Photoinduced Electron Transfer from *N,N*-Dimethylaniline to Pyrrolidinofullerenes ($C_{60}(C_3H_6N)R$): Emphasized Substituent Effects with Solvent Polarity Change

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Photoinduced electron-transfer reactions of pyrrolidinofullerenes {$C_{60}(C_3H_6N)R$; R = H (**1**), $C_6H_4NO_2$-*p* (**2**), C_6H_4CHO-*p* (**3**), C_6H_5 (**4**), C_6H_4OMe-*p* (**5**), and $C_6H_4NMe_2$-*p* (**6**)} with *N,N*-dimethylaniline have been systematically studied by means of nanosecond laser photolysis. From the direct observation of the rises of the anion radicals accompanied by the decays of the triplet states of the fullerenes, the rate constants of electron-transfer reactions (k_{ET}) via the triplet states were evaluated in polar solvents. Although the k_{ET} values are considerably decreased by the substituents as compared with that of pristine C_{60}, the electron is accepted by the C_{60} moiety. Among the derivatives, the k_{ET} values of **2** and **3** with electron-withdrawing groups are larger than those of **4** and **1**. In less polar solvent, such a substituent effect becomes prominent with decrease in the k_{ET} values, which is in accord with the reactivity−selectivity principle. This behavior can be explained by the Rehm−Weller relation and/or Marcus equation in consideration of the solvent polarity change. Back-electron-transfer rate constants in less polar solvent are larger than those in polar solvent, which is related to the desolvation process and/or loose ion pair formation.

Introduction

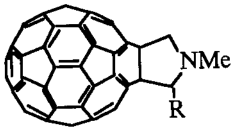
The electron-transfer phenomena of fullerenes with various kinds of organic reagents have been well studied with relation to both scientific and practical interests.[1−16] C_{60} and C_{70} act as excellent acceptors because of their low multiply degenerate LUMO states.[17] With electron donors such as aromatic amines,[6] fullerenes can form charge-transfer (CT) complexes in the ground state. In particular, C_{60} forms an ion radical complex with strong electron donors such as tetrakis(dimethylamino)ethylene (TDAE).[18]

Excited states of fullerenes can be efficiently quenched by the electron donors with the formation of exciplex,[4] or ion pair,[5] or free ion radicals,[9] indicating that electron-acceptor abilities increase in the singlet and triplet excited states of fullerenes. In addition, the triplet state of C_{60} can act as an electron donor with strong electron acceptors such as tetracyanoethylene.[19−21]

Intramolecular electron transfer has been reported for several donor−spacer−fullerene dyads,[22−27] in which charge separation occurs via the singlet state of fullerene moieties; [22−24] then, charge recombination occurs within the picosecond time scale, producing triplet-state fullerenes in addition to the direct deactivation to the ground state.[25] On the other hand, only a few studies reported the intermolecular electron transfer of fullerene derivatives in the presence of electron donors.[28−31] Since many of the fullerene derivatives have been expected to apply to material and biological sciences,[18,32−34] it is important to evaluate their photophysical and photochemical properties.

In the present work, photoinduced intermolecular electron-transfer reactions for pyrrolidinofullerenes ($C_{60}(C_3H_6N)R$; Scheme 1) with *N,N*-dimethylaniline (DMA) are systematically studied by observing the transient absorption spectra of the triplet states and ion radicals of $C_{60}(C_3H_6N)R$. It is found that the functional groups play an important role in the electron-transfer reactions.

SCHEME 1



R = H(**1**), $C_6H_4NO_2$-*p* (**2**), C_6H_4CHO-*p* (**3**), C_6H_5(**4**), C_6H_4OMe-*p* (**5**), $C_6H_4NMe_2$-*p* (**6**)

Experimental Section

Materials. C_{60} (>99.9%) was purchased from Texas Fullerenes Corp. Dimethylaniline (DMA), tetrakis(dimethylamino)ethylene (TDAE), and $(n\text{-Bu})_4NPF_6$ were of the best grade commercially available. Pyrrolidinofullerenes (Scheme 1) were synthesized according to methods described in previous paper.[35] Solvents were of spectroscopic or HPLC grade.

Measurements. Transient absorption spectra and time profiles were measured using a laser photolysis apparatus with SHG light (532 nm) of a Nd:YAG laser (6 ns fwhm) as the exciting source. For the transient absorption in the near-IR region, a Ge-APD photodiode module (Hamamatsu, C5331-SPL) attached to a monochromator was employed to detect the monitoring light from a pulsed Xe lamp (15 J/pulse, 60 μs fwhm). The details of the experimental setup are described elsewhere.[36]

Electrochemical measurements were carried out as described in the previous report.[35] Steady-state absorption spectra were

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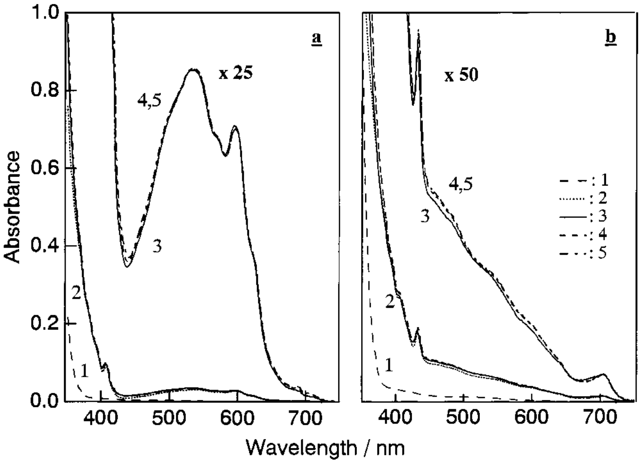

Figure 1. Steady-state absorption spectra of (a) C_{60} and (b) **2** with DMA in benzonitrile: (1) DMA (a, 6.0 mM; b, 23.7 mM); (2) (a) C_{60} (0.034 mM) and (b) **2** (0.056 mM); (3) synthesized spectra; (4) observed spectra of mixtures; (5) observed spectra of mixtures after repeated laser photolysis.

measured using an optical cell (1 cm) with a JASCO/V-570 spectrophotometer. All measurements were carried out under an Ar atmosphere at room temperature.

Results and Discussion

Steady-State Absorption Spectra of C_{60} and $C_{60}(C_3H_6N)R$ with DMA. The absorption spectra of C_{60} and $C_{60}(C_3H_6N)R$ with DMA are shown in Figure 1. Although a drastic change in the absorption band of C_{60} was reported on adding a high concentration of DMA (>100 mM),[3,6] no noticeable change in the absorption spectra was observed when the concentration of DMA was lower than 30 mM, indicating that any ground-state interaction such as charge transfer should be negligibly weak under our experimental conditions. After repeated photolysis of the benzonitrile solution containing C_{60} (or $C_{60}(C_3H_6N)R$) and DMA with a 532 nm laser, a noticeable spectral change due to some photochemical reactions was not observed. This finding suggests that the present photolysis systems of C_{60} (or $C_{60}(C_3H_6N)R$) and DMA are stable, although some aliphatic amines have been reported to react photochemically with C_{60}.[37]

Electron Transfer via $^{T}C_{60}(C_3H_6N)R^*$. The studies on electron transfer in the excited triplet states of $C_{60}(C_3H_6N)R$ were carried out by nanosecond laser photolysis by excitation of $C_{60}(C_3H_6N)R$ with light at 532 nm, which does not excite DMA. Since similar transient absorption spectra and kinetic behavior were observed for all $C_{60}(C_3H_6N)R$ with DMA in benzonitrile (BN), the transient absorption spectra of derivative **2** are shown in Figure 2 as an example. In the absence of DMA in benzonitrile (Figure 2a), immediately after laser pulse, a sharp absorption band was observed at 680 nm, which is attributed to $^{T}C_{60}(C_3H_6N)R^*$.[38,39] The absorbance of $^{T}C_{60}(C_3H_6N)R^*$ did not appreciably decay without DMA. In the presence of DMA, on the other hand, the absorbance of $^{T}C_{60}(C_3H_6N)R^*$ decayed completely in 1000 ns. Concomitant with the decay at 680 nm, a new absorption band appeared at 1000 nm.

To assign the 1000 nm band, $C_{60}(C_3H_6N)R$ were reduced by TDAE, which is one of the strongest organic electron donors.[18] Figure 3 shows the changes of steady-state absorption spectra of C_{60} and **2** in benzonitrile caused by addition of TDAE. The absorption bands that appeared at 1070 nm accompanying weak bands in the 900−1000 nm region can be assigned to $C_{60}^{\bullet-}$.[38,40] Similarly, the absorption bands that appeared at 1000 nm with shoulders at 790 and 840 nm can be ascribed to $2^{\bullet-}$. For other $C_{60}(C_3H_6N)R^{\bullet-}$, the absorption maxima (λ_{max}^{a}) are listed in Table 1.

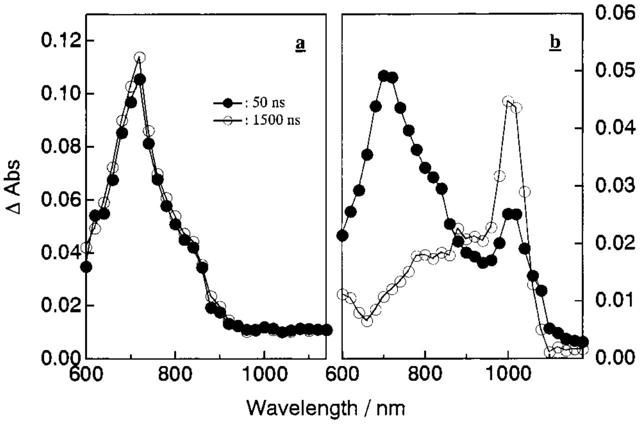

Figure 2. Transient absorption spectra of **2** (0.11 mM) with DMA in benzonitrile: (a) [DMA] = 0; (b) [DMA] = 16 mM.

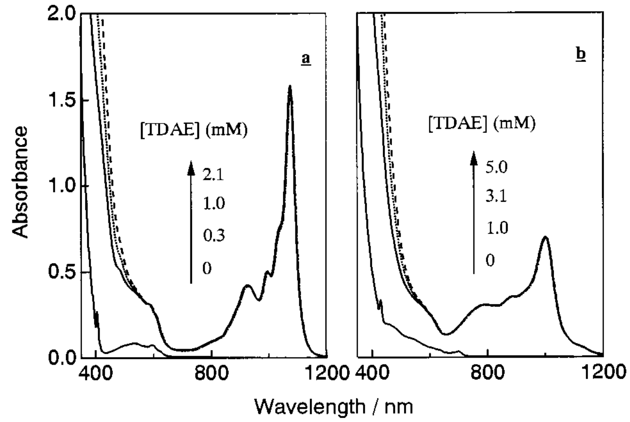

Figure 3. Steady-state absorption spectra of (a) C_{60} (0.11 mM) and (b) **2** (0.093 mM) with TDAE in argon bubbled benzonitrile.

Upon adding TDAE to a large excess, the absorbance of $C_{60}^{\bullet-}$ and $C_{60}(C_3H_6N)R^{\bullet-}$ saturated, indicating that the fullerenes were completely reduced into their radical anions; thus, the molar extinction coefficients (ϵ_a) were calculated on assuming that $[C_{60}^{\bullet-}]$ and $[C_{60}(C_3H_6N)R^{\bullet-}]$ are equal to the initial concentrations of C_{60} and $C_{60}(C_3H_6N)R$, respectively, as summarized in Table 1. Since the ϵ_a value of $C_{60}^{\bullet-}$ evaluated by this method is close to the reported one,[38,41] the ϵ_a values for $C_{60}(C_3H_6N)R^{\bullet-}$ are reliable. In Table 1, the reduction potentials of C_{60} and $C_{60}(C_3H_6N)R$ measured in this study are also listed as well as the data about the triplet states reported in our previous paper.[39]

From Figures 2 and 3, it is certain that the electron-transfer reaction occurs via $^{T}C_{60}(C_3H_6N)R^*$ (or $^{T}C_{60}^*$) as shown in eq 1, in which $C_{60}(C_3H_6N)R$ is simply represented as $C_{60}R$. The quantum yields and rate constants for intersystem crossing (k_{ISC}) are ca. 1 and ca. 1 × 10^9 s^{-1}, respectively, as reported previously.[9,39]

$$C_{60}R \xrightarrow{h\nu} {}^{S}C_{60}R^* \xrightarrow{k_{ISC}} {}^{T}C_{60}R^* \xrightarrow[+DMA]{k_{ET}} C_{60}R^{\bullet-} + DMA^{\bullet+} \quad (1)$$

For **6**, the triplet formation was strongly quenched by intramolecular electron transfer in the singlet state in benzonitrile.[21,39] However, intermolecular electron transfer to the triplet state of **6** from DMA was also observed, although the transient absorption intensities of the triplet state and anion radical of **6** are weak.

TABLE 1: Properties of C_{60} and $C_{60}(C_3H_6N)R$ in Their Neutral, Radical Anion (a) and Excited Triplet State (T)

	C_{60}	H (**1**)	$C_6H_4NO_2$ (**2**)	C_6H_4CHO (**3**)	Ph (**4**)	C_6H_4OMe (**5**)	$C_6H_4NMe_2$ (**6**)
$E_{red}{}^a$ (V vs SCE)	−0.50	−0.61	−0.62	−0.64	−0.65	−0.67	−0.67
$\lambda^a_{max}{}^b$ (nm)	1076	992	1002	1001	996	995	991
$\epsilon_a{}^b$ ($\times 10^3$ M^{-1} cm^{-1})	14.6	8.4	7.4	8.6	8.6	9.5	9.2
$\epsilon_T{}^c$ ($\times 10^4$ M^{-1} cm^{-1})	1.88	1.61	1.48	1.45	1.69	1.41	1.40
${}^T\Delta E_{0,0}{}^c$ (eV)	1.57	1.50	1.50	1.50	1.50	1.50	1.50

[a] Reduction potentials (E_{red}) of C_{60} and $C_{60}(C_3H_6N)R$ measured in dichloromethane solution of $(n\text{-Bu})_4NPF_6$ (0.1 M) at −10 °C. Scan rates = 200 mV/s. [b] Absorption maxima (λ^a_{max}) and molar extinction coefficients (ϵ_a) of $C_{60}{}^{\bullet -}$ and $C_{60}(C_3H_6N)R^{\bullet -}$. [c] Molar extinction coefficients (ϵ_T) and lowest energy (${}^T\Delta E_{0,0}$) of ${}^TC_{60}$ and ${}^TC_{60}(C_3H_6N)R^*$ (ref 39).

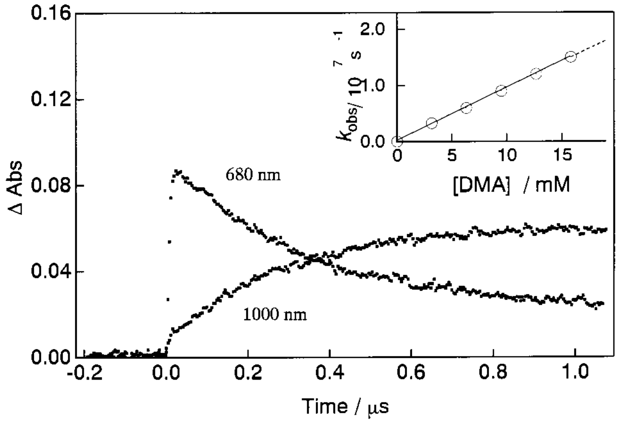

Figure 4. Decay at 680 nm and rise at 1000 nm of **2** (0.11 mM) in the presence of DMA (3.1 mM) in benzonitrile. Insert: pseudo-first-order plots.

Substituent Effect on Electron-Transfer Reactions. The decay profile of ${}^TC_{60}(C_3H_6N)R^*$ at 680 nm and the rise profile of $C_{60}(C_3H_6N)R^{\bullet -}$ at 1000 nm seem to be mirror images as shown in Figure 4. The decay curve consists of two-component kinetics; the slower decay part is due to the absorption tail of $C_{60}(C_3H_6N)R^{\bullet -}$ extending to 680 nm. By use of a large excess of DMA (3 mM) with respect to $[{}^TC_{60}(C_3H_6N)R^*]$ (ca. 6×10^{-3} mM), the second-order rate constants (k_{ET}^{obs}) for quenching of ${}^TC_{60}(C_3H_6N)R^*$ by DMA can be obtained from the pseudo-first-order plots of the observed first-order decay rate constants. The k_{ET}^{obs} values are $(4.2-9.5) \times 10^8$ M^{-1} s^{-1} for ${}^TC_{60}(C_3H_6N)R^*$ in benzonitrile.

The efficiency (E_{ET}) of the $C_{60}(C_3H_6N)R^{\bullet -}$ formation via ${}^TC_{60}(C_3H_6N)R^*$ can be estimated from eq 2, where A_T and A_a refer to the respective maximal absorbance; molar extinction coefficients (ϵ_T and ϵ_a) can be cited from Table 1.

$$E_{ET} = [C_{60}(C_3H_6N)R^{\bullet -}]/[{}^TC_{60}(C_3H_6N)R^*] = (A_a/A_T)(\epsilon_T/\epsilon_a) \tag{2}$$

Figure 5 shows that E_{ET} increases with the concentration of DMA, reaching a plateau at [DMA] = ca. 20 mM, from which the quantum yield (Φ_{ET}) for electron transfer via the triplet state was estimated to be 1.00 for **3**. For other $C_{60}(C_3H_6N)R$, the Φ_{ET} values are also 1.00 in benzonitrile (Table 2), indicating that all of these electron-transfer reactions are very efficient in benzonitrile. The electron-transfer rate constants (k_{ET}) are calculated by $k_{ET}^{obs}\Phi_{ET}$ as listed in Table 2.

The k_{ET} value for ${}^TC_{60}^*$ with DMA is close to the diffusion-controlled limit ($k_{diff} = 5.8 \times 10^9$ M^{-1} s^{-1} in benzonitrile), while the k_{ET} values for ${}^TC_{60}(C_3H_6N)R^*$ are slightly lower than k_{diff}. Therefore, the introduced substituents decelerate the rate of electron transfer via ${}^TC_{60}(C_3H_6N)R^*$, even though R are electron-withdrawing groups. This reason may be considered from the Rehm−Weller equation as follows:[42]

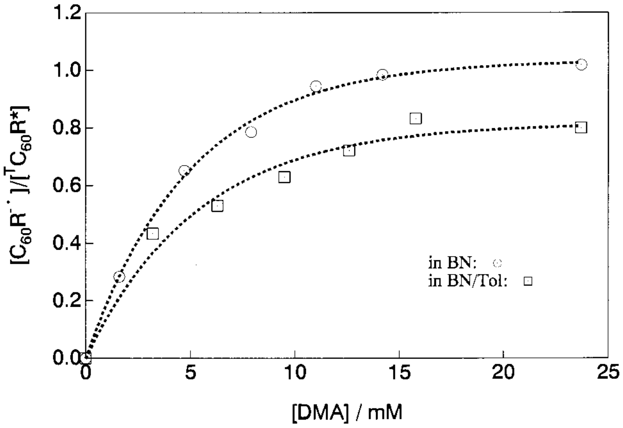

Figure 5. Efficiency of anion radical formation via triplet state of **3** in benzonitrile (BN) and benzonitrile/toluene (BN/Tol, v/v 1:1).

$$\Delta G^0_{et} = E_{ox} - E_{red} - {}^T\Delta E_{0,0} - e^2/\epsilon d \tag{3}$$

where ΔG^0_{et} refers to free energy change, E_{ox} and E_{red} to the oxidation potential of DMA and the reduction potentials of fullerenes respectively, ${}^T\Delta E_{0,0}$ to the lowest triplet energy of fullerenes, e to the electric charge of an electron, ϵ to the dielectric constant, and d to the distance between ion radicals. From Table 1, the ${}^T\Delta E_{0,0}$ values of ${}^TC_{60}(C_3H_6N)R^*$ are smaller than that of C_{60} by 0.07 eV (1.61 kcal mol^{-1}), leading to less negative ΔG^0_{et}, which results in a decrease in k_{ET} values of $C_{60}(C_3H_6N)R$ in comparison with that of C_{60}. The E_{red} values of $C_{60}(C_3H_6N)R$ are 0.1 V more negative than that of C_{60}, predicting the deceleration of electron-transfer rates. Both decreases in E_{red} and ${}^T\Delta E_{0,0}$ result from the increase of LUMO energy levels of $C_{60}(C_3H_6N)R$ relative to that of C_{60}, which may be caused by the reduction of fullerene symmetry.[43]

Among the derivatives, the k_{ET} values decrease in the order of **2** > **3** > **1** ≈ **4** ≈ **5** ≈ **6**; i.e., the electron-withdrawing groups NO_2 and CHO (in **2** and **3,** respectively) slightly accelerate electron-transfer reactions as compared with those of **1** and **4**. Such slight changes indicate that an electron from DMA is accepted by the C_{60} moiety in $C_{60}(C_3H_6N)R$, but not by the nitrobenzene (or benzaldehyde) moiety. A more prominent substituent effect was observed in a less polar solvent as described below.

Solvent Effect on Electron Transfer. On mixing benzonitrile ($\epsilon_{BN} = 25.70$) with toluene ($\epsilon = 2.40$), solvent dielectric constant (ϵ) decreases; $\epsilon_{1:1} = 14.05$ for 1:1 (v/v) mixture. The observed decay rates of ${}^TC_{60}(C_3H_6N)R^*$ in the presence of DMA were slower than those in benzonitrile (Figure 6). The absorption intensities of $C_{60}(C_3H_6N)R^{\bullet -}$ were also weaker than those in benzonitrile. All of the kinetic data are listed in Table 2.

The quantum yields (Φ_{ET}) in benzonitrile/toluene (BN/Tol, 1:1) in Table 2 indicate that the electron-transfer reactions take place in less efficient ways as compared with those in benzoni-

TABLE 2: Electron-Transfer Rate Constants and Back-Electron-Transfer Rate Constants of $^TC_{60}$ and $^TC_{60}R$ with DMA in Benzonitrile (BN) and Benzonitrile/Toluene (BN/Tol, v/v 1:1)

	C_{60}	H (**1**)	$C_6H_4NO_2$ (**2**)	C_6H_4CHO (**3**)	Ph (**4**)	C_6H_4OMe (**5**)	$C_6H_4NMe_2$ (**6**)
				In BN			
Φ_{ET}	1.00	1.00	1.00	1.00	1.00	1.00	1.00
k_{ET} ($\times 10^9$ M^{-1} s^{-1})	3.5	0.57	0.95	0.73	0.44	0.42	0.57
k_{BET} ($\times 10^9$ M^{-1} s^{-1})	19	13	6.2	8.7	8.4	7.1	7.9
				In BN/Tol			
$\Phi_{ET}^{1:1\,a}$	0.52	0.58	0.95	0.80	0.50	0.61	0.60
$k_{ET}^{1:1}$ ($\times 10^9$ M^{-1} s^{-1})	2.1	0.026	0.12	0.078	0.025	0.013	0.017
$k_{BET}^{1:1}$ ^{a} ($\times 10^9$ M^{-1} s^{-1})	41	20	16	18	12	16	25

[a] ϵ_a values were assumed to be same to those in benzonitrile.

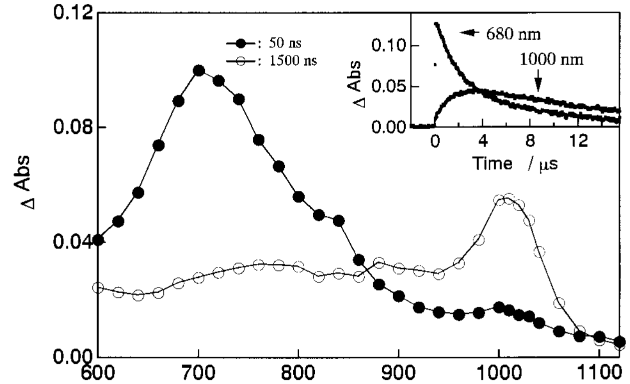

Figure 6. Transient absorption spectra of **2** (0.1 mM) with DMA in BN/Tol: (a) [DMA] = 0; (b) [DMA] = 16 mM. Insert: decay at 700 nm and rise at 1000 nm in the presence of DMA.

trile. The Φ_{ET} values in BN/Tol (1:1) also show a prominent functional group effect; i.e., the C_{60} moiety of **2** and **3** with electron-withdrawing groups can accept an electron more efficiently than others. The k_{ET} values for $C_{60}(C_3H_6N)R$ in BN/Tol (1:1) are smaller than those in benzonitrile by factors of ca. 1/10, while the change for C_{60} is not so large. In less polar BN/Tol (1:1), the substituent effect becomes prominent; the k_{ET} values decrease in the order of C_{60} > **2** > **3** > **4** ≈ **1** > **5** ≈ **6**, implying not only an accelerating effect by electron-withdrawing groups (NO_2 and CHO in **2** and **3**) but also a decelerating effect by electron-donating groups (OMe and NMe_2 in **5** and **6**). A large substituent effect accompanying a decrease of the k_{ET} values in less polar solvents is in accord with the reactivity–selectivity principle;[44,45] i.e., the lower the reactivity, the higher is the selectivity with electronic factor of substituents. In general, this principle can be interpreted according to the Hammond postulate that the productlike transition state with high activation energy shows high selectivity.[46]

In the present electron-transfer reactions, the observed tendency can be explained by the Rehm–Weller relation taking the solvent polarity change into consideration as shown in Figure 7. The k_{ET} values can be calculated using the semiempirical Weller equation on the basis of free energy changes for activation ($\Delta G^{\ddagger}_{et}$), which were evaluated from ΔG^0_{et}.[47] The calculated curves for k_{ET} vs ΔG^0 in two different solvents are plotted in Figure 7, in which the general shapes of the curves both in benzonitrile and in BN/Tol (1:1) are the same. An upward slight shift of the calculated k_{ET} in mixed solvent is due to the lower viscosity.[42] The ΔG^0_{et} values of $^TC_{60}(C_3H_6N)$-R* with DMA in BN/Tol (1:1) ($(\Delta G^0_{et})_{1:1}$) were calculated from eq 4, in which $(\Delta G^0_{et})_{BN}$ values were evaluated by correction due to the solvation energy from acetonitrile;[42,48] r_D and r_A refer to radii of DMA and $C_{60}(C_3H_6N)R$ (or C_{60}), respectively.

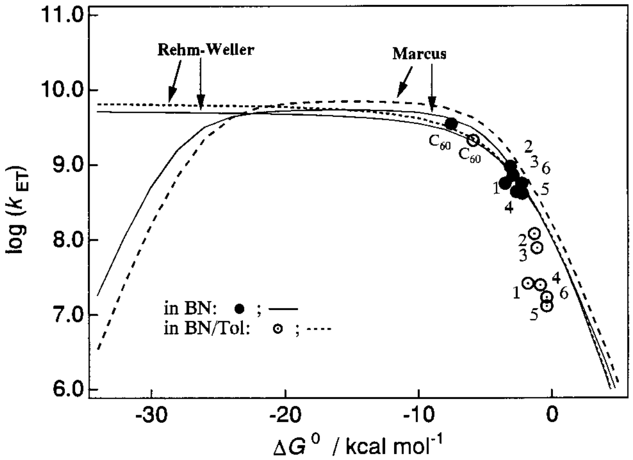

Figure 7. Plot of log k_{ET} vs ΔG^0. Solid line (in BN) and dotted line (in BN/Tol) were calculated by the Rehm–Weller equation[42] and Marcus equation.[22,47]

$$(\Delta G^0_{et})_{1:1} = (\Delta G^0_{et})_{BN} - (e^2/2)(1/r_D + 1/r_A)(1/\epsilon_{BN} - 1/\epsilon_{1:1}) \tag{4}$$

Marcus theory was also applied for explaining the substituent effect with solvent polarity change (Figure 7).[20,22,47] The calculated curve of k_{ET} vs ΔG^0 in BN/Tol slightly shifts to the right relative to that in benzonitrile because of the decrease of solvent reorganization energy.[49] From Figure 7, the curves of k_{ET} vs ΔG^0_{et} calculated by the Marcus equation in the normal region are quite similar to those calculated by the Rehm–Weller relation.

In Figure 7, the experimental k_{ET} values are plotted against the calculated ΔG^0_{et} from eq 4; the ΔG^0_{et} values shift to less negative when the solvent polarity decreases. In Figure 7, although the observed k_{ET} values deviate downward from the calculated lines as pointed by Arbogast et al.,[1] our finding that the substituent effect on k_{ET} in benzonitrile is smaller than that in less polar solvents can be successfully explained; i.e., the dots of experimental k_{ET} values of polar solvents lie in the flat negative ΔG^0_{et} region, while the dots of less polar solvents lie in the less negative ΔG^0_{et} region, showing steep downward curvature.

Back Electron Transfer. By the observation of the time profiles of $C_{60}(C_3H_6N)R^{\bullet-}$ in the long time scale (Figure 8), the absorbance of $C_{60}(C_3H_6N)R^{\bullet-}$ begins to decrease after reaching a maximum, obeying second-order kinetics. This can be attributed to the back-electron-transfer reaction:

$$C_{60}R^{\bullet-} + DMA^{\bullet+} \xrightarrow{k_{BET}} C_{60}R + DMA \tag{5}$$

From the slopes of the second-order plots (insert in Figure 8), the ratios of the back-electron-transfer rate constants (k_{BET})

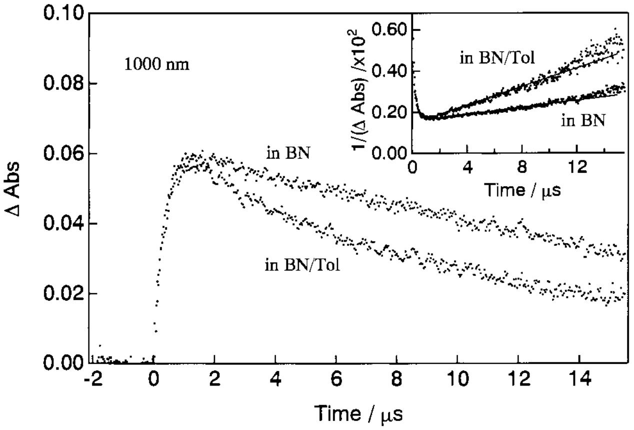

Figure 8. Rise and decay of $\mathbf{2}^{\bullet-}$ at 1000 nm in BN and BN/Tol. Insert: second-order plots for decay of $\mathbf{2}^{\bullet-}$.

to ϵ_a can be obtained (Table 2). Then, k_{BET} can be evaluated by substituting ϵ_a values; k_{BET} values for $C_{60}(C_3H_6N)R^{\bullet-}$ are smaller than that of $C_{60}{}^{\bullet-}$ itself. This may be related to the size of $C_{60}(C_3H_6N)R^{\bullet-}$ and/or to steric hindrance of the substituents attached to C_{60} rather than the electronic effect.

The k_{BET} values in BN/Tol (1:1) are ca. 2−3 times larger than the corresponding values in benzonitrile for $C_{60}(C_3H_6N)R^{\bullet-}$ and $C_{60}{}^{\bullet-}$. In both solvent systems, decay kinetics was second-order, suggesting that the ion radicals are present as free ones and/or loose ion pairs, but not as the contact ion pairs, in which first-order decay kinetics would be anticipated.[9] In benzonitrile, it is confirmed that the ion radicals are present as free ones, since k_{BET} values are close to k_{diff} ($=5.8 \times 10^9$ M^{-1} s^{-1}) in benzonitrile. In BN/Tol (1:1), k_{diff} is 7.4×10^9 M^{-1} s^{-1}, which is 1.3 times larger than that in benzonitrile; thus, a part of the increase in k_{BET} can be attributed to its low viscosity. In addition, since the desolvation energy of the ion radicals is small in less polar solvents, the faster back electron transfer would be anticipated. However, for the reason $k_{BET} > k_{diff}$ in BN/Tol (1:1), it is presumed that the ion radicals are present as loose ion pairs in less polar solvents, in which the oppositely charged ion radicals easily transfer an electron in reverse, returning to the neutral molecules.

Conclusion

Triplet excited states of pyrrolidinofullerenes are capable of accepting an electron from DMA in appropriately polar solvents. The electron-transfer rate constants are decreased by the introduction of the substituents, because of a decrease in the π-conjugation of the C_{60} moiety, which causes an increase in LUMO energy level and a decrease in the lowest triplet energy. The electron is obviously accepted by the C_{60} moiety, which the substituents affect indirectly. Among pyrrolidinofullerenes, electron-transfer rate constants are increased by the introduced electron-withdrawing groups, while the electron-donating groups slightly decelerated the electron-transfer reaction. This substituent effect becomes prominent in less polar solvent, which is reasonably interpreted by the shift of ΔG^0_{et} to positive, reaching the steep curvature of the Rehm−Weller relation and/or Marcus theory.

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