Nature of the Potential Energy Surfaces for the S_N1 Reaction: A Picosecond Kinetic Study of Homolysis and Heterolysis for Diphenylmethyl Chlorides

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Abstract: The picosecond dynamics for the photoinduced homolysis and heterolysis of (4-methylphenyl)phenylmethyl chloride and bis(4-methylphenyl)methyl chloride in acetonitrile are examined. In less than 20 ps, both the geminate radical pair and contact ion pair are formed from the first excited singlet state. The geminate radical pair decays by either diffusional separation to free radicals or electron transfer back to the ground state surface which partitions between reactant and contact ion pair. The contact ion pair decays by diffusional separation to the solvent separated ion pair or by collapse to form the carbon−chlorine bond. The kinetics for these processes are employed in the development of the potential energy surfaces for the S_N1 reaction for diphenylmethyl chlorides in polar solvents.

Introduction

The development of a detailed molecular description for the S_N1 reaction mechanism still presents a challenge to both organic and physical chemists. Since the overall mechanism was initially presented by Hughes and Ingold[1] in the 1930's and further expanded upon by Winstein and co-workers,[2] there have been innumerable studies, both experimental and theoretical, seeking to provide insight into the molecular nature of this most important class of organic reaction.[3−12] The form of the electronic barrier for the S_N1 reaction, first addressed by Ogg and Polanyi[13] and then further elaborated upon by Pross and Shaik,[4] has been developed from the perspective of the reaction surface, which results from the coupling of two diabatic states, one purely covalent and one purely ionic. An underlying assumption of these theoretical models is that equilibrium solvation of the solute is maintained throughout the entire reaction process, including passage through the transition state. Recently Hynes and co-workers have questioned this assumption of equilibrium solvation within the transition state in a series of theoretical studies on the S_N1 reaction mechanism for *tert*-butyl halides.[14−16]

An important aspect in the formulation of the S_N1 reaction mechanism is the elucidation of the nature of the barrier for the collapse of the contact ion pair (CIP) to form the covalent bond. Previously there have been no experimental methodologies that allowed for the direct observation of this kinetic process. A few years ago we found that irradiation of diphenylmethyl chloride (DPMC) in a polar solvent, such as acetonitrile, leads, within 20 ps, to the CIP.[17,18] By monitoring the time dependence of the diphenylmethyl cation, we determined the dynamics of the collapse of the CIP to form the carbon−chlorine bond as well as the dynamics of diffusional separation to the solvent separated ion pair (SSIP). From the temperature and solvent dependence of the kinetics for CIP collapse, deviations from the predictions of equilibrium solvation transition state theory were found and we proposed that the reaction occurs within the polarization caging regime where the dynamics of solvent reorganization determines the rate of the collapse of the CIP.[18]

More recently we presented a study of the photochemical processes which give rise to the CIP.[19] For the molecules DPMC, (4-methoxyphenyl)phenylmethyl chloride (MeOC), and bis(4-methoxyphenyl)methyl chloride (DiMeOC), we found that both the CIP and the geminate radical pair are formed directly from a common excited state and, in turn, the geminate radical pair decays by either diffusional separation or electron transfer to the ground state surface to form either the CIP or a covalent bond. In this paper we expand these studies of the mechanism of photoinduced homolysis and heterolysis to include the molecules (4-methylphenyl)phenylmethyl chloride (MC) and bis(4-methylphenyl)methyl chloride (DiMC). With this set of molecules, we begin to address the question of the effect of substituents upon the free energy barrier for the collapse of the CIP and the effect of substitutents upon the decay of the geminate radical pair.

Experimental Section

(4-Methylphenyl)phenylmethyl chloride (MC) and bis(4-methylphenyl)methyl chloride (DiMC) were prepared from the corresponding alcohols (Aldrich) with thionyl chloride and purified by vacuum distillation to >95% purity as measured by gas chromatography (HP5890, FID, DB17 column) and NMR. Acetonitrile (Burdick and Jackson, UV-grade) was distilled from calcium hydride.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

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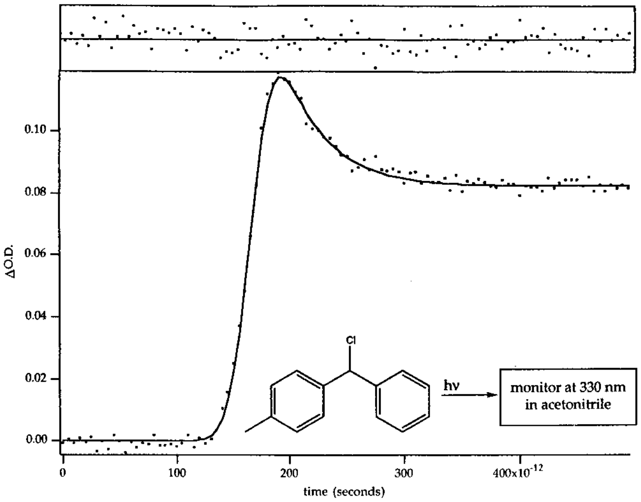

Figure 1. Transient absorption of the MC radical formed upon the photolysis of MC in acetonitrile at 23 °C, fit to the model shown in Scheme 1. Laser excitation at 266 nm. Radical monitored at 330 nm. Rate constants: $k_d = 1.34 \times 10^{10}$ s^{-1}, $k_{esc} = 1.36 \times 10^{10}$ s^{-1}. $\sigma = 15.5$ ps and $t_0 = 171$ ps.

A detailed description of our picosecond pump-probe experiment, based upon a Continuum (PY61C-10) Nd:YAG (30 ps fwhm) laser has been reported elsewhere.[20] The optical density of the samples at the photolysis wavelength, 266 nm, were 1.5 OD. The samples were stirred in a 1-cm quartz cuvette throughout the experiment; flowing the sample through the cuvette had no effect upon the experimental results. The MC and DiMC radicals were monitored at 330 nm while the corresponding cations were monitored at 440 nm. For a given kinetic study, 200 data points at 5-ps intervals were collected for each run where each point is the average of 25 laser shots. The reported decays are the average of 3 to 6 runs.

The method of deconvolution of the kinetic data has been presented.[20] The observed transient signal A(t) results from the convolution of the instrument response function I(t) with the transient signal, F(t).

$$\mathrm{A}(t) = \int_{-\infty}^{t} \mathrm{I}(\tau)\, \mathrm{F}(t-\tau)\, \mathrm{d}\tau \qquad (1)$$

The instrument response function, I(t), is produced by the convolution of the pump and probe pulse, and is assumed to have the analytical form of a Gaussian

$$\mathrm{I}(t) = (2\pi\sigma)^{-0.5} \exp(-(t-t_0)^2/2\sigma^2) \qquad (2)$$

where σ is the width and t_0 the position of the peak of the Gaussian.

To measure the response time of our instrument, we use the instantaneous excited state absorption of pyrene at 440 nm and of naphthalene at 330 nm. For naphthalene, it is necessary to subtract fluorescence from the data before optical density is calculated. The response function of our instrument at both wavelengths of interest is 20 ± 3 ps as measured by repeated experiments.

Results

Kinetics of Diphenylmethyl Chloride Radicals. The dynamics of the photoinduced homolysis of MC and DiMC in acetonitrile at 23 °C were monitored at 330 nm following irradiation at 266 nm. Steenken and co-workers reported λ_{max} of 336 nm for the MC radical and λ_{max} of 338 nm for the DiMC radical.[21] Figure 1 displays the formation and decay kinetics of MC. The radical is formed within the duration of the laser pulse and then decays on the time scale of 100 ps to a constant absorbance. The radical decays are fit to the model depicted in Scheme 1. The geminate radical pair (GRP), created within the duration of the laser pulse, is assumed to decay by two pathways: the first pathway is diffusional separation, k_{esc}, to free radical, FR, and the second pathway is an electron transfer process, k_d, which returns the system to the ground state surface, GS. As will be shown, once on the ground state surface the system may then evolve into the CIP or re-form the carbon−chlorine bond. Figure 1 shows the fit of the model outlined in Scheme 1 to the kinetic data. For MC GRP, the rate of radical cage escape, k_{esc}, to FR is 1.36×10^{10} s^{-1} and the rate of return to GS, k_d, is 1.34×10^{10} s^{-1} leading to a lifetime ($1/k$) of the GRP of 37 ps. For DiMC GRP (data not shown), the rate of radical cage escape, k_{esc}, to FR is 1.40×10^{10} s^{-1} and the rate of return to GS, k_d, is 1.33×10^{10} s^{-1} leading to a lifetime ($1/k$) of the GRP of 36 ps. These results as well as the results of our previous study of the dynamics of the GRP for DPMC, MeOC, and DiMeOC are presented in Table 1.

Scheme 1

Table 1. Kinetics Parameters for Decay of the Geminate Radical Pairs of Diphenylmethyl Chlorides at 23 °C in Acetonitrile

compd	k_d ($\times 10^{10}$ s^{-1})[a]	k_{esc} ($\times 10^{10}$ s^{-1})[a]
DPMC	0.82	1.30
MC	1.34	1.36
DiMC	1.33	1.40
MeOC	0.70	0.50
DiMeOC	0.51	0.40

[a] Uncertainties in fits are estimated at ±20%.

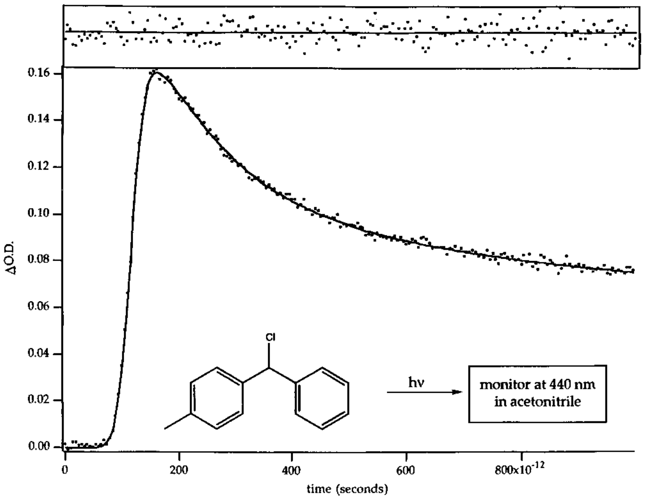

Figure 2. Transient absorption of the MC cation formed upon the photolysis of MC in acetonitrile at 23 °C, fit to the model shown in Scheme 2. Laser excitation at 266 nm. Cation monitored at 440 nm. Rate constants: $k_1 = 3.88 \times 10^{10}$ s^{-1}, $k_2 = 3.51 \times 10^{9}$ s^{-1}, $k_3 = 1.2 \times 10^{9}$ s^{-1}, and $k_4 = 1.15 \times 10^{9}$ s^{-1} with $R = 0.2$. $\sigma = 18.4$ ps and $t_0 = 118$ ps.

Kinetics of Diphenylmethyl Chloride Ions. The dynamics of the photoinduced heterolysis of MC and DiMC in acetonitrile at 23 °C were monitored at 440 nm following irradiation at 266 nm. Steenken and co-workers reported λ_{max} of 450 nm for the MC cation and λ_{max} of 464 nm for the DiMC cation.[21] Figure 2 shows the decay of the MC cation. The model we use in the analysis of the kinetic data is presented in Scheme 2. The model assumes that the CIP is formed by two pathways. The first pathway is directly from the excited singlet state whose kinetics are not resolved in the present experiment due to the limited time resolution of 20 ps. The second pathway comes from the GRP through an electron transfer process. The model assumes

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Scheme 2

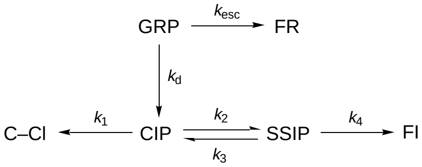

Table 2. Kinetics Parameters for Decay of the Contact Ion Pairs of Diphenylmethyl Chlorides at 23 °C in Acetonitrile

compd	R	k_1 ($\times10^9$ s^{-1})[a]	k_2 ($\times10^9$ s^{-1})[a]	k_3 ($\times10^9$ s^{-1})[b]	k_4 ($\times10^9$ s^{-1})[b]
DPMC	0.0	4.1	3.6	0.7	0.6
MC	0.2	3.9	3.5	1.2	1.2
DiMC	0.2	3.4	3.6	1.6	1.7
MeOC	0.3	3.5	3.6	1.2	0.9
DiMeOC	0.4	1.7	2.0	0.9	1.1

[a] Uncertainties in fits are estimated at ±20%. [b] Uncertainties in fits are estimated at ±50%.

that GRP and diphenylmethyl chlorides (C−Cl) do not absorb at 440 nm and that the extinction coefficients of the CIP, SSIP, and free ion (FI) at 440 nm are the same. The rate constants k_d and k_{esc} reflect the kinetics for the decay of the GRP and are obtained from the corresponding radical data at 330 nm, Table 1. During the fitting procedure we vary the rate constants k_1 through k_4 as well as a parameter R defined by

$$R = [\mathrm{GRP}]_0/([\mathrm{GRP}]_0 + [\mathrm{CIP}]_0)$$

where $[\mathrm{GRP}]_0$ is the total number of GRP that decay into CIP and $[\mathrm{CIP}]_0$ is the initial amount of CIP formed directly from the excited singlet state.

We developed the model depicted in Scheme 2 based on our previous studies of DPMC, MeOC, and DiMeOC. For DPMC, the cation data was well modeled by Scheme 2 where $R = 0.0$; that is, all of the CIP was derived from the first excited singlet state. For MeOC, an acceptable fit to the observed kinetic data could not be obtained assuming that all of the CIP came from the first excited singlet state. It was only when $R = 0.3$ that an acceptable fit between the experimental data and the model was obtained so that 30% of the CIP came from the GRP.

In fitting the experimental data for MC cation in Figure 2 to the model displayed in Scheme 2, R was varied from 0.0 to 1.0. The best fit occurred when $R = 0.2$, which is shown in Figure 2. Similarly, the best fit of the model to the experimental data for DiMC also occurred with $R = 0.2$. The results of the kinetic study of the ion pair dynamics for MC and DiMC as well as previous results for DPMC, MeOC, and DiMeOC are given in Table 2.

Discussion

Dynamics of Covalent Bond Formation from CIP. A very successful theoretical perspective for examining organic reactivity in both gas and condensed phases is the valence-bond configuration mixing model (VBCM) developed by Pross and Shaik.[4] This formulation has been applied to a great variety of organic reaction mechanisms including S_N1, S_N2, E1, and E2. The reaction profile potential energy surfaces, the adiabatic states, are developed by the mixing of the appropriate valence bond electronic configurations which serve as the diabatic states. For the S_N1 reaction of alkyl halides, the two most important valence bond states are the purely covalent state R••X where, for the two active electrons, one electron is associated with R and the other with X, and the purely ionic state R^+X^- where both active electrons are associated with X. In the gas phase when the two valence bond electronic configurations mix to produce the S_0 and S_1 adiabatic surfaces, at bonding distances the ground state surface acquires some ionic character resulting in a stabilization of S_0 relative to diabatic surface R••X and destabilization of S_1 relative to the diabatic surface R^+X^-, Figure 3.

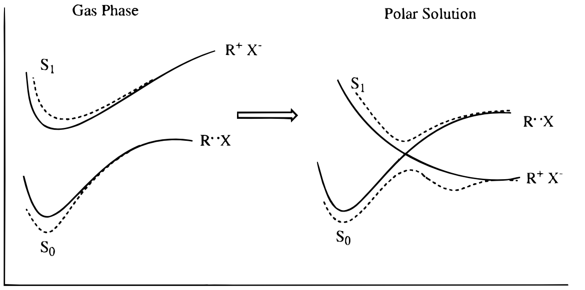

Figure 3. Potential energy surfaces for homolysis and heterolysis in the gas phase and in polar solution. Solid curves: diabatic surfaces. Dashed curves: adiabatic surfaces.

When the system is placed in a polar solvent, the order of stability of the two valence bond states reverse as R and X separate leading to a curve crossing between the two diabatic states.[4] In the vicinity of this curve crossing there is a large electronic coupling between the two diabatic surfaces leading to an avoided crossing between the two adiabatic surfaces S_0 and S_1, Figure 3; thus, in polar solution, the dissociation of R−X leads adiabatically to the formation of a contact ion pair. The representation of the heterolytic and homolytic dissociation pathways in polar solvents shown in Figure 3 is however misleading for the dissociation pathways depend not only on the bond extension coordinate but also upon a solvent coordinate which is not depicted. Figure 3 should be viewed as the solvent fully equilibrated to the bond extension reaction coordinate where the solvent structure continously changes with bond extension. Furthermore, the solvation structure along the S_0 and S_1 surfaces will differ given the difference in ionic character for the two surfaces. From the mixing of the two diabatic states a maximum is produced on the S_0 surface, corresponding to the transition state for heterolytic dissociation, and a minimum is produced on the excited state surface. However, the fully equilibrated solvent structure for the transition state for heterolytic dissociation will certainly be different from the fully equilibrated solvent structure for the minimum on S_1. Furthermore, because of the role of the solvent, it is unlikely that the minimum in the bond extension coordinate on S_1 will correspond to the maximum on the bond extension coordinate on S_0. This difference in position of the S_1 minimum and S_0 maximum on the bond extension coordinate may play an important role in governing the product outcome upon the relaxation from the S_1 surface onto the S_0 surface.

One of the difficulties in determining the magnitude of the electronic barrier for the collapse of a CIP in a polar solvent is that the dynamics of covalent bond formation are dependent upon the restructuring of the polar solvent about the reacting ions and thus the activation parameters for this process will be affected by both the electronic and solvent components. Hynes and co-workers have developed a theoretical formulation, based upon the generalized Langevin equation, for the effect that polar solvent dynamics have upon chemical reactions involving charge displacement.[22−24] One of the fundamental assumptions of transition state theory is that during the displacement of charge in a reaction, such as an S_N1 process, the solvent fully

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equilibrates to the motion of charge through the transition state. When viewed from transition state theory, the dynamics of the reaction will not depend upon the dynamics of the solvent restructuring. However, in polar solvents, the medium may produce a significant retarding force upon the motion of charge through the transition state and the rate of reaction, k, will be reduced from the rate of reaction predicted by transition state theory, k_{TST}.

The parameter that measures the deviation from transition state theory is κ, defined by $\kappa = k/k_{TST}$. As Hynes has shown,[24] the principal factors governing the value of κ are the reaction barrier frequency for the transition state, ω_b, and electrostatic solvent frequency, ω_s, associated with the nondissipative restoring force due to the solvent. In the limit of strong solvent forces, $\omega_s^2/\omega_b^2 > 1$, Hynes found that as the charge moves off of the top of the transition state barrier, the system finds itself trapped in a solvent well or a "polarization cage". While the polarization cage is maintained, the system will oscillate within the transition state, reducing the rate of the reaction k relative to k_{TST}, and it is only when the solvent cage relaxes that the system evolves into product. The time scale for the relaxation of the solvent cage is of the order τ_l, the longitudinal relaxation time of the solvent.

Recently we reported a kinetic study of the collapse of the CIP for DPMC in acetonitrile and propionitrile.[18] From the analysis of the temperature dependence for this process, the derived activation parameters are $A = 9.2 \times 10^{11}$ s^{-1} (ln $A = 25.55 \pm 0.53$) and $E_a = 3.2 \pm 0.3$ kcal/mol. Modeling this reaction within the assumptions of transition state theory, the A factor should have been 5.7×10^{12} s^{-1}. Thus the κ value for the reaction is 0.16 which, within the Hynes model,[24] places the reaction in the domain of polarization caging. If the dynamics of the solvent are important in governing the rate of the reaction, then κ should be dependent upon the τ_l of the solvent. Indeed when the solvent is changed from acetonitrile, with $\tau_l = 0.2$ ps, to propionitrile, with $\tau_l = 0.3$ ps, the value of κ decreased from 0.16 to 0.09. Since the restructuring of the solvent appears to play an important role in determining the activation parameters for the collapse of the CIP, the energy of activation E_a must contain contributions from both the electronic free energy barrier, $\Delta G^{\ddagger}$, and energy of activation for τ_l. As the energy of activation associated with τ_l is approximately 0.8 kcal/mol, the value for the free energy barrier for the collapse of the CIP to form R$-$X is approximately 2.4 kcal/mol. Clearly, the barrier produced by the mixing of the two diabatic states for collapse of the CIP, Figure 3, is indeed small.

In the present study we have not determined the activation parameters associated with the collapse of the CIP for MC, DiMC, MeOC, and DiMeOC. However, the energy of activation can be estimated if it is assumed that the A factor, determined for DPMC, is the same for the other four diphenylmethyl chlorides. With this assumption, the E_a for CIP collapse is 3.2 kcal/mol for MC, 3.3 kcal/mol for DiMC, 3.3 kcal/mol for MeOC, and 3.6 kcal/mol for DiMeOC. Excluding DiMeOC, a change of more than 5 kcal/mol in the CIP energy has virtually no effect upon the barrier for the collapse of the CIP. Thus it appears that the electronic barrier for the collapse of the CIP within this series of compounds shows virtually no dependence on the overall free energy for reaction.

Dynamics of S_1 Decay into Radical Pairs and Contact Ion Pairs. Another interesting question that arises within the context of the valence-bond approach to reactivity is the photochemical reaction pathway leading to homolysis and heterolysis. The reaction diagrams depicted in Figure 3 are not directly applicable to the photochemistry of diphenylmethyl chlorides as only carbon$-$halogen valence bond states have been considered; formally the S_1 surface which correlates with R^+X^- in the gas phase and correlatives with R••X in the polar condense phase corresponds to the $\sigma \rightarrow \sigma^*$ transition. However, for diphenylmethyl chlorides, account must be taken of the $\pi \rightarrow \pi^*$ states which will be of lowest energy at bonding distances.[25] As the bond distance increases in the lowest excited singlet state the $\pi \rightarrow \pi^*$ state will increase in energy and at the same time the $\sigma \rightarrow \sigma^*$ state will decrease in energy leading to a crossing of the two states.[25] Since the $\sigma \rightarrow \sigma^*$ state is ionic at short bond distances, increasing the solvent polarity will lead to an earlier crossing between the $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ states reducing the barrier to bond cleavage. In acetonitrile, the bond cleavage occurs in less than 20 ps and thus the electronic barrier separating the $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ states must be exceedingly small along the bond stretch coordinate in S_1.

Table 3. Quantum Yield Data, Taken from Steenken and Co-workers, for Radical Pair, Φ(RP), and Ion Pair, Φ(IP), Measured at 10 ns[21]

	Φ(RP)	Φ(IP)
DPMC	0.23	0.13
MC	0.18	0.11
DiMC	0.27	0.18
MeOC	0.26	0.32
DiMeOC	0.24	0.31

The details of the reaction pathways for photoinduced homolysis and heterolysis, both occurring in less than 20 ps, have yet to be elucidated and thus we can only speculate on the processes leading to dissociation. Based upon the Miller and Spears model for solvent gating of intramolecular electron transfer,[26] it is a fluctuation in the solvent structure that governs the decay of S_1. Immediately following excitation, the solvent structure surrounding the first excited singlet state will be that corresponding to the equilibrium solvation structure for the reactant. Since the equilibrium solvent structure surrounding the radical pair will differ from the equilibrium solvent structure surrounding the ion pair, both of which differ from the equilibrium solvent structure for the reactant, there must be two distinct solvent motions to allow for the formation radical and ion pairs. Formation of the CIP may come from a solvent fluctuation that lowers the $\sigma\sigma^*$ ionic surface, causing a development of a conical intersection between the radical and ionic surfaces.[27] Presumably the radical pairs, formed adiabatically, are produced by a solvent fluctuation in a different coordinate.

If this model for radical pair and ion pair formation were complete, then the sum of the quantum yields for production of radical pair and ion pair should be unity. Recently the quantum yields for the formation of the radical pair and ion pair for a number of diphenymethyl chlorides in acetonitrile, measured at 10 ns by nanosecond flash photolysis, have been reported by Steenken and co-workers and are given in Table 3.[21] Given 10 ns quantum yield data it is then possible to derive the initial quantum yield for radical pair production, Φ_0(RP). Similarly, the initial quantum yield for total ion pair production, Φ_0(IP), coming from both the excited singlet state and the radical pair can be derived from the kinetic data given in Table 2. The quantum yields for initial radical pair production and ion pair production are given in Table 4. Taking into account the amount of the total ion pair that is formed from the radical

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Table 4. Quantum Yields for Initial Radical Pair Formation, Φ_0(RP); Initial Total Ion Pair Formation, Φ_0(IP); Ion Pair Formation Formed Directly from S_1, $\Phi_{ip}(S_1)$; Total Transients Formed from S_1, Φ_T; Radical Decay through Kinetic Process k_d, $\Phi(k_d)$; and Ion Pair Formation from Radical Pair, $\Phi_{ip}(k_d)$

	Φ_0(RP)	Φ_0(IP)	$\Phi_{ip}(S_1)$	Φ_T	$\Phi(k_d)$	$\Phi_{ip}(k_d)$
DPMC	0.37	0.28	0.28	0.65	0.14	0.00
MC	0.35	0.23	0.18	0.53	0.17	0.05
DiMC	0.52	0.35	0.28	0.80	0.25	0.07
MeOC	0.62	0.62	0.43	1.05	0.36	0.19
DiMeOC	0.54	0.57	0.34	0.88	0.30	0.23

pair, which is reflected in the *R* value given in Table 2, it is then possible to derive the amount of ion pair that is formed directly from the excited singlet state, $\Phi_{ip}(S_1)$. Thus the total amount of transient species produced directly from the excited singlet state, Φ_T, is the sum of Φ_0(RP) and $\Phi_{ip}(S_1)$, shown in Table 4. Finally, the quantum yield for the decay of the radical pair onto the ground state surface through the kinetic process k_d, $\Phi(k_d)$, is just the difference between Φ_0(RP) and Φ(RP), again give in Table 4. The quantum yield for the formation of the CIP from the decay of the radical pair, $\Phi_{ip}(k_d)$, is the difference between Φ_0(ip) and $\Phi_{ip}(S_1)$.

From the data given in Table 4, the quantum yield for the decay of S_1 into radical pairs and ion pairs is approximately unity for MeOC and DiMeOC but is significantly less than unity for DPMC, MC, and DiMC. The model that has been developed for the decay of S_1 into radical pairs and ion pairs, which predicts unit efficiency for the formation of transient species, requires further development. Critical to the formation of ion pairs is an evolution in the solvent coordinate. Importantly, the solvent structure at the conical intersection will differ from the equilibrium solvent structure about the CIP.[27] Thus when the electronic transition is made from the S_1 surface onto the S_0 surface, the solvent structure at that point in time will not support the full development of the CIP. Upon reaching the ground state hypersurface, with coordinates encompassing both bond extension−compression and solvent reorientation, the system may evolve among many coordinates one of which will take the system over into the CIP while another will return the system back to the initial reactant. Since the point at which the system crosses from the S_1 surface onto the S_0 surface will be a function of the electronic structure of the system, each of the diphenylmethyl chlorides will appear at a different point on the ground state hypersurface upon internal conversion. Apparently MeOC and DiMeOC appear on the ground state surface in a region close to CIP given the unity efficiency for creation of the CIP. Conversely, DPMC, MC, and DiMC must appear in a region away from the CIP so that reformation of the initial reactant is competitive with CIP formation. At this stage, it is not possible to predict for a given molecular system in what region, in terms of bond and solvent coordinates, internal conversion will place the system on the ground state hypersurface.

Dynamics of Radical Pair Decay. The standard valence bond approach for developing potential energy surfaces for both the ground and excited state dissociation processes, assuming equilibrium solvation along the two diabatic surfaces, produces adiabatic surfaces where the position of the transition state on the ground state surface correlates with a minimum on the excited state surface, Figure 3.[4] The wave function for the transition state on the S_0 surface is the in-phase linear combination of the covalent, Ψ_C, and ionic, Ψ_I, structures each making an equal contribution.

$$\Psi_S = (1/\sqrt{2})(\Psi_I + \Psi_C) \tag{3}$$

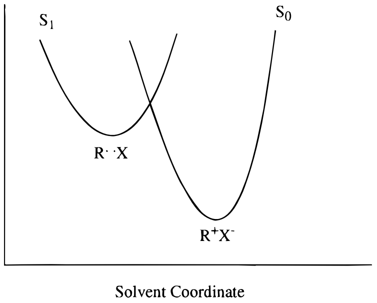

Figure 4. Solvent reaction coordinate for electron transfer within the radical pair placing the system onto the ground state surface. The equilibrium nuclear separation at which electron transfer occurs within the radical pair does not correspond to the equilibrium nuclear separation within the CIP.

The excited state of the transition state, which is a minimum on the S_1 surface, is the out-of-phase combination of the two valence bond structures.

$$\Psi_A = (1/\sqrt{2})(\Psi_I - \Psi_C) \tag{4}$$

The transition state and its excited singlet state have equal contributions from the two valence bond covalent and ionic states, resulting in a 50% ionic character for the two states.

Hynes' theoretical study of the S_N1 reaction of *tert*-butyl chloride reveals that this valence bond approach is incomplete for it does not properly take into account the effect of solvent.[14] From the nonlinear Schrodinger formulation of the S_N1 reaction, the transition state for heterolysis is shifted to longer bond distances from that predicted by the standard valence bond approach. Furthermore, the amount of ionic contribution to the transition state is greater than 50% and is a function of the polarity of the solvent. For the example of *tert*-butyl chloride in acetonitrile, the ionic contribution to the transition state is 61%. Although the ionic contribution to the wave function on the excited state surface at the minimum was not addressed in the Hynes study, it should be less than 50%.

An important consequence of properly accounting for solvent interactions is that position of the transition state on the S_0 surface no longer corresponds to the minimum on the excited singlet state surface. Furthermore, given that the two species have differing ionic contributions, the equilibrium solvent structure for the S_0 transition state will differ from the equilibrium solvent structure for the S_1 minimum. For fast internal conversion to occur at the minimum position of the S_1 surface through a conical intersection between the two surfaces,[27] a fluctuation in the solvent coordinate must occur, Figure 4. This transition will place the sytem on the group state surface, but not necessarly in the vicinity of the CIP. This process is formally an electron transfer reaction and the kinetics of the process should be described by Marcus electron transfer theory.[28] The role of electron transfer in the conversion of radical pairs to ion pairs has been presented by Pinock and co-workers in the study of the photosolvoysis of benzylacetates in methanol.[29,30] Their model differs somewhat form the model proposed herein in that they suggest that electron transfer occurs within the radical pair to directly produce the ion pair.

From the experimental perspective, there is the issue as to the evidence for the existence of a local minimum on the surface correlating with radical dissociation. In the absence of such a minimum, the dynamics of geminate radical separation would

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be limited by the reorganization of the solvent to allow for the two radicals to separate. The rate of diffusional separation (Scheme 1, k_{esc}) should be controlled by the rate of diffusion of the smaller particle, the chlorine atom, away from the larger radical. Substitution on the phenyl rings should produce only a negligible effect upon the dynamics of geminate radical pair diffusional separation. Although the rate constant k_{esc} is virtually identical for DPMC, MC, and DiMC, the rate constants for MeOC and DiMeOC are reduced by almost a factor of 3. Clearly more than just solvent reorganization is contributing to the barrier for diffusional separation of the geminate radical pair. If a local minimum does exist on the radical surface, the depth of the minimum will be sensitive to the electronic structure for the interacting species, and thus one would predict that the rate of diffusional separation should vary with substituents. Exactly how this well depth will vary with substituent cannot be predicted given our limited understanding of the nature of the diabatic surfaces, the magnitude for the electronic coupling between the two diabatic surfaces, and how this coupling will be influenced by the interaction with the solvent.

For efficient internal conversion between the radical pair and the ground state surface (Scheme 1, k_d), a fluctuation in the solvent coordinate should lead to an intersection between the radical and ionic surfaces allowing for an electron transfer. The rate of this internal conversion should be sensitive to the energy gap between the radical surface and ionic surface and thus the rate should vary with substituents, as is observed. However, given the limited knowledge pertaining to effect of substituents on the energetics of the minimum for the radical surface as well as the effect on the energetics for the ionic surface, it is not possible to derive the free energy change for the electron transfer reaction and consequently a Marcus analysis of the kinetic data is precluded.

Once the internal conversion from the radical surface onto the ground state ionic surface has occurred, the system may then either evolve into CIP or return to initial ground state reactants. Comparing the quantum yields for return of the radical pair to the ground state surface, $\Phi(k_d)$, Table 4, to the quantum yield for the formation of CIP from the radical pair, $\Phi_{ip}(k_d)$, reveals that the efficiency for CIP formation from the radical pair is very sensitive to substituents. For example, when the DPMC radical pair returns to the ground state surface, none of the population evolves into the CIP. In contrast when the DiMeOC radical pair returns to the ground state surface, 63% of the population evolves into the CIP. It would appear that the process of internal conversion through an electron-transfer process places the system on the ground state hypersurface whose position is very sensitive to the electronic structure of the reacting species.

Conclusion

The present kinetic study of the photoinduced homolysis and heterolysis of diphenylmethyl chlorides reveals that in a polar solvent such as acetonitrile both radical pairs and ion pairs are produced from the excited singlet state. The CIP is found to decay by diffusional separation to SSIP or collapse to form the carbon−chlorine bond. The electronic barrier for collapse of CIP is approximately 2.4 kcal/mol and varies little with substituents. Furthermore, the kinetics for the collapse of the CIP are controlled by solvent dynamics placing the system in the polarization caging regime. The geminate radical pair is found to decay by diffusional separation or by electron transfer to form ion pairs. Given the effect of substituents on the kinetics of geminate radical pair diffusional separation, there is evidence that a local minimum exists on the electronic surface correlating with the radical pair, in accord with predictions of valence bond theory.

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