for these three PZ follow a concerted mechanism while the stepwise mechanism is operative for PTH. The reactions described above in AN are presented by Scheme 2.

The differences in the decay behavior of $PZ^{\bullet+}$ for PTH and other three PZ can be explained on the basis of the difference in the driving force for the ET reactions, which governs the mechanism of the overall reaction.

3.2. Energetics of the ET Reaction. The oxidation potential ($E_{1/2}$) of PZ and the $\Delta G°$ for the ET reactions between PZ and CCl_4 have been listed in Table 1, and indicate that PTH is the strongest donor among all of the PZ used. In the other three PZs used, the *N*-hydrogen atom in PTH has been replaced by either alkyl or aminoalkyl group. It is expected that such a substitution by electron donating alkyl or aminoalkyl groups should make PZ the better donor. However, the opposite trend observed in the $E_{1/2}$ values of PZ results from the nonplaner structure of the phenothiazine moiety with dihedral angle of ∼150° between the two benzene rings.[22] Because of the H-intra configuration[23] of PTH, the lone-pair electron orbital on the nitrogen atom is directed outwardly and hence is easily accessible to the electron acceptor. However, due to substitution of the *N*-hydrogen atom by a bulkier group, PTH moiety is forced to attain H-extra configuration, in which the lone-pair electron orbital is directed inside and is less available for electron acceptors. Because of this, the PTH derivatives used are weaker donors than PTH. Hence, the $E_{1/2}$ values of MPTH, CPZ, and PMZ are higher than PTH.

The free energy change, $\Delta G°$, for the ET reaction between PZ and CCl_4 is given by the following equation

$$\Delta G° = E(\mathrm{PZ/PZ^{\bullet+}}) - E(\mathrm{CCl_4/CCl_3^{\bullet} + Cl^{-}}) - E_{00} - \frac{e^2}{\epsilon_s r} \tag{3}$$

where $E(\mathrm{PZ/PZ^{\bullet+}})$ and E_{00} are oxidation potential and the excited state (S_1) energy of PZ 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 E_{00} values for PZ in AN obtained from the crossing points of the normalized fluorescence and excitation spectra are listed in Table 1. 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 estimated using Edward's atomic volume addition method.[24] The $E(\mathrm{CCl_4/CCl_3^{\bullet}+Cl^{-}})$ value is calculated from the following equation:

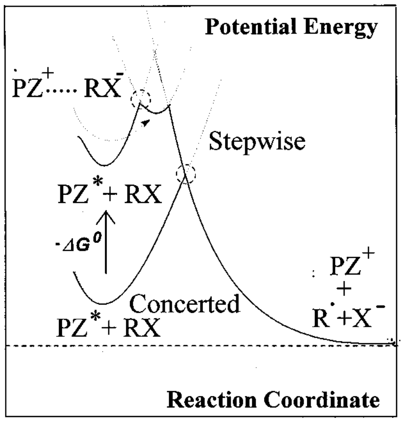


Figure 3. Potential energy diagram for the passage from stepwise to a concerted mechanism as a function of the $\Delta G°$ of the reaction. The transition between the stepwise and concerted mechanism takes place on increasing $-\Delta G°$.

$$E(\mathrm{CCl_4/CCl_3^{\bullet} + Cl^{-}}) = E(\mathrm{Cl/Cl^{-}}) - \mathrm{BDFE(CCl_3{-}Cl)} \tag{4}$$

where BDFE is the bond dissociation free energy for the C−Cl bond in CCl_4 and is equal to 2.55 eV[17] and the $E(\mathrm{Cl/Cl^{-}})$ value in acetonitrile is +1.89 V vs SCE.[17] These values give $E(\mathrm{CCl_4/CCl_3^{\bullet} + Cl^{-}})$ values equal to −0.66 vs SCE in acetonitrile.

The calculated values of the driving force ($-\Delta G°$) for the PDET reaction between PZ in the excited singlet state (S_1) and CCl_4 have been given in Table 1, which shows a wide variation of $\Delta G°$. How this difference in $\Delta G°$ value for the PDET reaction affects the overall reaction mechanism can be explained by a potential energy diagram as shown in Figure 3. Figure 3 is purely a qualitative representation, and hence the activation energy shown is also a qualitative. In general, 3D coordinates represent reaction coordinates, namely the stretching of the C−Cl bond from equilibrium, solvent coordinate, and the vibrational coordinate of all other bonds of the reactants that are not being dissociated during the ET process. However, the contribution from all of these parameters is regarded as independent and additive and thus can be treated separately. As the present work deals with the dissociation of the C−Cl bond, the progress of the reaction is represented in terms of the extent of stretching of the C−Cl bond.

The predominance of one mechanism over the other depends on the relative (vertical) position of the potential energy surface (PES) of the reactants and the intermediate (cf. Figure 3). If the minima of these two PES are (vertically) close, there is a possibility that the reactant PES can cross the same of the intermediate. In such a case, the reactions pass through an intermediate state and follow a stepwise mechanism. But if the driving force of the reaction decreases, the position of the

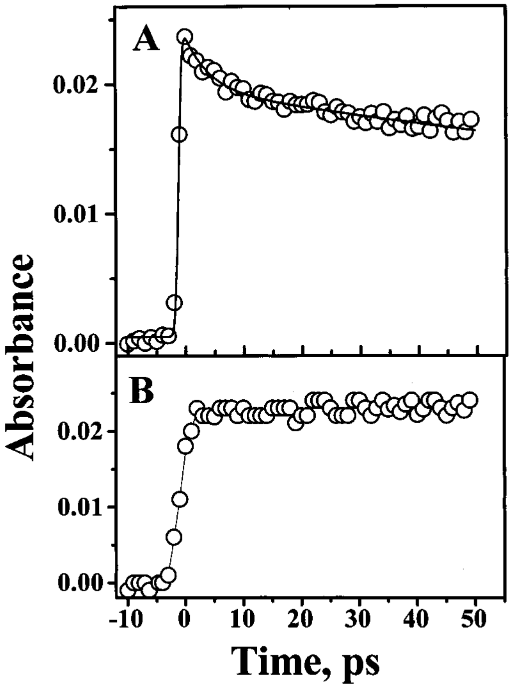


Figure 4. The kinetic trace recorded at 530 nm for MPTH in dimethyl sulfoxide (A) and PTH in 3:2 (v/v) acetonitrile−ethyl acetate solvent mixture (B) with 0.5 M CCl_4.

minimum of the PES of the reactants goes down (vertically), reducing the possibility of crossing its PES with that of the intermediate. In other words, the energy of the intermediate is so high, with respect to the energy of the reactants, that the reaction passing through an intermediate is not favorable. At low enough driving force, the PES of the reactants crosses the PES of the final product directly. In this case, the latter is the dissociative PES for CCl_4.[3] Hence, the possibility of direct dissociation of $CCl_4^{\bullet-}$ to $CCl_3^{\bullet}$ and Cl^- is favored at lower driving force via the concerted rather than the stepwise mechanism, which is associated with higher activation energy. Thus for PTH, with a higher $-\Delta G°$ value, the stepwise mechanism operates, whereas for other PZ, with lower $-\Delta G°$ values, the concerted mechanism is favored.

3.3. Effect of Solvent Polarity on the Reaction Mechanism. The driving force for the ET reaction ($-\Delta G°$) is a solvent-dependent parameter. Thus, a change in the solvent polarity can also cause a crossover from one mechanism to the other. As the products in the present ET reaction are highly polar in nature, a polar solvent will stabilize the products better as compared to a relatively less polar solvent. According to the Born equation,[25] the free energy of solvation of an ion is given by eq 5.

$$\Delta G^{\text{solv}} = -\frac{e^2}{r}\left(1 - \frac{1}{\epsilon_S}\right) \qquad (5)$$

From this equation, it is evident that the more polar the solvent (i.e., the higher the ϵ_S), the better is the stabilization for the ion. Thus, a more polar medium always provides a higher driving force than does a low polar solvent for a given donor−acceptor pair. To validate this idea, we have recorded the transient spectra and their temporal evolution in solvents other than AN ($\epsilon_S = 37.5$). Figure 4 shows the temporal evolution recorded at 530 nm for the MPTH−CCl_4 system in dimethylsulfoxide (DMSO, $\epsilon_S = 46.6$) and PTH−CCl_4 system in AN-ethylacetate (EA) (3:2 v/v, $\epsilon_S = 25$) mixed solvent. It is evident from Figure 4A that the absorption due to $MPTH^{\bullet+}$ shows a decay up to ~50 ps, whereas no such decay has been observed for the $PTH^{\bullet+}$ absorption in the mixed AN−EA solvent. Thus it can be concluded that the BET process takes place even for MPTH in a higher polarity solvent. As DMSO is a more polar solvent than AN, the former can provide more driving force for the ET reaction with CCl_4. However, for PTH in a less polar mixed AN−EA medium, the BET process that was clearly taking place in more polar AN is now hindered. This clearly shows that in more polar solvent the system follows a stepwise mechanism, whereas in less polar medium the concerted mechanism seems to be operative. The absence of decay of the absorbance due to the $PTH^{\bullet+}$ in less polar medium indicates that the observed decay in more polar AN is not due to the proton-transfer reaction from $PTH^{\bullet+}$ to Cl^-. If the decay in AN was due to proton transfer, one should expect that such reaction will be enhanced in a less polar solvent as the products of this reaction are two neutral species formed from two charged reactants. Again, the appearance in the decay for MPTH, a tertiary amine, indicates that the decay in the absorbance of $MPTH^{\bullet+}$ is not due to any reaction with Cl^-.

It is important to mention here that the occurrence of the concerted mechanism does not depend on whether the intermediate exists or not. It rather depends on the lowest available free energy path. The anion radical may exist, but the activation barrier for going through such an intermediate might be higher than that for the concerted path. The nonexistence of the anion radical is a sufficient condition, but not necessary for the concerted mechanism to be operative. In other words, depending on the energetics, the DET can follow a concerted path even if the $RX^{\bullet-}$ has a finite lifetime.

In the present study, the transient is a radical anion, $CCl_4^{\bullet-}$, which dissociates in the bond breaking step. Although the existence of the $CCl_4^{\bullet-}$ is not reported at room temperature, several results show its existence at low temperatures. For example, in 3-methylpentane glass at 95 K, the $CCl_4^{\bullet-}$ has an absorption peak at 370 nm and is stable up to 1 ms.[26] Naturally, such decay will be much faster at room temperature. Although we could not detect the absorption for $CCl_4^{\bullet-}$, because of the limited detection range (400−930 nm) of our instrument, our results clearly show that the intermediate, $CCl_4^{\bullet-}$, exists for at least a few picoseconds and participates in the BET process with the geminate radical cation partner, $PTH^{\bullet+}$, as the kinetic trace (curve b) in Figure 2A and Figure 4A indicates.

4. Conclusion

Depending on the free energy of the reaction, PZ was found to follow a different mechanism in an electron-transfer reaction with CCl_4 in acetonitrile. It is demonstrated nicely that the higher driving force for the electron-transfer reaction favors the stepwise mechanism, whereas a decrease in driving force triggers the crossover of the stepwise mechanism to a concerted mechanism. Polarity of the medium plays an important role in determining the mechanism. Higher polarity solvent favors the stepwise mechanism as compared to a less polar medium. It has also demonstrated that the CCl_4 anion radical exists at room temperature for a extremely short time.

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Supporting Information Available: Structure of PZ molecules. This material is available free of charge via the web at http://pubs.acs.org.

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