

Electron-Transfer Reactions between Fullerenes (C₆₀ and C₇₀) and Tetrakis(dimethylamino)ethylene in the Ground and Excited States

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Electron-transfer reactions between tetrakis(dimethylamino)ethylene (TDAE) and fullerenes (C₆₀ and C₇₀) in solution have been studied in the ground and excited states. Analyses of the thermal equilibria indicate that the radical ions are present as free radical ions in appropriate polar solvents, while the radical ion pairs are predominant in less polar solvents. On the laser excitation of C₆₀/C₇₀ in the presence of TDAE, the concentration of the radical anions (C₆₀^{•−}/C₇₀^{•−}) was increased by photoinduced electron transfer via the triplet state of C₆₀/C₇₀. The photochemically generated C₆₀^{•−}/C₇₀^{•−} decayed rapidly by the back-electron transfer returning to the thermal equilibrium. In polar solvents the back-electron-transfer reactions obey bimolecular kinetics, suggesting that radical ions are separately solvated. In less polar solvents, on the other hand, first-order kinetics of the decay of C₆₀^{•−}/C₇₀^{•−} indicates that the back-electron transfer occurs within the ion pairs. On combination of the rate constants of the back-electron transfer with the equilibrium constants, the rate constants of the electron transfer in the ground states were evaluated, which are 1/3 to 1/45 of those in the excited triplet states.

Introduction

Fullerenes show various interesting properties when they are chemically treated with some electron donors or acceptors; superconductivity,¹ ferromagnetism,² and photoconductivity³ attracted much attention. Among the organic electron donors, tetrakis(dimethylamino)ethylene (TDAE) is one of the strongest donors to form radical ion salts with electron acceptors.⁴ Mixing C₆₀ with TDAE easily forms the radical ion salt of C₆₀–TDAE, which shows a ferromagnetic transition at low temperature.^{2a} Properties of various fullerene–TDAE salts have been investigated extensively by means of magnetic susceptibility, magnetization, EPR, and X-ray diffraction measurements.² On the other hand, the EPR study of the solution of C₆₀/C₇₀–TDAE also revealed useful information on the nature of radical ions, such as disproportionation.^{2g}

In the present paper, we report the results of a detailed study on the electron-transfer reaction of fullerene (C₆₀/C₇₀)–TDAE systems in solution. The present reaction system seems to be quite a unique one that allowed us to investigate electron transfer both in the ground and excited states. Within our knowledge, the study that evaluates the reactivity both in the ground and excited states quantitatively is quite rare, although such information is essential to understand and design novel materials; charge generation is a key process for interesting and useful properties such as photoconductivity.³ We examine the thermal equilibrium of radical ion formation in several solvents using steady-state spectroscopic measurements such as vis–near-IR and EPR spectra to make clear the radical ion states. For such solutions containing C₆₀/C₇₀, TDAE, and their radical ions, we employ a laser flash photolysis method to investigate photoinduced electron transfer and back-electron-transfer phenomena. On combining the kinetic data with the equilibrium data, we can compare electron-transfer phenomena of the fullerene–TDAE systems in the ground state with those in the excited state.

Experimental Section

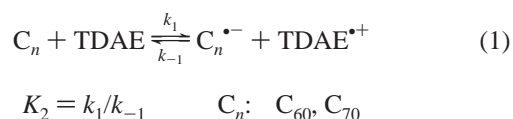
Materials. C₆₀ (purity = 99.5%) and C₇₀ (purity = 98%) were obtained from Texas Fullerene Corp. and Southern

Chemical Group LLC, respectively. TDAE was purchased from Aldrich and used as received. Solvents used were the best grades available commercially.

Apparatus. Steady-state absorption spectra in the vis–near-IR region were measured with a JASCO V-570DS spectrometer at room temperature. EPR spectra were measured with a Varian E-4. EPR measurements were carried out just after the sample preparation and deaeration. Transient absorption spectra in the near-IR region were measured using the second harmonic generation (SHG) (532 nm) of a Nd:YAG laser (6 ns fwhm) as the excitation source. Light from a pulsed Xe lamp was detected with a Ge avalanche photodiode (APD) detector through the sample. Details of the transient absorption measurements were described in our previous reports.⁵ All the samples in a quartz cell (1 cm × 1 cm) were deaerated by bubbling Ar through the solution for 10 min for both steady and transient measurements.

Results and Discussions

Radical Ion Formation in the Ground State. When TDAE was added to C₆₀ in *o*-dichlorobenzene (*o*-DCB), sharp absorption bands appeared with some structures in the vis–near-IR region as shown in Figure 1. The absorption band at λ_{max} = 1078 nm with peaks at 1041 (sh), 998, and 929 nm was attributed to C₆₀^{•−}.⁶ The absorption in 500–600 nm may also be due to C₆₀^{•−} because TDAE^{•+} does not show peaks in the visible region.⁸ At a constant concentration of C₆₀, the absorption bands increase with TDAE concentration, indicating that neutral molecules and radical ions were in equilibrium, as shown in eq 1:



where K₂ is an equilibrium constant. The subscript 2 implies that the back-electron transfer is a bimolecular reaction.

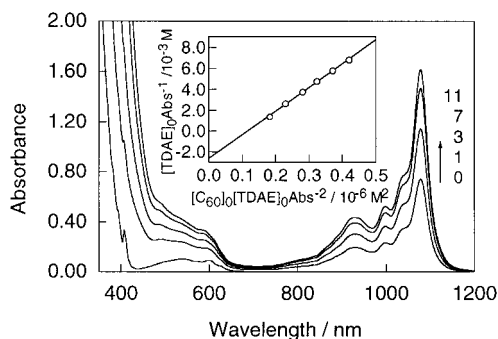


Figure 1. Steady-state absorption spectra of C_{60} (0.1 mM) and various concentrations of TDAE in deaerated *o*-DCB at room temperature. The numbers show the concentration of TDAE in mM. Inset shows a plot of eq 2.

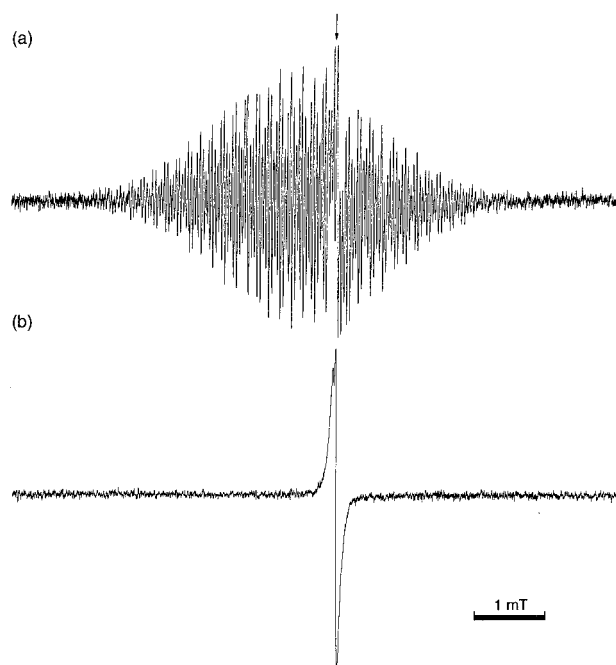


Figure 2. EPR spectra of mixture of C_{60} (0.1 mM) and TDAE (20 mM) in deaerated (a) *o*-DCB and (b) anisole at room temperature.

Although the absorption peak at 929 nm in Figure 1 seems to resemble the reported absorption band of the dianion of C_{60} (C_{60}^{2-}) at 945 nm, the ratio of the absorption peak at 929 nm to that at 1078 nm was 0.24, which is in good agreement with the reported one for $C_{60}^{•-}$.^{6a,b} Therefore, the generation of C_{60}^{2-} due to second reduction or other processes can be neglected. The ratio of absorbances at the peaks did not vary in the course of the present experiments.

The sharp absorption peak at 1078 nm indicates that $C_{60}^{•-}$ and $TDAE^{•+}$ are present as free radical ions or solvent-separated ion pairs in *o*-DCB. This was supported by the finding that the absorption peak at 1078 nm did not shift even under such high concentrations of $C_{60}^{•-}$ and $TDAE^{•+}$ that the formation of the contact ion pair may be favorable. The formation of $TDAE^{•+}$ was confirmed by the EPR spectra of C_{60} -TDAE system in *o*-DCB as shown in Figure 2a. $TDAE^{•+}$ can be identified by the hyperfine structure; the observed signal was analyzed well by assuming the reported coupling constants (4 N atoms with 0.49 mT, 12 H atoms with 0.33 mT, and 12 H atoms with 0.28 mT).⁸ In the EPR signals of $TDAE^{•+}$, a narrow signal shown by the arrow in Figure 2a and a broad background signal may be hidden; they are attributed either to $C_{60}^{•-}$ or to C_{60}^{2-} , although some arguments for the assignment of these narrow

TABLE 1: Equilibrium Constants (K) and Molar Extinction Coefficients of Fullerenes Radical Anions (ϵ)

fullerene	solvent ^a (ϵ_s)	$K_1^{b/}$ M^{-1}	K_2^b	$\epsilon^c/$ $M^{-1} cm^{-1}$	$\lambda_{max}/$ nm	$[TDAE]_0/$ mM
C_{60}	BN (25.70)	240		14000	1076	0.2–1
	BN/Tol (14.04)	6.34		23900	1072	1–10
	<i>o</i> -DCB (9.93)	0.016		22800	1078	1–11
	CB (5.61)	43		10700	1073	5–25
	<i>m</i> -DCB (5.04)	26		14500	1074	1–25
	anisole (4.33)	42		13000	1070	2–25
	Bz (2.28)	1.1		(7000) ^d	1067	10–200
C_{70}	BN/Tol (14.04)	>100		^d	1372	1–11
	<i>o</i> -DCB (9.93)	0.043		7030	1373	1–11
	CB (5.61)	50		3400	1365	7–20
	anisole (4.33)	115		3000	1369	1–25
	Bz (2.28)	^e		^e	1366	10–200

^a BN, benzonitrile; BN/Tol, benzonitrile/toluene = 1:1; *o*-DCB, *o*-dichlorobenzene; CB, chlorobenzene; *m*-DCB, *m*-dichlorobenzene; Bz, benzene. ^b Estimation error: $\pm 5\%$. ^c Estimation error: $\pm 2\%$. ^d Reasonable ϵ was not obtained. ^e Absorption peaks of $C_{70}^{•-}$ was not observed even on addition of high concentrations of TDAE.

and broad signals still remain.^{2,9} The g value of the C_{60} anion species was estimated to be 2.0007, which is in good agreement with the previously reported value for the C_{60} -TDAE salt.^{2f,g,9} In the more polar benzonitrile/toluene mixture (1:1), similar EPR signals consisting of broad and narrow signals of $C_{60}^{•-}$ with hyperfine structures of $TDAE^{•+}$ were confirmed. Thus, the EPR spectrum in Figure 2a suggests that $C_{60}^{•-}$ and $TDAE^{•+}$ are present as solvent-separated ion pairs or free radical ions; at least, it is not necessary to take the contact ion pair into consideration from these sharp signals.

For the equilibrium (eq 1), eq 2 can be derived by assuming that $[C_n^{•-}]$ is negligibly small compared with the initial concentration of TDAE, $[TDAE]_0$,

$$\frac{[TDAE]_0}{Abs} = \frac{[C_n]_0[TDAE]_0}{Abs^2} \epsilon - \frac{1}{K_2 \epsilon} \quad (2)$$

where $[C_n]_0$, Abs, and ϵ are the initial concentration of C_n , absorbance, and the extinction coefficient of $C_n^{•-}$, respectively. In the inset of Figure 1, $[TDAE]_0/Abs$ was plotted against $[C_{60}]_0[TDAE]_0/Abs^2$. From the intercept and slope, the ϵ and K_2 values were evaluated as listed in Table 1. The ϵ value of $C_{60}^{•-}$ is slightly larger than the reported one in benzonitrile.⁶ Compared with *o*-DCB, K_2 in the benzonitrile/toluene (1:1) mixture shows drastic increase by a factor of 400, although the increase in the dielectric constant was small. A drastic increase of K_2 will result from segregation of polar benzonitrile around radical ions. In highly polar solvents such as benzonitrile, the K_2 value further increases, indicating that most of the C_{60} is converted into $C_{60}^{•-}$ on addition of only a slight excess of TDAE.

In nonpolar benzene, only a small amount of $C_{60}^{•-}$ appeared on the addition of a large excess of TDAE, although a blue shift (about 10 nm) and broadening of absorption bands were observed compared to absorption bands in highly polar solvents. The relationship between the concentration and the absorbance does not obey eq 2 (Figure 3a), indicating that the generated radical ions are not solvated as free radical ions. On the basis of an assumption that the radical ions are present as contact ion pairs (eq 3), the equilibrium constant (K_1) and ϵ values in benzene were evaluated by the Benesi-Hildebrand method (eq 4);¹⁰ subscript 1 of the equilibrium constant implies that the back-electron transfer of eq 3 is a monomolecular reaction. This assumption is confirmed by the fact that a plot of eq 4 shows good linear relationship, as shown in Figure 3b. Furthermore,

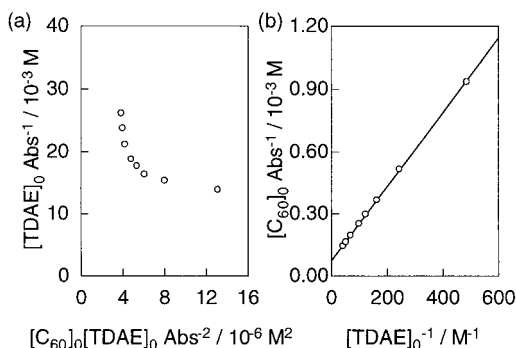


Figure 3. Analyses of absorption spectral change observed in an anisole solution containing C_{60} and TDAE by (a) eq 2 and (b) Benesi-Hildebrand plot (eq 4).

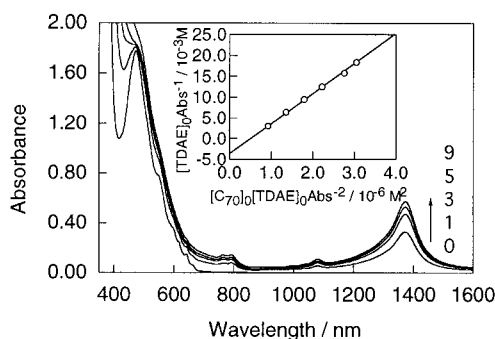
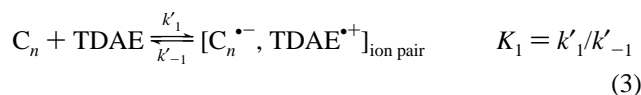


Figure 4. Steady-state absorption spectra of C_{70} (0.1 mM) and various concentrations of TDAE in deaerated *o*-DCB at room temperature. The numbers show the concentration of TDAE in mM. Inset shows a plot of eq 2.

the results of the laser photolysis experiments in the later section of the present paper indicate contact ion pair formation in less polar solvents, which support the present assumption.



The estimated K_1 and ϵ values are added to Table 1 for C_{60} .

$$\frac{[C_n]_0}{\text{Abs}} = \frac{1}{K_1 \epsilon [TDAE]_0} + \frac{1}{\epsilon} \quad (4)$$

The ϵ value in benzene is much smaller than those in polar solvents. The finding can be partly attributed to the ion pair formation in benzene.

In the EPR spectra of C_{60} -TDAE in less polar solvents such as anisole and *m*-dichlorobenzene (*m*-DCB), the hyperfine structure due to $TDAE^{\bullet+}$ was diminished as shown in Figure 2b even immediately after the sample preparation. This finding indicates that the radical ions will take a different solvated form other than solvent-separated ion pairs or free radical ions as considered above.

For the C_{70} -TDAE system in *o*-DCB, the generation of $C_{70}^{\bullet-}$ was confirmed by the appearance of an absorption band at 1373 nm (Figure 4).¹¹ Two weak absorption peaks appeared at 780 and 1080 nm, in which the 1080 nm band is due to $C_{60}^{\bullet-}$ with a large ϵ value contained as an impurity. Since the amount of $C_{60}^{\bullet-}$ is estimated to be ca. 0.1% of $C_{70}^{\bullet-}$ in Figure 4, effects of $C_{60}^{\bullet-}$ on the present equilibrium and kinetic study on $C_{70}^{\bullet-}$ can be negligible. The 780 nm band may be due to an unknown impurity. The ϵ value at 1373 nm for $C_{70}^{\bullet-}$ estimated by eq 2 shows good agreement with the reported ones.¹¹ The K_2 value

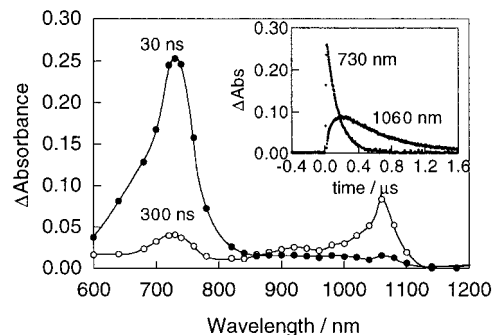
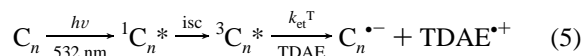


Figure 5. Transient absorption spectra of C_{60} (0.1 mM) in the presence of TDAE (1 mM) in *o*-DCB at room temperature. Inset shows time profiles.

for C_{70} is similar to that for C_{60} in *o*-DCB (Table 1), suggesting similar electron-accepting ability of C_{60} and C_{70} .¹² In the benzonitrile/toluene (1:1) mixture, most of the C_{70} is converted to $C_{70}^{\bullet-}$ on adding only a slight excess of TDAE; the K_2 value was evaluated to be larger than 100. In more polar benzonitrile, the absorption spectra of $C_{70}^{\bullet-}$ were essentially the same as those in *o*-DCB with a slight shift of the absorption peaks, but K_2 was too large to evaluate. In benzene, on the other hand, the appreciable absorption band of $C_{70}^{\bullet-}$ was not observed even after addition of a large excess of TDAE, indicating its small K and ϵ values.

Radical Ion Formation in the Excited State. By 532 nm laser excitation of the solution, in which C_{60} , TDAE, $C_{60}^{\bullet-}$, and $TDAE^{\bullet+}$ are in equilibrium concentrations, both C_{60} and $C_{60}^{\bullet-}$ were irradiated, resulting in the shift of the equilibrium.¹³ In Figure 5, the transient absorption spectra observed by laser excitation of the C_{60} -TDAE system in *o*-DCB are shown. The absorption band of $^3C_{60}^*$ appeared at 740 nm immediately after laser excitation.¹⁴ With the decay of $^3C_{60}^*$, extra $C_{60}^{\bullet-}$ appeared at 1060 nm as shown in the time profiles in Figure 5. Since the time profiles of the decay of $^3C_{60}^*$ and the rise of $C_{60}^{\bullet-}$ show a mirror image, it is evident that $C_{60}^{\bullet-}$ is formed via $^3C_{60}^*$ (eq 5).¹⁵ The electron transfer between $^3C_{60}^*$ and TDAE was supported by enhancement of the decay rate of $^3C_{60}^*$ and the rise rate of $C_{60}^{\bullet-}$ with an increase of TDAE concentration.



From the ratio of $[C_{60}^{\bullet-}]_{\text{max}}$, which was estimated by using ϵ in Table 1 to $[^3C_{60}^*]_{\text{init}}$, the quantum yield of electron transfer (Φ_{et}^T) was evaluated as summarized in Table 2. In solvents with low dielectric constants, the Φ_{et}^T values are not high, suggesting that other deactivation processes of $^3C_{60}^*$ are competitive with the electron transfer. Each decay of $^3C_{60}^*$ obeys a first-order decay function ($k_{1st}(^3C_{60}^*)$) under the pseudo-first-order condition ($[^3C_{60}^*] \ll [TDAE]$). From the relation between $[TDAE]$ and $k_{1st}(^3C_{60}^*)$, the second-order rate constant (k_{obs}^T) was estimated. The rate constant of electron transfer (k_{et}^T) was evaluated using the relation $k_{\text{et}}^T = \Phi_{\text{et}}^T k_{\text{obs}}^T$,¹⁶ as listed in Table 2.

After reaching a maximum, $C_{60}^{\bullet-}$ begins to decay gradually as shown in the time profile in Figure 5. This decay curve obeys a first-order decay function (Figure 6), although $C_{60}^{\bullet-}$ usually decays slowly following a second-order decay function when the same amounts of $C_{60}^{\bullet-}$ and $TDAE^{\bullet+}$ are present as a solvent-separated ion pair or as free ions.¹⁷ This first-order rate constant ($k_{1st}(C_{60}^{\bullet-})$) increases with $[TDAE^{\bullet+}]_0$, which refers to the concentration of $TDAE^{\bullet+}$ before the laser irradiation and was calculated using K_2 in Table 1. Under the present experimental

TABLE 2: Rate Constants of the Forward and the Back-Electron-Transfer Reaction between Fullerenes and TDAE

fullerenes	solvent	Φ_{et}^T ^a	k_{obs}^T /M ⁻¹ s ⁻¹	k_{et}^T /M ⁻¹ s ⁻¹	$k_{\text{bet}}^{\text{1st}}$ /s ⁻¹	$k_{\text{bet}}^{\text{2nd}}$ /M ⁻¹ s ⁻¹	$k_1 (=k_{\text{et}}^G)^{b,c}$ /M ⁻¹ s ⁻¹
C ₆₀	<i>o</i> -DCB	0.33	5.7×10^9	1.9×10^9		4.0×10^{10}	6.4×10^8
	CB	0.25	1.2×10^{10}	3.3×10^9	1.2×10^7		5.2×10^8
	<i>m</i> -DCB	1.00	7.8×10^9	7.8×10^9	1.5×10^7		3.9×10^8
	anisole	0.36	9.2×10^9	3.3×10^9	1.7×10^7		7.1×10^8
	Bz	0.13	1.1×10^{10}	1.4×10^9	1.3×10^7		1.4×10^7
C ₇₀	<i>o</i> -DCB	0.87	5.8×10^9	5.0×10^9		4.1×10^{10}	1.8×10^9
	CB	1.00	1.1×10^{10}	1.1×10^{10}	1.7×10^7		8.5×10^8
	anisole	1.00	8.7×10^9	8.7×10^9	1.8×10^7		2.1×10^9
	Bz	0.14	1.3×10^{10}	1.5×10^9	2.0×10^7		d

^a Estimation error: $\pm 5\%$. ^b Estimation error: $\pm 7\%$. ^c $k_{\text{bet}}^{\text{2nd}} = k_{-1}$, from $K = k_1/k_{-1}$ and $k_1 = k_{\text{et}}^G$. ^d K was not obtained.

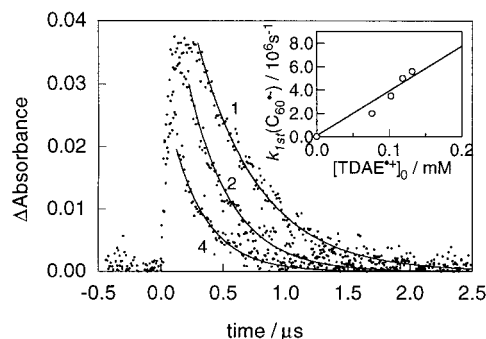


Figure 6. Decay curves of C₆₀*⁻ at 990 nm in different [TDAE]₀ in *o*-DCB. The numbers show the [TDAE]₀ in mM. Solid lines show fitted curves. Inset shows the dependence of the first-order rate constants of the decay of C₆₀*⁻ ($k_{1\text{st}}(\text{C}_{60}^{*-})$) on [TDAE*⁺]₀ in *o*-DCB.

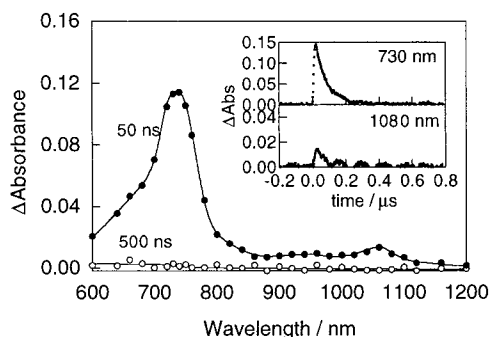
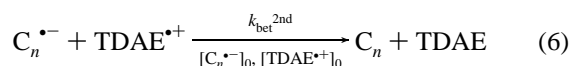


Figure 7. Transient absorption spectra of C₆₀ (0.1 mM) in the presence of TDAE (1 mM) in benzene at room temperature. Inset shows time profiles.

conditions, the laser irradiation produced 0.005 mM of C₆₀*⁻ additionally at the maximum, which is far less than [TDAE*⁺]₀. This indicates that the pseudo-first-order condition is achieved in the back-electron-transfer reaction (eq 6). The plot of $k_{1\text{st}}(\text{C}_{60}^{*-})$ vs [TDAE*⁺]₀ is shown in the inset of Figure 6, in which a linear relation is found. The slope gives the second-order rate constant of the back-electron-transfer reaction, $k_{\text{bet}}^{\text{2nd}}$, as listed in Table 2. In the benzonitrile/toluene (1:1) mixture and in benzonitrile, the transient absorption band due to ³C₆₀* was not observed because most of the C₆₀ is converted to C₆₀*⁻ in the presence of only a slight excess of TDAE before the laser illumination.



In nonpolar benzene, both ³C₆₀* and C₆₀*⁻ were observed immediately after the laser pulse (Figure 7), although the absorption of C₆₀*⁻ is smaller than that in *o*-DCB, indicating low Φ_{et}^T . The decay rate of ³C₆₀* and rise rate of C₆₀*⁻ in benzene are as fast as those in *o*-DCB; however, k_{et}^T was small

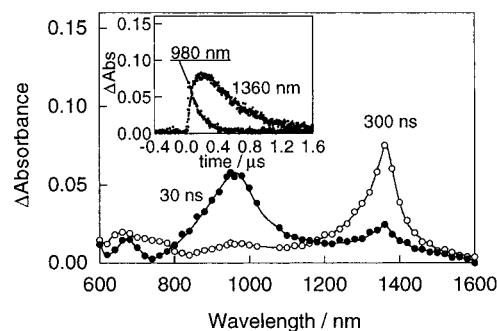
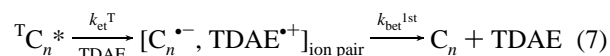


Figure 8. Transient absorption spectra of C₇₀ (0.1 mM) in the presence of TDAE (1 mM) in *o*-DCB at room temperature. Inset shows time profiles.

because of low Φ_{et}^T . The decay of C₆₀*⁻ was fitted well by a first-order decay function. The decay rate constant was quite larger than that in *o*-DCB. In benzene, since [TDAE*⁺]₀ is negligibly low before laser irradiation, first-order kinetics of C₆₀*⁻ decay indicates that C₆₀*⁻ and TDAE*⁺ are present as ion pairs (eq 7).¹⁷ The first-order rate constants of back-electron-transfer within the ion pair ($k_{\text{bet}}^{\text{1st}}$) were evaluated in benzene and in other solvents with low dielectric constants (Table 2).



Generation of radical ions by laser irradiation was also observed in the transient absorption spectra of C₇₀ in the presence of TDAE in *o*-DCB (Figure 8). The electron-transfer reaction via ³C₇₀* (eq 5) was confirmed. The generated radical ions decayed by second-order kinetics in highly polar solvents, while first-order kinetics was confirmed in less polar solvents. The rate constants and Φ_{et}^T are summarized in Table 2.

From a comparison of eq 1 (eq 3) with eq 6 (eq 7), we can put $k_{\text{bet}}^{\text{2nd}}$ ($k_{\text{bet}}^{\text{1st}}$) equal to k_{-1} (k'_{-1}) to estimate k_1 as listed in Table 2. In each solvent, the k_1 is smaller than k_{et}^T by a factor of $1/45$ to $1/3$. The different reactivity can be explained on the basis of the free energy change of the electron-transfer reactions, which can be calculated by the expression developed by Weller.¹⁸ From the reduction potential of C₆₀ in the excited triplet state or ground state,¹⁵ the oxidation potential of TDAE,¹⁹ and the dielectric constants of the solvents,^{20,21} -28 to -45 kcal mol⁻¹ of sufficiently negative free energy changes are expected for the electron transfer in the triplet excited state (ΔG_T) in the solvents in this study, while smaller changes are expected for those in the ground state (ΔG_G). The ΔG_G of the C₆₀-TDAE system in *o*-DCB, chlorobenzene, *m*-DCB, anisole, and benzene were calculated to be -8.8, -5.0, -4.0, -2.4, and 7.8 kcal mol⁻¹, respectively. The positive ΔG_G of the reaction in benzene explains well the finding that k_1 in benzene was on the order of 10^7 M⁻¹ s⁻¹, while in other solvents k_1 was on the order of 10^8 M⁻¹ s⁻¹. Furthermore, $k_{\text{bet}}^{\text{1st}} < k_1$ can be

explained on the basis of calculated ΔG_G : the forward electron-transfers in all solvents except benzene are exothermic reactions. The k_1 values are smaller than diffusion-limited rate by factors of $1/40$ to $1/60$, suggesting that the ground-state electron transfer needs slightly positive activation energy.

The electron-transfer systems employed in this study will be the first example to afford both rate constants k_{et}^T and k_{et}^G . Usually, photoinduced electron transfer systems did not show electron transfer in the ground state and vice versa. In this respect, the fullerene-TDAE systems are quite interesting not only from the points of practical use but also from a physical chemistry viewpoint.

Conclusion

In the present study, we showed that fullerenes and TDAE afford a unique system in which the electron-transfer reactions take place both in the ground and excited states in solution. On the basis of the results of steady-state absorption, transient absorption, and EPR measurements, we can consistently show that the generated radical ions take different solvated forms (free radical ions or radical ion pair) depending on the solvent polarity. Furthermore, by combining the equilibrium data with the kinetic data, the rate constants of electron transfer in the ground state can be compared with those in the excited triplet state. The latter rate constants are larger than the former rate constants by factors of 3–45.

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References and Notes

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