Charge Recombination Reactions in Photoexcited C_{60}–Amine Complexes Studied by Picosecond Pump Probe Spectroscopy

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Abstract: Photoexcitation of complexes between fullerene C_{60} and organic amines in benzene solutions is known to result in charge separation (CS) and subsequent charge recombination (CR) reactions, which lead to varying yields of fullerene triplet formation. Picosecond flash photolysis studies are carried out on C_{60}–diphenylamine (DPA), C_{60}–triethylamine (TEA), C_{60}–diazabicyclooctane (DABCO), and C_{60}–triphenylamine (TPA) systems to find out mechanistic details of the triplet formation on CR by inducing heavy atom and polarity effects by using suitable solvents. It is found that in the case of C_{60}–DPA, C_{60}–TEA, and C_{60}–DABCO systems proton transfer from the amine cation to the C_{60} anion in the ion pair state dominates, leading to poor triplet yields, which improve in heavy atom containing solvents. In TPA, proton transfer is not possible and hence fullerene triplet yields are high. Increase of solvent polarity for this system results in decreased C_{60} triplet yields with a consequent increase in the ion dissociation yield. A suitable reaction scheme is proposed to explain the results obtained.

Introduction

Fullerenes C_{60} and C_{70} have been found to display interesting charge-transfer chemistry in both their ground and excited electronic states.[1-5] Due to the good electron-accepting properties, the fullerenes form weak ground-state complexes with amine donors such as triethylamine (TEA), *N,N*-dimethylaniline (DMAN), *N,N*-diethylaniline (DEAN), diphenylamine (DPA), and triphenylamine (TPA). Such charge-transfer complexes are being studied to improve the second- and third-order polarizabilities of the fullerenes.[3,6] Fullerene amine complexes are potential materials which possess large nonlinear properties with good chemical stability. Molecular ferromagnetism is observed in the tetrakis(dimethylamino)ethylene salt of C_{60}.[7] Photoexcitation of the C_{60}–DMAN complex was found to result in charge separation (CS), giving an ion pair (DMAN cation and C_{60} anion) which undergoes geminate recombination in 20–55 ps.[1] We observed the formation of weak charge-transfer complexes between C_{60} and DPA, TPA, and TEA in the ground state. Picosecond time-resolved absorption studies showed that on photoexcitation of these complexes ion pairs are formed which undergo charge recombination (CR) to give either the ground state or the triplet state of the fullerene.[4] It is interesting to note that, in benzene solutions, the C_{60} triplet formation was found to be the major path in the CR of the C_{60}–TPA ion pair, while in the case of the C_{60}–DPA and C_{60}–TEA systems, triplet formation was found to be the minor route. The present work was undertaken to resolve the mechanistic details of the CR process and analyze the varying amounts of triplet yields in different C_{60}–amine systems.

Since the oxidation potentials of the amines[8] are closer ($E_{ox}^{DPA} = 0.64$ V, $E_{ox}^{TPA} = 0.55$ V, and $E_{ox}^{TEA} = 0.66$ V vs Ag/Ag^+ in acetonitrile), the energy change (ΔG_0) associated with the electron transfer from amine to C_{60} does not seem to be the governing factor for the large differences observed in the triplet production following CR in the three systems. The factor which governs the predominance of the routes seems to be related to the molecular structure of the amines. Structurally, DPA [$HN(C_6H_5)_2$], is a secondary amine and TPA [$N(C_6H_5)_3$] is a tertiary amine. Thus, the hydrogen atom attached to the nitrogen in DPA (absent in TPA) may be responsible for the observed differences in the CR processes in the C_{60}–DPA and C_{60}–TPA systems. In the C_{60}–DPA system, the transfer of a proton from the DPA cation to the C_{60} anion in the ion pair state may compete with the formation of a triplet. Such a process will be absent in the case of the C_{60}–TPA system, and hence it will give a high triplet yield following CR. A proton transfer of the above type suggested for the C_{60}–DPA system has already been reported for a number of hydrocarbon–amine systems.[9-12] In the case of the C_{60}–TEA system, although there is no hydrogen atom attached to nitrogen, the C_{60} triplet yield is negligible. This observation in the C_{60}–TEA system suggests that, in the ion pair state of the system, there could be a very fast proton transfer from the α-position of one of the alkyl groups of the TEA cation to the C_{60} anion. Such α-proton-transfer processes from alkyl groups are well-known in the photoreduction of carbonyl compounds in the presence of an amine such as TEA, resulting in the formation of ketyl radicals.[13,14] Photoreduction of carbonyl compounds in alcoholic solvents is also due to a similar kind of α-proton transfer.[15,16] In the present

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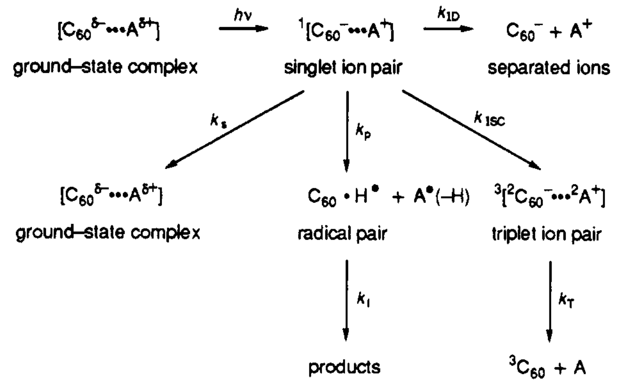
Scheme I



work we have investigated the mechanistic aspects of the CR processes in C_{60}–DPA, C_{60}–TPA, C_{60}–DABCO ($E_{ox}^{DABCO} = 0.28$ V vs Ag/Ag$^+$ in acetonitrile),[8] and C_{60}–TEA systems using picosecond flash photolysis techniques with the help of the heavy atom effect, the solvent polarity effect, and the effect of deuteration of DPA.

Results and Discussion

The time-resolved picosecond transient absorption studies on complexes of C_{60} with DPA, TPA, and TEA in benzene solutions showed that the ion pair $[C_{60}^{-}\cdots A^{+}]$ formed immediately after a 35-ps laser pulse excitation undergoes CR, producing a triplet state of the fullerene to a varying extent depending upon the amine used.[4] The ion pairs formed immediately after photoexcitation of C_{60}–DPA and C_{60}–TPA complexes with a laser pulse (35 ps, 532 nm) show transient absorption spectra similar to those of DPA and TPA cations reported earlier.[17-19] To understand the mechanistic aspects of the CR processes, Scheme I is proposed. In Scheme I, the singlet ion pair state $^1[^2C_{60}^{-}\cdots {}^2A^{+}]$ produced by the excitation of the ground-state fullerene–amine complex can undergo various processes as follows: (1) a simple charge recombination process producing the ground state of the complex with a rate constant k_s; (2) ion dissociation (ID) to produce the solvent-separated ions, the rate constant being represented by k_{ID}; (3) intersystem crossing (ISC) from the singlet ion pair $[^2C_{60}^{-}\cdots {}^2A^{+}]$ to the corresponding triplet ion pair $^3[^2C_{60}^{-}\cdots {}^2A^{+}]$ with a rate constant k_{ISC},[20,21] the triplet ion pair in turn giving the C_{60} triplet on recombination with a rate constant k_T; (4) proton transfer from the amine cation to the fullerene anion wherever possible (depending on the structure of the amine) in the singlet ion pair state, resulting in the formation of a radical pair with a rate constant of k_p. This proton-transferred radical pair ultimately gives products (mostly the ground-state complex[9-12]) other than the C_{60} triplet with a rate constant k_f. With the above-mentioned mechanistic Scheme I, experiments were planned to throw light on the various steps proposed. In the following sections we discuss the results obtained under different conditions for the above-mentioned C_{60}–amine systems.

C_{60}–DPA System. Our previous studies[4] showed that C_{60} triplet formation is a minor process following CR in the C_{60}–DPA system in benzene. In the present work attempts were made to increase k_{ISC} and thus enhance triplet formation in this system. A common way to enhance the ISC rate is by using the external heavy atom effect. Bromobenzene and iodobenzene were used as solvents to induce the external heavy atom effect in this system. In solutions containing C_{60} alone or C_{60}–DPA in iodobenzene it was seen that, at the end of a 35-ps laser pulse, formation of the C_{60} triplet was complete. These results indicate that ISC rate enhancement in iodobenzene is too fast to study the comparative influence of the external heavy atom effect on k_{ISC} with reference to the other rate constants for the C_{60}–DPA system in neat iodobenzene. Hence, various mixtures of benzene and iodobenzene were used, and it was found that at about 15% iodobenzene in benzene the decrease of DPA cation absorption[17,22] at 710 nm with time and the growth of the C_{60} triplet at 740 nm could be resolved at different time delays following laser excitation (Figure 1A). With bromobenzene as solvent, no significant C_{60} triplet formation was observed immediately after the laser pulse in the absence of DPA. In the presence of DPA, however, the amine cation peak at 710 nm decreases with simultaneous increase in the fullerene triplet peak at 740 nm, as shown in Figure 1B. The results obtained for C_{60}–DPA in benzene alone are shown in Figure 1C, for comparison with the above results. All the above results show that the external heavy atom effect increases the ISC rate and changes the course of the reaction.

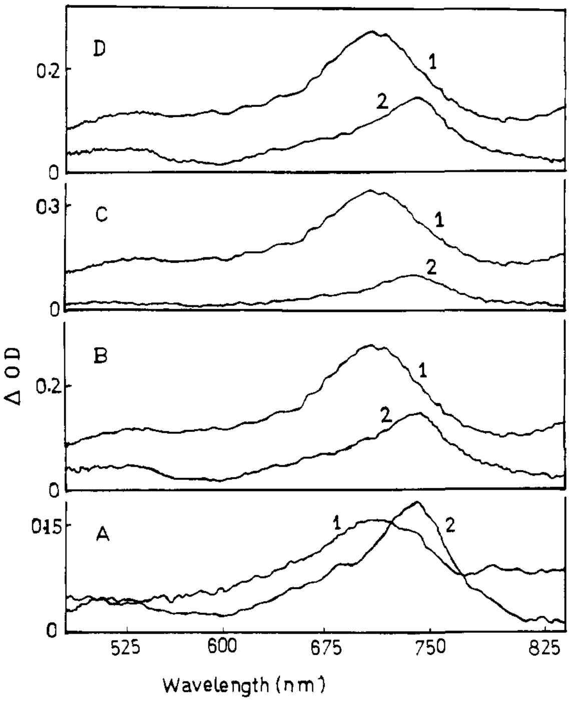


Figure 1. Picosecond transient absorption spectra obtained for the C_{60}–DPA system in different solvents ($[C_{60}] = 1.5 \times 10^{-4}$ mol dm^{-3}; [DPA] = 2.0 mol dm^{-3}): (A) in 15% iodobenzene in benzene; 1, at 0 ps; 2, at 3.8-ns delay; (B) in bromobenzene; 1, at 0 ps; 2, at 3.8-ns delay; (C) in benzene; 1, at 0 ps; 2, at 3.8-ns delay; (D) DPA-*d* in benzene; 1, at 0 ps; 2, at 3.8-ns delay.

The proton-transfer rate constants are known to be reduced on deuteration.[11] Hence, experiments were carried out with deuterated DPA (DPA-*d*) in benzene solutions. In these experiments it was found that C_{60} triplet yields increase in comparison to those in the undeuterated DPA as shown in Figure 1D. The results are in accordance with the expectation that the deuterium ion transfer rates are slower than proton-transfer rates ($k_d < k_p$), and hence ISC dominates in the solutions containing DPA-*d*, giving higher yields of the C_{60} triplet.

The triplet yields (Φ_T) under different conditions were estimated from the amount of conversion of the DPA cation ($\epsilon = 9000$ dm^3 mol^{-1} cm^{-1}),[22] formed immediately after the laser excitation, to the C_{60} triplet formed 4 ns after the pulse (ϵ at 740 nm for the C_{60} triplet, 12 000 dm^3 mol^{-1} cm^{-1}),[23,24] measured after the

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Table I. Photophyscial Parameters Associated with Ion Recombination of C-60–DPA and C-60–DPA-*d* Ion Pairs[a]

system	τ (ps)	ϕ_T	$\phi_{p/d}$	ϕ_{s+ID}	k_{ISC}[b]	$K_Q[Q]$[b]	(k_Q)[b]	k[b]	$k_{p/d}$[b]	$(k_s + k_{ID})$[b]
C-60–DPA in										
BZ	240	0.23	0.75	0.02	9.6				31.2	0.9
Br-BZ	210	0.37			17.6	8.0	(0.84)			
15% I-BZ in BZ	200	0.59			29.5	19.9	(14.8)			
C-60–DPA-*d* in										
BZ	390	0.38	0.59	0.03	9.7			16.1	15.1	0.8

[a] BZ = benzene; Br-BZ = bromobenzene; I-BZ = iodobenzene. [b] In units of $10^8\ s^{-1}$.

completion of formation of the latter (about 4 ns after the laser pulse). Thus, ϕ_T values are calculated as

$$\phi_T = [\epsilon(A^+)/\epsilon(^3C_{60})](OD_T/OD_{A^+}) \qquad (1)$$

where OD_{A^+} is the optical density of the DPA cation at 710 nm immediately after the laser pulse and OD_T is the optical density of the C_{60} triplet at 740 nm, measured after the completion of its formation. The values thus obtained are tabulated in Table I.

Following Scheme I, the fraction of the amine cation formed at the end of the pulse which gets converted into the C_{60} triplet can be written as

$$\phi_T = k_{ISC}/(k_s + k_p + k_{ISC} + k_{ID}) \qquad (2)$$

From the rate of disappearance of the DPA cation absorption at 710 nm with time, total rate constants ($k_s + k_{ISC} + k_p + k_{ID}$) have been estimated following single exponential decay analysis, the inverse of which is the lifetime of the ion pair and are listed in Table I. A typical single-exponential analysis for the C_{60}–DPA system in benzene was already reported in ref 4. Using these values for the total rate constants and the corresponding ϕ_T values calculated using eq 1, absolute values of k_{ISC} were calculated using eq 2. When the value of k_{ISC} in benzene is subtracted from those obtained in bromobenzene and 15% iodobenzene solutions, the effective quenching rate parameter $k_Q[Q]$ and hence k_Q were estimated for external heavy atom effects. The values of $k_Q[Q]$ and k_Q so obtained are also listed in Table I. It is clear from Table I that the external heavy atom effect is very strong for iodobenzene.

In the case of C_{60}–DPA and C_{60}–DPA-*d* ion pairs the same k_{ISC} values are obtained (within experimental error) as expected since deuteration will affect only the proton-transfer rate. Assuming the deuterium ion transfer rate $k_d = k_p - k$, where k is the decrease in the proton-transfer rate due to deuteration, the latter can be estimated as

$$k = k_p - k_d = \tau^{-1} - \tau_d^{-1} \qquad (3)$$

where τ and τ_d are the lifetimes of the ion pairs [$C_{60}^{-}\cdots DPA^+$] and [$C_{60}^{-}\cdots DPA\text{-}d^+$], respectively.

Again, from the definition of the quantum yield for the proton transfer (ϕ_p) and the deuterium ion transfer (ϕ_d) we have

$$\phi_p = k_p\tau = 1 - \phi_T - \phi_s - \phi_{ID} \qquad (4)$$

$$\phi_d = k_d\tau_d = 1 - \phi_{T,d} - \phi_s - \phi_{ID} \qquad (5)$$

Subtracting eq 5 from eq 4 and using the experimentally observed ratio of

$$\tau_d/\tau = 1.6$$

we get

$$(k_p - 1.6k_d)\tau = \phi_{T,d} - \phi_T = 0.15 \qquad (6)$$

Using eqs 3 and 6, the values of k_p and k_d are calculated and are listed in Table I. Knowing k_{ISC}, k_p, and k_d, the sum of the rate constants ($k_s + k_{ID}$) is also estimated. The values of different rate constants associated with Scheme I and the quantum yields for each channel are tabulated in Table I. It is seen from Table I that in the C_{60}–DPA system k_p is very high compared to the other rate constants, resulting in low ϕ_T and negligible ϕ_{s+ID} values.

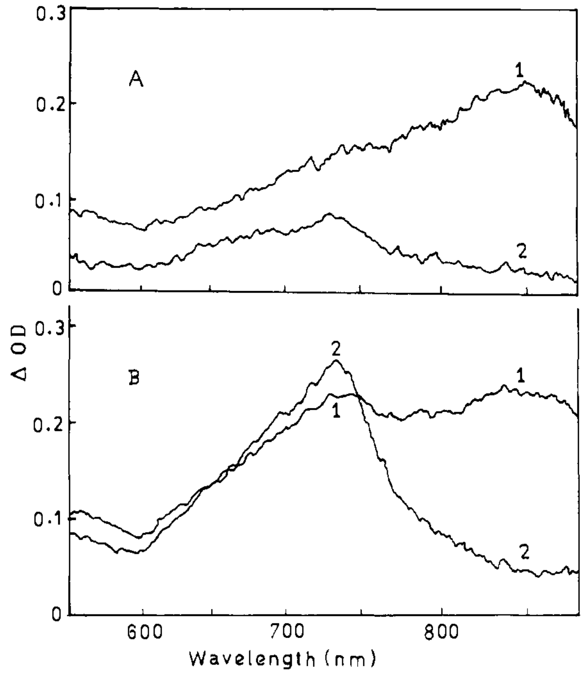

Figure 2. Picosecond transient absorption spectra obtained for the C_{60}–TEA system in different solvents ([C_{60}]) = 1.5×10^{-4} mol dm^{-3}; [TEA] = 3.0 mol dm^{-3}); (A) in benzene; 1, at 0 ps; 2, at 3.8-ns delay; (B) in 15% iodobenzene in benzene; 1, at 0 ps; 2, at 3.8-ns delay.

C_{60}–TEA System. It was earlier observed that,[4] for C_{60}–TEA in benzene solutions, the ion pair does not give the C_{60} triplet on CR, although TEA is a tertiary amine. In fact, on careful observation it is seen that, in the case of C_{60}–TEA in benzene, only a small amount of the C_{60} triplet is formed and the lifetime of the ion pair is ~200 ps. It is therefore reasonable to expect that the α-H atom of the alkyl group of TEA can participate in very fast proton transfer from the TEA cation to the C_{60} anion in the ion pair state. Hence, the reaction goes via a route similar to one seen for the C_{60}–DPA ion pair. In the C_{60}–TEA system the proton-transfer rate seems to be so high that k_{ISC} is negligible ($k_p \gg k_{ISC}$), and hence a small amount of the C_{60} triplet is formed following the recombination in benzene solutions. To enhance k_{ISC}, iodobenzene in benzene and neat bromobenzene were used as solvents, where a reasonable absorption due to the triplet of C_{60} is seen. Figure 2 shows the effect of 15% iodobenzene in benzene on the C_{60} triplet yield in the CR process of the C_{60}–TEA system in comparison to benzene solutions. It is therefore evident that proton transfer appears to be the predominant decay path for the C_{60}–TEA ion pair. It is already seen that, for the C_{60}–DPA system, ($k_s + k_{ID}$) is negligible in comparison to k_{ISC}. In the case of C_{60}–TEA in benzene it seems that both k_{ISC} and ($k_s + k_{ID}$) are negligible in comparison with k_p ($k_p \gg (k_{ISC} + k_s + k_{ID})$) and hence ϕ_p will be quite high (almost unity) for this

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Table II. Effect of Solvent Parity on Ion Recombination and Ion Separation in the C-60–TPA System

solvent	D	η^c (mN s/m^2)	τ^a (ps)	$\phi_T{}^b$	$\phi_{ID}{}^b$	k_{ISC} ($\times10^8$ s^{-1})	k_{ID} ($\times10^8$ s^{-1})
benzene	2.275	0.6	1300	0.9	0	6.9	
benzene + Cl-benzene^d (1:1)	3.94		1260	0.79	0	6.3	
Cl-benzene	5.62	0.8	1250	0.7	0.04	5.6	0.32
benzene + diCl-benzene^e (1:1)	6.1		1200	0.63	0.06	5.3	0.5
benzyl chloride	7.0	1.4	470	0.61	0.08	13.0	1.7
Cl-benzene + diCl-benzene (1:1)	7.78		1060	0.5	0.08	4.7	0.75
diCl-benzene	9.93	1.3	1150	0.34	0.11	3.0	1.0
benzyl alcohol	13.1	7.8	350	0.16	0.13	4.6	3.7
benzonitrile + diCl-benzene (4:6)	16.1		150	0.2	0.18	13	12
benzonitrile + diCl-benzene (6:4)	19.1		100	0.13	0.19	13	19
benzonitrile + diCl-benzene (2:8)	22.15		80	0.08	0.23	10	29
benzonitrile	25.2	1.45	50	0	0.25		50

[a] Error limit for the lifetimes <50 ps. [b] Error limit for quantum yield values ±0.02. [c] η is viscosity. [d] Cl-benzene is chlorobenzene. [e] diCl-benzene is *o*-dichlorobenzene.

system. The exact values for the quantum yields for the various kinetic routes and the rate constants, however, could not be evaluated for the C_{60}–TEA ion pair, as the optical absorption of the TEA cation (λ_{max} = 380 nm) lies beyond the spectral region of our detection system and hence quantum yields of either of the channels could not be measured.

Recently Kajii and co-workers[25] have found that photoirradiation of the C_{60}–TEA system in toluene results in the formation of stable photoproducts. According to Scheme I, we also expect likewise, as the proton-transferred radical species can give either the ground-state complex or its own products. However, the mechanism of product formation in this system proposed by the authors[25] is different. The authors also observe quenching the C_{60} triplet by TEA. However, in our present studies carried out using 3.0 mol dm^{-3} TEA in benzene no quenching of the C_{60} triplet could be seen up to 4 ns. In fact, in this system the ion pair lifetime is only ~200 ps, due to the fast proton transfer, and the triplet formation channel compete with the proton-transfer channel to give limited triplet yields. The apparent difference between the results obtained by us and by Kajii et al.[25] is not clear at this stage. Probably, the quenching rate is not high enough to show effective quenching in about 4 ns.

C_{60}–TPA System. In the TPA molecule no transferable proton exists, and hence, k_p will be 0 for TPA. This is indicated by a high C_{60} triplet yield in benzene as compared to that in the C_{60}–DPA system in the same solvent.[4] To understand the details of the mechanistic path, the C_{60}–TPA system was studied in several solvents and solvent mixtures of varying polarity. With an increase in the solvent polarity it is expected that k_{ID} will increase and hence the yield of the separated ion pairs will increase, and consequently, the yield of C_{60} triplets will decrease. The solvents used in the present study and their dielectric constants[26] are tabulated in Table II. For the mixed solvents the dielectric constants were calculated using the relation[27–29]

$$D_{mix} = f_A D_A + f_B D_B \qquad (7)$$

where the coefficients f_A and f_B represent the volume fractions of the solvents A and B and D_A and D_B represent their dielectric constants in the pure state. In all these solvent systems, the quantum yield for C_{60} triplet formation (ϕ_T) in C_{60}–TPA solutions was estimated by following eq 1 and assuming that the molar extinction coefficient of the TPA cation[18,19] at its absorption peak (665–670 nm) is the same in all the solvents and solvent mixtures studied. The value of ϵ_{TPA^+} in benzene was determined by comparing the OD of TPA^+ at 666 nm, formed at 4 ns after the laser pulse in the solutions of C_{60}–TPA in benzene with 20% (v/v) iodobenzene. To make sure that all [C_{60}^-–TPA^+] ion pairs recombined to give the fullerene triplet, a number of such measurements were carried out with varying amounts of iodobenzene, whereby it was confirmed that with >15% iodobenzene in benzene the fullerene triplet yield reaches the maximum.

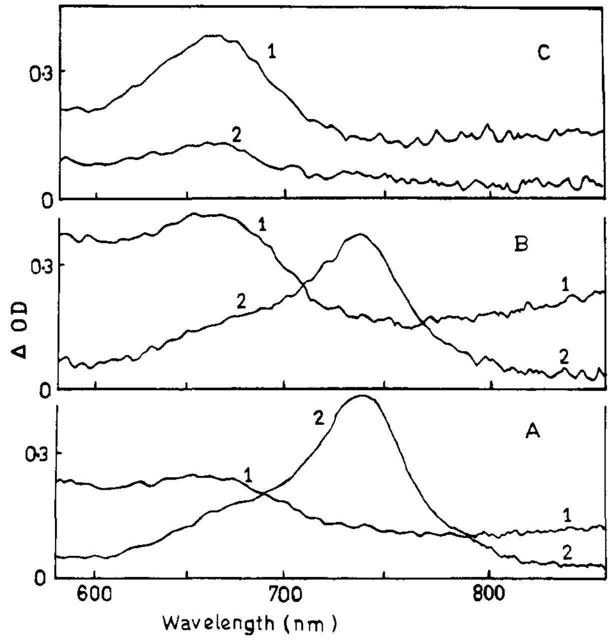

Figure 3. Picosecond transient absorption spectra obtained for the C_{60}–TPA system in various solvents ([C_{60}] = 1.5 × 10^{-4} mol dm^{-3}; [TPA] = 1.2 mol dm^{-3}): (A) in benzene; 1, at 0 ps; 2, at 3.8-ns delay; (B) in *o*-dichlorobenzene; 1, at 0 ps; 2, at 3.8-ns delay; (C) in benzonitrile; 1, at 0 ps; 2, at 3.8-ns delay.

The ϕ_T values obtained for the C_{60}–TPA system in different solvents and solvent mixtures are listed in Table II. It is seen that ϕ_T gradually decreases as the solvent dielectric constant is increased. The effect of solvent polarity on ϕ_T is clearly seen from Figure 3 for three solvents of different dielectric constants. Such observations are in accordance with the expectation that increased solvent polarity results in an increase in k_{ID}, increasing the separated ion pair yield and consequently reducing the C_{60} triplet yield. The increase in separated ion pair formation is clearly seen from Figure 3C, which shows the distinct transient absorption spectrum band for TPA^+ in the absorption spectrum obtained 4 ns after the laser pulse in benzonitrile solvent. The quantum yields for the separated ion pairs (ϕ_{ID}) in different solvents and solvent mixtures were calculated from the residual absorption at 665–670 nm due to the TPA cation 4 ns after the laser pulse. Wherever necessary, correction for the absorption of fullerene triplet at the wavelength of observation was made by subtracting the normalized C_{60} triplet absorption from the residual absorption at 665–670 nm, obtained 4 ns after the laser pulse. The normalization of the C_{60} triplet absorption was done from the observed C_{60} triplet spectrum in each solvent in the absence

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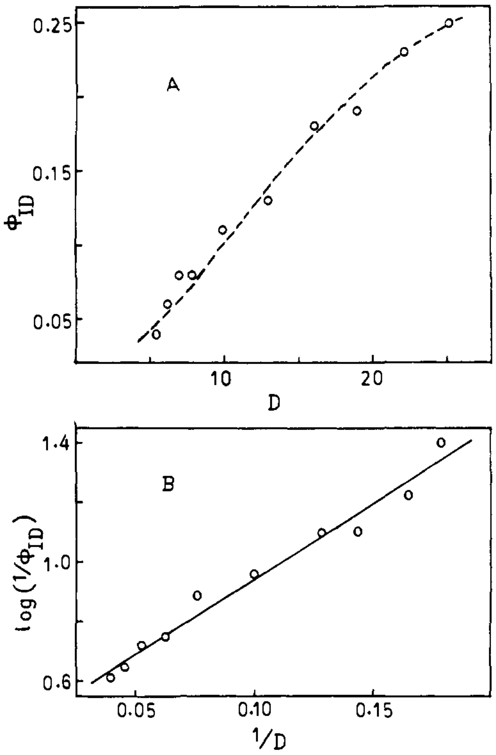

Figure 4. (A) Plot of the free ion yield (ϕ_{ID}) vs the dielectric constant (D) for the C_{60}–TPA system in the various solvents studied. (B) Plot of $\log(1/\phi_{ID})$ vs $1/D$ for the C_{60}–TPA system in the various solvents studied.

of TPA and normalizing it with respect to the OD_T value (λ = 740 nm) obtained for the C_{60}–TPA system in the same solvent.

The ϕ_{ID} values obtained for the C_{60}–TPA system in different solvents and solvent mixtures are listed in Table II. As expected, it is seen that the ϕ_{ID} value gradually increases as the solvent dielectric constant (D) is increased. A plot of ϕ_{ID} vs D shows a typical S-shaped curve (Figure 4A) usually observed for the separated ion pair yields as a function of the solvent dielectric constant.[27–29]

Using Mozumder's extension of Onsager's ion recombination model, Masuhara and co-workers[27] have shown that the variation of ϕ_{ID} with D follows the semilogarithmic relation

$$\log(1/\phi_{ID}) = a + b/D \tag{8}$$

where a and b are constants independent of D. A plot of $\log(1/\phi_{ID})$ vs $1/D$ for the present system shows good linearity, as shown in Figure 4B.

Considerations of energy changes in the ion separation process leads to another semilogarithmic relation (9) given by Masuhara et al.[27]

$$\log(1/\phi_{ID} - 1) = a + b/D \tag{9}$$

where a and b are constants. For the present systems, the plot of $\log(1/\phi_{ID}-1)$ vs $1/D$ is also seen to be linear. However, the data fit eq 8 better than eq 9, directly confirming the validity of the steps proposed in Scheme I. A linear correlation was also observed on plotting $\log(k_{ID})$ vs $1/D$ as done by Mataga for the tetracyanobenzene–toluene system.[30] Since in the present situation the effect of solvent polarity on the geometrical changes of the ion pair cannot be measured, it is not possible to calculate the ΔG_0 associated with the charge recombination process. Thus, a correlation between the CR rate and ΔG_0 is not possible for the present system, as is observed in a large number of recent papers[31–34] for chemically related donor–acceptor pairs in a suitable solvent.

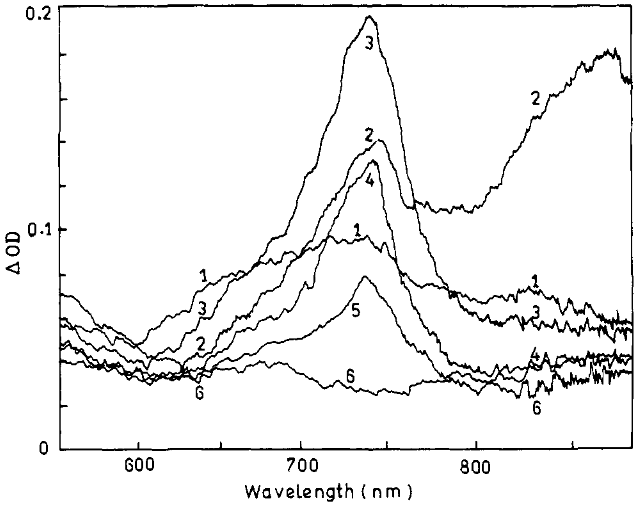

Figure 5. Picosecond transient absorption spectra obtained for the C_{60}–DABCO system at different delay times after the laser pulse in mixed solvent (benzonitrile–o-dichlorobenzene–iodobenzene; 2:2:1) ([C_{60}] = 1.5×10^{-4} mol dm^{-3}; [DABCO] = 0.5 mol dm^{-3}): (1) 0 ps; (2) 50 ps; (3) 200 ps; (4) 550 ps; (5) 1050 ps; (6) 4.1 ns.

Effect of Viscosity. In the solvents and solvent mixtures used, except for benzyl alcohol, the viscosity changes by a factor of 2.[26] Increase of viscosity should result in reduction of the ion pair lifetimes as a result of increase in k_s. However, the lifetime values (Table II) do not seem to change drastically even in the case of viscous benzyl alcohol. On the other hand, the ion pair lifetime follows a reasonably good correlation with the dielectric constant of the solvent, as seen from Table II. Hence, it is considered that the viscosity effect on the CR reactions is marginal and the main governing factor is the solvent polarity.

C_{60}–DABCO System. The DABCO molecule has no H atom attached to the two aza nitrogens. However, the DABCO molecule has α-hydrogen atoms in its three bridged alkyl groups. Hence, it is expected that DABCO should behave either like TPA to give good C_{60} triplet yields or like TEA, in which case the C_{60} triplet yields will be poor. Since DABCO is not sufficiently soluble in most of the solvents studied, except benzonitrile, a 50:50 (v/v) mixture of benzonitrile, and o-dichlorobenzene was used as solvent for this system. Neat benzonitrile was not used as solvent to avoid strong polarity effects, as observed in the case of the C_{60}–TPA system. In mixed benzonitrile–dichlorobenzene (50:50) it is seen that for the C_{60}–DABCO system the triplet yield is poor. Since in the mixed solvent, too, the DABCO concentration (saturated solution; 0.5 mol dm^{-3}) was not high enough, it was expected that part of the C_{60} triplet could also be coming from direct excitation of free, uncomplexed C_{60}. Thus, it is seen that DABCO behaves like TEA. It is also seen that, with the addition of 20% iodobenzene, in the C_{60}–DABCO system in the mixed solvent (2:2:1), the fullerene triplet yield increases significantly (Figure 5). These observations clearly indicate that DABCO behaves like TEA. An interesting point observed with DABCO, in the prsence or absence of iodobenzene, is the quenching of the C_{60} triplet. It is seen that, with the present amine donor (DABCO), fullerene triplet absorption initially increases with time for 100–200 ps (depending on the presence or absence of iodobenzene) and thereafter the C_{60} triplet decreases with time and vanishes completely in 4 ns (Figure 5). This type

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of triplet quenching is not observed with any other amine studied. However, due to limited solubility, triplet quenching by DABCO, and poor DABCO cation absorption at 525 nm, it was not possible to extract the detailed kinetic information and various quantum yields for the processes given in Scheme I.

The present results on various C_{60}–amine complexes show that C_{60} resembles closely aromatic hydrocarbons such as naphthalene and pyrene[9-12] with respect to photoexcited CS and CR processes, proton-transfer reactions, ISC processes, and ionic dissociation of the ion pair states. No special properties of C_{60} as a dome structure could be seen in the present studies.

Experimental Section

Fullerene C_{60} obtained from SES Corp. was used after checking its purity by UV–vis spectrophotometry. Diphenylamine and triphenylamine were purified by repeated crystallization from methanol. Triethylamine was purified by fractional distillation in the presence of NaOH. Spectroscopic grade benzene and benzonitrile (both from Spectrochem, Bombay) were used as received. Benzyl chloride (Aldrich 99%), iodobenzene (Fluka), bromobenzene (Fluka), benzyl alcohol (Spectrochem, Bombay), chlorobenzene, dichlorobenzene, and triethylamine were used after distillation. Deuterated DPA was prepared by repeated shaking of the benzene solution of DPA with D_2O (>99%) and separating out the organic layer. Solid DPA-*d* was obtained by evaporating the solvent, and its purity was estimated to be >90% by IR spectroscopy. 1,4-Diazabicyclo[2.2.2]octane (DABCO, Fluka) was used as received.

Steady-state absorption spectra were recorded on a Shimazdu Model 160 A spectrophotometer. Transient optical absorption spectra were recorded by a picosecond laser flash photolysis system described in detail elsewhere.[23,24] Briefly, the second harmonic output (532 nm, 35 ps, 15 mJ) from an actively–passively mode locked Nd:YAG laser was used for excitation of the solutions. The transients thus generated were monitored by a white-light continuum (400–900 nm) produced by focusing the residual fundamental 1064-nm light on a 10-nm cell containing a 50:50 (v/v) H_2O–D_2O mixture. The delay between the pump and probe pulses was adjusted by a combination of a delay rail and different lengths of optical fibers. The probe beam was bifurcated by an optical fiber beam splitter to generate reference and analyzing beams. Both the reference and analyzing beams were dispersed through a spectrograph and recorded by a dual diode array based optical multichannel analyzer system.

Conclusions

The photoexcitation of the C_{60}–DPA, C_{60}–TEA, C_{60}–TPA, and C_{60}–DABCO complexes results in the production of ion pairs $^1[C_{60}^{-}\cdots\text{amine}^{+}]$. In the C_{60}–DPA, C_{60}–TEA, and C_{60}–DABCO systems the ion pairs undergo very fast proton transfer from the amine cations to the fullerene anion. The intersystem crossing from the singlet ion pair state to the triplet ion pair state and the consequent formation of the C_{60} triplet by ion recombination are thus small or negligible for the C_{60}–DPA, C_{60}–TEA, and C_{60}–DABCO systems. Experiments carried out using solvents such as bromobenzene and benzene–iodobenzene mixtures, where ISC processes are enhanced, prove the hypothesis. In the case of the C_{60}–TEA and C_{60}–DABCO systems the α-hydrogen atom in the alkyl chain participates in very fast proton transfer in the singlet ion pair state of the fullerene amine complexes. Use of deuterated DPA also gives results concurrent with the proposed scheme.

In the C_{60}–TPA system, no proton transfer is possible and the ion pair $^1[C_{60}^{-}\cdots TPA^{+}]$ is subjected to competing processes such as intersystem crossing to the triplet ion pair state, dissociation of the ion pair to give free ions, and the recombination of the ion pair to give the ground state of the complex back. In the low-polarity solvents, the ISC process dominates, resulting in the formation of the fullerene triplet as the major product. In solvents of more polarity, ion dissociation predominates, producing more solvent-separated free ions. The inverse of the free ion yield follows a semilogarithmic relation with the inverse of the dielectric constant, as suggested by Masuhara and co-workers[27-29] following Onsager's ion recombination model and energy considerations in the ion separation process. In our opinion, in the present studies C_{60} behaves like a typical aromatic hydrocarbon acceptor with respect to organic amine donors.

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