Selective One-Electron and Two-Electron Reduction of C_{60} with NADH and NAD Dimer Analogues via Photoinduced Electron Transfer

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Abstract: The selective one-electron reduction of C_{60} to $C_{60}^{\bullet-}$ is attained through photoinduced electron transfer from an NADH analogue, 1-benzyl-1,4-dihydronicotinamide (BNAH), and the dimer analogue [$(BNA)_2$] to the triplet excited state of C_{60}. The limiting quantum yield for formation of $C_{60}^{\bullet-}$ in the case of $(BNA)_2$ exceeds unity; $\Phi_\infty = 1.3$. In this case, the initial electron transfer from $(BNA)_2$ to the triplet excited state ($^3C_{60}^*$) is followed by fast C−C bond cleavage in the resulting $(BNA)_2^{\bullet+}$ to give $BNA^\bullet$ and BNA^+ and the second electron transfer from $BNA^\bullet$ to C_{60} yields BNA^+ and $C_{60}^{\bullet-}$, when $(BNA)_2$ acts as a two-electron donor to produce 2 equiv of $C_{60}^{\bullet-}$. When BNAH is replaced by 4-*tert*-butylated BNAH (*t*-BuBNAH), the photochemical reaction with C_{60} yields not $C_{60}^{\bullet-}$ but instead the *tert*-butylated anion ($t\text{-BuC}_{60}^-$) selectively. In this case, the initial electron transfer from *t*-BuBNAH to $^3C_{60}^*$ is also followed by fast C−C bond cleavage in $t\text{-BuBNAH}^{\bullet+}$ to give $t\text{-Bu}^\bullet$, which is coupled with $C_{60}^{\bullet-}$ produced in the electron transfer to yield $t\text{-BuC}_{60}^-$. The selective two-electron reduction of C_{60} to 1,2-dihydro[60]fullerene ($1,2\text{-}C_{60}H_2$) is also attained with the use of another NADH analogue, 10-methyl-9,10-dihydroacridine ($AcrH_2$), under visible light irradiation in deaerated benzonitrile solution containing trifluoroacetic acid. The studies on the quantum yields, the kinetic deuterium isotope effects, and the quenching of the triplet−triplet absorption of C_{60} by $AcrH_2$ have revealed that the photochemical reduction proceeds via photoinduced electron transfer from 10-methyl-9,10-dihydroacridine to the triplet excited state of C_{60}, which is followed by proton transfer from $AcrH_2^{\bullet+}$ to $C_{60}^{\bullet-}$ and a second electron transfer from the deprotonated acridinyl radical ($AcrH^\bullet$) to $C_{60}H^\bullet$ in the presence of trifluoroacetic acid to yield the final products 10-methylacridinium ion ($AcrH^+$) and $1,2\text{-}C_{60}H_2$. The transient spectra of the radical ion pair formed in the photoinduced electron transfer have been detected successfully in laser flash photolysis of each NADH analogue−C_{60} system. The mechanistic difference between the selective one- and two-electron reductions of C_{60} is discussed on the basis of the difference in the redox and acid−base properties of NADH and the dimer analogues.

Introduction

Buckminsterfullerene (C_{60}) and its homologues are known to act as electrophiles, and thus much attention has been focused on their functionalization with various nucleophiles.[1−4] The use of the photoexcited state of C_{60} has further expanded the scope of the reactions with nucleophiles since the early work by Foote et al.[5−9] We have recently reported that the photoinduced electron-transfer process from ketene silyl acetals to $^3C_{60}^*$ gives the fullerene with an ester functionality.[10] The selective photochemical allylation of C_{60} with allylic stannanes has also been established.[11] It is now well-known that the triplet excited

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state of C_{60} is formed by efficient intersystem crossing.[5,12] The triplet excited state of C_{60} has a reduction potential of $E^0_{red} = 1.14$ V versus SCE and can therefore be reduced by a variety of organic compounds giving the C_{60} radical anion.[5,13,14] A long-lived transient of $C_{60}^{\bullet-}$ has been reported to be formed in photoinduced electron transfer from ZnO or TiO_2 semiconductor colloids to C_{60}.[15] In homogeneous systems, however, the lifetime of the generated $C_{60}^{\bullet-}$ is generally extremely short as a result of fast back electron transfer to the reactant pair, resulting in no net formation of $C_{60}^{\bullet-}$.[16,17] We report herein that the photoinduced electron transfer from an NADH analogue, 1-benzyl-1,4-dihydronicotinamide (BNAH), and the dimer analogue $[(BNA)_2]$ to the triplet excited state of C_{60} ($^3C_{60}{}^*$) yields stable $C_{60}^{\bullet-}$ in benzonitrile solution with a surprisingly high quantum yield, exceeding unity in the latter case; $\Phi = 1.3$. We also report the selective two-electron reduction of C_{60} to the *tert*-butylated C_{60} anion (t-BuC_{60}^-) and 1,2-dihydro[C_{60}]-fullerene (1,2-$C_{60}H_2$) via photoinduced electron transfer from 4-*tert*-butyl-1-benzyl-1,4-dihydronicotinamide (*t*-BuBNAH) and 10-methyl-9,10-dihydroacridine ($AcrH_2$) to $^3C_{60}{}^*$, respectively.[18] The reduction of C_{60} has so far been achieved by the use of strong reductants such as BH_3, which yields not only $C_{60}H_2$ but also polyhydride mixtures.[19,20] The use of the triplet excited state of C_{60} has enabled us to attain the selective two-electron reduction of C_{60} to 1,2-$C_{60}H_2$ by using $AcrH_2$, which is a mild hydride donor. In this study we could observe the transient absorption spectra in the visible and near-IR region to confirm the formation of the radical ion pair produced upon photoinduced electron transfer from NADH analogues to the triplet excited state of C_{60}. This study provides an excellent opportunity to develop mechanistic insight into the selective one- and two-electron reductions of C_{60} depending on different NADH analogues.

Experimental Section

Materials. C_{60} (>99.95% pure) was purchased from Science Laboratories Co., Ltd., Japan, and used as received. C_{60} of 99.99% purity was obtained from Texas Fullerenes Corp. and used for the spectral measurements. 10-Methyl-9,10-dihydroacridine ($AcrH_2$) was prepared from 10-methylacridinium iodide ($AcrH^+I^-$) by reduction with $NaBH_4$ in methanol and was purified by recrystallization from ethanol.[21] The dideuterated compound, 10-methyl[9,9′-$^2H_2$]acridine ($AcrD_2$) was prepared from 10-methylacridone by reduction with $LiAlD_4$.[21] Preparation of 1-benzyl-1,4-dihydronicotinamide (BNAH) was described previously.[21] The *tert*-butylated BNAH (*t*-BuBNAH) was prepared by a Grignard reaction with BNA^+Cl^-.[22,23] The BNA dimer was prepared by the following procedure according to the literature.[24,25] To a stirred solution of 12 g of Zn dust in 20 mL of water, 4 g of cupric sulfate in 40 mL of water and then 20 mL of concentrated NH_3 and 100 mL of MeOH are added. While the solution was being stirred strongly, 10 g of BNA^+Cl^- in 40 mL of water is added. The solution immediately turns yellow. After 20 min, the mixture is filtered and the precipitate is extracted four times with 40 mL of hot ethanol under N_2. From the combined EtOH solutions EtOH is removed at 313−323 K under reduced pressure until the product starts to fall out. The solution is cooled to 253 K, and the product is filtered (still under N_2). Yield: 17.5%, light yellow crystals. The dimer is very sensitive to acid and somewhat sensitive to light and oxygen, especially in solution. UV (MeOH): 268 nm ($\epsilon = 6.3 \times 10^3$ M^{-1} cm^{-1}), 348 nm ($\epsilon = 7.3 \times 10^3$ M^{-1} cm^{-1}). Benzonitrile (PhCN, 99.9%) was purchased from Aldrich and purified by successive distillation over P_2O_5 prior to use.

Reaction Procedure. Typically, to a solution of C_{60} (10.1 mg, 0.014 mmol) in deaerated PhCN (50 mL) under an atmospheric pressure of argon was added 10-methyl-9,10-dihydroacridine (2.7 mg, 0.014 mmol), and the solution was irradiated with a Xe lamp ($\lambda > 540$ nm) equipped with a Toshiba O-54 cut filter for 30 min. After the solvent was evaporated under reduced pressure, the residue was separated by washing it with acetonitrile and centrifuged to give 1,2-$C_{60}H_2$ in 70% yield, and the recovered C_{60} was measured by HPLC equipped with an analytical “Buckyclutcher I” column (Regis, Morton Grove, IL). A hexane−toluene mixture was used as the eluent with a flow rate of 2 mL min^{-1}. The product was monitored at 434 nm with a UV−vis detector. ^1H NMR spectra were measured on a JEOL GSX-400 (400 MHz) spectrometer. Chemical shifts of ^1H NMR were expressed in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$). ^1H NMR (400 MHz, C_6D_6): δ 5.91 (s, 2H). The UV−vis spectra were measured on a Hewlett-Packard 8453 photodiode array spectrophotometer. UV−vis (λ_{max}, PhCN): 434, 714 nm.

Similarly, a deaerated PhCN solution (50 mL) containing C_{60} (10.1 mg, 0.014 mmol) and *t*-BuBNAH (0.014 mmol) was irradiated with a Xe lamp ($\lambda > 370$ nm) equipped with a Toshiba UV-37 cut filter for 1 h. The successive reaction with CF_3COOH (0.018 mmol) in deaerated PhCN at room temperature gave 1-*tert*-butyl-1,2-dihydro[60]fullerene (1,2-t-$BuC_{60}H$), which was isolated on an aluminum column using hexane as an eluent. 1,2-t-$BuC_{60}H$ (typically 60% yield) along with unreacted C_{60} was obtained. FAB-MS: mass calcd for $C_{64}H_{10}$, 778.8; found, 778.7. ^1H NMR (CS_2/$CDCl_3$ 3:1 v/v, 298 K): δ 2.06 (s, 9H), 6.64 (s, H). UV−vis (λ_{max}, CS_2): 437 nm.

Addition of $PhCH_2Br$ instead of CF_3COOH to the photolyzed PhCN solution of C_{60} and *t*-BuBNAH gave 1-*tert*-butyl-4-benzyl-1,4-dihydro-[60]fullerene [1,4-t-$Bu(PhCH_2)C_{60}$]. The final product was isolated and characterized by FAB-MS and ^1H NMR spectroscopy. FAB-MS: mass calcd for $C_{71}H_{16}$, 868.9; found, 868.7. ^1H NMR (CS_2/$CDCl_3$ 3:1 v/v, 298 K): δ 1.98 (s, 9H), 4.29 (d, 1H, $J_{ab} = 13.2$ Hz), 4.51 (d, 1H, $J_{ab} = 13.2$ Hz), 7.26 (m, 1H), 7.32 (m, 2H), 7.50 (m, 2H). UV−vis (λ_{max}, CS_2): 447 nm.

Quantum Yield Determinations. A standard actinometer (potassium ferrioxalate)[26] was used for the quantum yield determination of the photoreduction of C_{60} by electron donors. Square quartz cuvettes (10 mm i.d.) that contained a deaerated PhCN solution (3.0 cm^3) of C_{60} (3.0×10^{-4} M) with NADH and the dimer analogues at various concentrations were irradiated with monochromatized light of $\lambda = 546$ nm from a Shimadzu RF-5000 fluorescence spectrophotometer. Under the conditions of actinometry experiments, the actinometer and C_{60} absorbed essentially all the incident light of $\lambda = 546$ nm. The light

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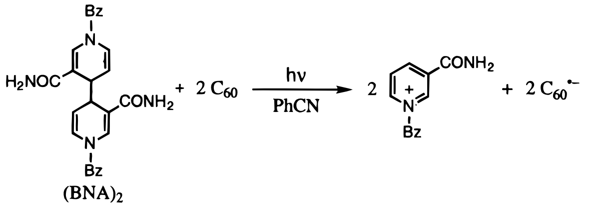
intensity of the monochromatized light of $\lambda = 546$ nm was determined to be 4.99×10^{-9} einstein s^{-1} with a slit width of 5 nm. The photochemical reaction was monitored using a Hewlett-Packard 8452A diode-array spectrophotometer. The quantum yields were determined from the increase in absorbance due to the C_{60} adducts at 434 nm and $C_{60}^{\bullet -}$ at 1080 nm, where the C_{60} absorbance at 434 nm has been taken into account. To avoid the contribution of light absorption of the products, only the initial rates were determined for determination of the quantum yields.

Laser Flash Photolysis. The procedure and the equipment for the measurements of the triplet−triplet absorption spectrum of $^3C_{60}^*$ were described previously.[10] The detailed procedures for the measurements of transient absorption spectra of $^3C_{60}^*$ and $C_{60}^{\bullet -}$ are available in Supporting Information.

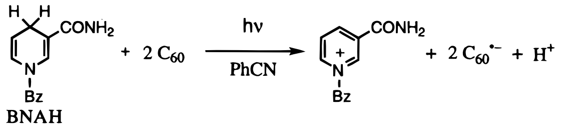
ESR Measurements. ESR spectra of the photolyzed PhCN solution of C_{60} and $(BNA)_2$ were taken on a JEOL JES-RE1XE and were recorded under nonsaturating microwave power conditions. The magnitude of the modulation was chosen to optimize the resolution and the signal-to-noise ratio (S/N) of the observed spectra. The *g* values were calibrated using a Mn^{2+} marker.

Results and Discussion

Selective One-Electron Reduction of C_{60} via Photoinduced Electron Transfer. When a dimeric NADH analogue $[(BNA)_2]$ is used as an electron donor, irradiation of a PhCN solution containing $(BNA)_2$ and C_{60} with daylight results in efficient one-electron reduction of C_{60} to $C_{60}^{\bullet -}$ (eq 1). No reaction occurs in the dark. The formation of $C_{60}^{\bullet -}$ is detected by the typical NIR spectrum ($\lambda_{max} = 1080$ nm).[27] The $C_{60}^{\bullet -}$ generated in the photochemical reaction is stable in deaerated PhCN, and the stoichiometry of the reaction is established as shown in eq 1, where $(BNA)_2$ acts as a two-electron donor to reduce 2 equiv of C_{60} to $C_{60}^{\bullet -}$.[28] The formation of $C_{60}^{\bullet -}$ was also confirmed by ESR spectroscopy after the photochemical reaction of C_{60} with $(BNA)_2$. A characteristic broad signal at $g = 2.0000$ is observed together with a sharp spike signal, which is always observed in the ESR spectrum of $C_{60}^{\bullet -}$.[29] Similarly, the photochemical reaction of C_{60} with the monomeric NADH analogue, 1-benzyl-1,4-dihydronicotinamide (BNAH), occurs to yield $C_{60}^{\bullet -}$ efficiently under irradiation with visible light from a Xe lamp ($\lambda > 540$ nm) equipped with a Toshiba O-54 cut filter (eq 2).



(1)



(2)

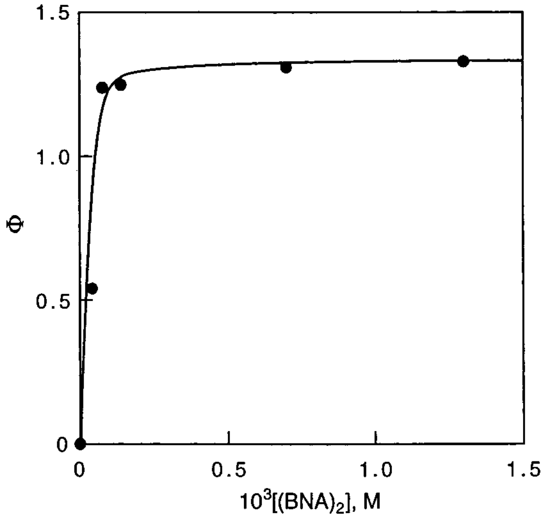


Figure 1. Dependence of the quantum yields on $[(BNA)_2]$ for the photoreduction of C_{60} (2.8×10^{-4} M) by $(BNA)_2$ in deaerated PhCN at 298 K.

The quantum yields (Φ) for the one-electron photoreduction of C_{60} were determined from an increase in absorbance due to $C_{60}^{\bullet -}$ by using a ferrioxalate actinometer[26] under irradiation of monochromatized light of $\lambda = 546$ nm. The Φ value for the photoreduction of C_{60} by $(BNA)_2$ in PhCN increases with an increase in the concentration of $(BNA)_2$ to reach a limiting value (Φ_∞) as shown in Figure 1. It should be noted that the Φ_∞ value exceeds unity; $\Phi_\infty = 1.3$. Such a large quantum yield exceeding unity is consistent with the stoichiometry in eq 1, where $(BNA)_2$ can reduce 2 equiv of C_{60}. The dependence of Φ on the BNAH concentration was also examined, and the Φ_∞ values for $(BNA)_2$ and BNAH are listed in Table 1.

The singlet excited state of C_{60} produced initially upon irradiation is known to be efficiently converted to the triplet excited state by the fast intersystem crossing.[5,12] The transient absorption spectra in the visible and near-IR region are observed by the laser flash photolysis of a deaerated PhCN solution of C_{60} containing BNAH with 532 nm laser light as shown in Figure 2. The triplet−triplet absorption band of $^3C_{60}^*$ at 740 nm appearing immediately after nanosecond laser exposure decays accompanied by concomitant appearance of new absorption bands at 600 and 1080 nm (Figure 2). The absorption band at 1080 nm in the near-IR region in Figure 2 is readily assigned to $C_{60}^{\bullet -}$.[27] The absorption band at 600 nm in the visible region can be assigned as $BNAH^{\bullet +}$, since the radical cation of an NADH analogue has a similar absorption band.[30,31] The transient absorption spectrum of $C_{60}^{\bullet -}$ is also observed by the laser flash photolysis of a deaerated PhCN solution of C_{60} containing $(BNA)_2$. The lifetime of the transient $^3C_{60}^*$ triplet−triplet (T−T) absorption at $\lambda_{max} = 740$ nm is significantly reduced by the presence of $(BNA)_2$ or BNAH. The bimolecular quenching rate constants (k_q) of $^3C_{60}^*$ by $(BNA)_2$ and BNAH were determined from the decay kinetics of transient T−T absorption at 740 nm. In each case, the first-order decay rate constant of $^3C_{60}^*$ (k_d) increases linearly with an increase in the concentration of $(BNA)_2$ or BNAH as shown in Figure 3 for $(BNA)_2$.

The k_q values of $(BNA)_2$ and BNAH are listed in Table 1, where the oxidation potentials (E^0_{ox}) of $(BNA)_2$[25] and BNAH[21]

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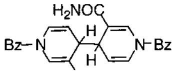
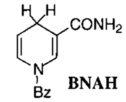
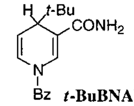
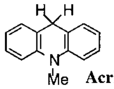
Table 1. Free Energy Change ΔG^0_{et} and Rate Constants k_{et} of Photoinduced Electron Transfer from NADH Analogues to $^3C_{60}{}^*$, Triplet Quenching Rate Constants k_q, and Limiting Quantum Yields Φ_∞ in the Photoreduction of C_{60} by NADH Analogues in PhCN at 298 K

NADH analogue	E^0_{ox} vs SCE, V	ΔG^0_{et},[a] kcal mol^{-1}	k_q,[b] M^{-1} s^{-1}	k_{et},[c] M^{-1} s^{-1}	Φ_∞
 **$(BNA)_2$**	0.26	-20.3	3.4×10^9	3.5×10^9	1.30
 **BNAH**	0.57	-13.1	2.9×10^9	4.1×10^9	0.80
 ***t*-BuBNAH**	0.71	-9.9	2.1×10^9	3.6×10^9	0.21
 **$AcrH_2$**	0.81	-7.6	4.3×10^9	4.6×10^9	0.33

[a] Obtained from the E^0_{ox} values of NADH analogues[21,25] and the E^0_{red} value of $^3C_{60}{}^*$ (1.14 V vs SCE)[5] by using the equation $\Delta G^0_{et} = F(E^0_{ox} - E^0_{red})$. [b] Experimental error is ±5%. [c] Evaluated by using the Rehm–Weller equation (eq 4).[32] The $\Delta G^{\neq}_0$ values of the electron transfer are taken as 4.0, 2.6, 4.0, and 5.5 kcal mol^{-1} for *t*-BuBNAH, $AcrH_2$, BNAH, and $(BNA)_2$, respectively.[21,25] The diffusion-limited electron-transfer rate constant is taken as 5.6×10^9 M^{-1} s^{-1}.[5]

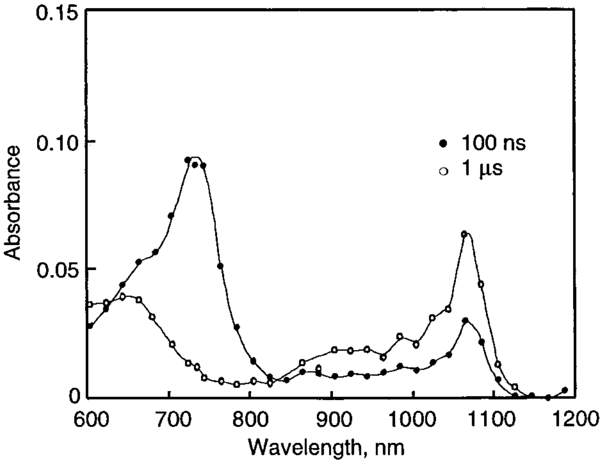


Figure 2. Transient absorption spectra observed in the photoreduction of C_{60} (1.0×10^{-4} M) by BNAH (1.1×10^{-3} M) at 100 ns (●) and 1 μs (○) after laser excitation in deaerated PhCN at 295 K.

as well as the free energy change of electron transfer from the donor to $^3C_{60}{}^*$ (ΔG^0_{et}) are also given. The ΔG^0_{et} value is obtained from the one-electron oxidation potential of the donor (E^0_{ox}) and the one-electron reduction potential of $^3C_{60}{}^*$ (E^0_{red}) by eq 3. The E^0_{ox} values (vs SCE) of $(BNA)_2$ (0.26 V)[25] and BNAH (0.57 V)[21] have been reported previously, and the E^0_{red}

$$\Delta G^0_{et} = F(E^0_{ox} - E^0_{red}) \tag{3}$$

value of $^3C_{60}{}^*$ is known to be 1.14 V.[5] In each case the ΔG^0_{et} value is highly negative, suggesting that the rate of the electron-transfer reaction may be diffusion-limited. The dependence of the activation free energy of photoinduced electron transfer $\Delta G^\ddagger_{et}$ on the free energy change of electron transfer (ΔG^0_{et}) has well been established as given by the Rehm–Weller free-energy relation (eq 4),[32,33] where $\Delta G^\ddagger_0$ is the intrinsic barrier

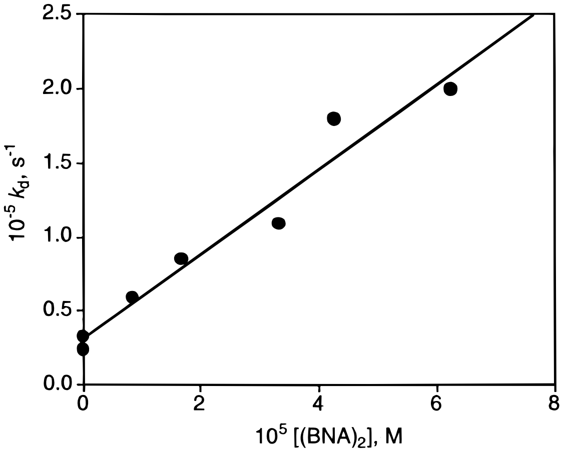


Figure 3. Plots of k_d vs $[(BNA)_2]$ for the quenching of $^3C_{60}{}^*$ (2.8×10^{-5} M) by $(BNA)_2$ in deaerated PhCN at 298 K.

$$\Delta G^\ddagger_{et} = (\Delta G^0_{et}/2) + [(\Delta G^0_{et}/2)^2 + (\Delta G^\ddagger_0)^2]^{1/2} \tag{4}$$

that represents the activation free energy when the driving force of electron transfer is zero, that is, $\Delta G^\ddagger_{et} = \Delta G^\ddagger_0$ at $\Delta G^0_{et} = 0$. The $\Delta G^\ddagger_{et}$ values are related to the rate constant of electron transfer (k_{et}) as given by eq 5, where Z is the collision frequency that is taken as 1×10^{11} M^{-1} s^{-1}; F is the Faraday constant,

$$\Delta G^\ddagger_{et} = 2.3RT \log[Z(k_{et}{}^{-1} - k_{diff}{}^{-1})] \tag{5}$$

and k_{diff} is the diffusion rate constant in PhCN (5.6×10^9 M^{-1} s^{-1}).[5] Then, the k_{et} values can be calculated from the ΔG^0_{et} and $\Delta G^\ddagger_0$ values[21,25] by using eqs 4 and 5. The k_{et} values thus evaluated are listed in Table 1 and agree well with the observed k_q values (Table 1).

Such an agreement between the k_{et} and k_q values as well as the direct observation of the products of electron transfer indicates that the photochemical reaction proceeds via photoinduced electron transfer to $^3C_{60}{}^*$ as shown in Scheme 1 for the case of $(BNA)_2$. The photoinduced electron transfer from $(BNA)_2$ to $^3C_{60}{}^*$ gives $(BNA)_2{}^{\bullet+}$ and $C_{60}{}^{\bullet-}$ in competition with the decay to the ground state. This step is followed by a fast cleavage of the C–C bond of the dimer (k_c) to produce *N*-benzylnicotinamide radical ($BNA^\bullet$) and BNA^+.[25] The subsequent second electron transfer from $BNA^\bullet$ to C_{60} should be faster by far than the first, as $BNA^\bullet$ is a strong reductant ($E^0_{ox} = -1.08$ V vs SCE).[21] Thus, once photoinduced electron transfer from $(BNA)_2$ to $^3C_{60}{}^*$ occurs, two $C_{60}{}^{\bullet-}$ molecules are produced.[34]

By application of the steady-state approximation to the reactive species, $^3C_{60}{}^*$, $(BNA)_2{}^{\bullet+}$, and $BNA^\bullet$ in Scheme 1, the dependence of Φ on $[(BNA)_2]$ can be derived as given by eq 6, which agrees with the observed dependence of Φ on $[(BNA)_2]$ in Figure 2. The limiting quantum yield Φ_∞ corresponds to

$$\Phi = \Phi_\infty k_{et}\tau_T[(BNA)_2]/(1 + k_{et}\tau_T[(BNA)_2]) \tag{6}$$

$2k_c/(k_c + k_b)$. Thus, the Φ_∞ value exceeding unity, $\Phi_\infty = 1.3$,

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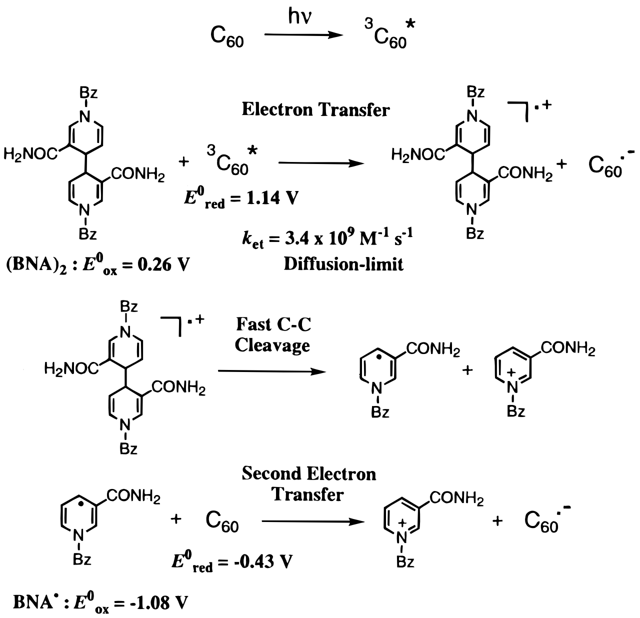
[32] Rehm, A.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

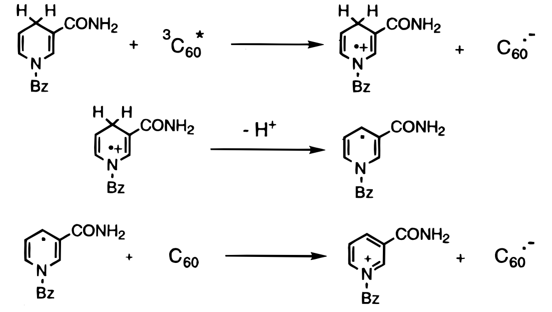
[33] Fukuzumi, S.; Fujita, M.; Otera, J.; Fujita, Y. *J. Am. Chem. Soc.* **1992**, *114*, 10271.

[34] Although electron transfer from $BNA^\bullet$ to $C_{60}{}^{\bullet-}$ may occur to produce $C_{60}{}^{2-}$, the fast comproportionation between $C_{60}{}^{2-}$ and C_{60} should take place to yield $C_{60}{}^{\bullet-}$ as the final product. Once all C_{60} is converted to $C_{60}{}^{\bullet-}$, there would be no further photoinduced electron transfer from $(BNA)_2$ to $C_{60}{}^{\bullet-}$.

Scheme 1



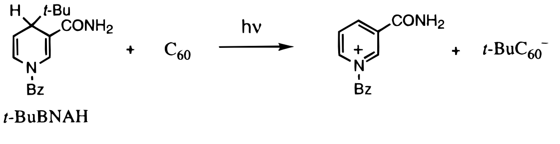
Scheme 2



may be ascribed to the efficient competition of C−C bond cleavage in $(BNA)_2^{\bullet +}$ (k_c) with the back electron transfer process (k_b). Once $C_{60}^{\bullet -}$ is produced, it is stable under the present experimental conditions.

The one-electron photoreduction of C_{60} by BNAH may also proceed via photoinduced electron transfer from BNAH to ${}^3C_{60}^*$ (Scheme 2). In this case, the deprotonation of $BNAH^{\bullet +}$ gives $BNA^{\bullet}$, which can further reduce C_{60} to $C_{60}^{\bullet -}$.

Selective Two-Electron Photoreduction of C_{60} to t-BuC_{60}^-. When BNAH is replaced by 4-*tert*-butylated BNAH (*t*-BuBNAH), no one-electron reduction of C_{60} by *t*-BuBNAH occurs, but instead the selective two-electron reduction of C_{60} to the *tert*-butylated anion (*t*-BuC_{60}^-) is attained accompanied by the two-electron oxidation of BNAH to BNA^+ (eq 7). Figure 4 shows the visible−near-IR spectral change observed in the photochemical reaction of *t*-BuBNAH with C_{60} in deaerated PhCN. The new absorption bands at 660 and 955 nm seen in Figure 4 agree with those of *t*-BuC_{60}^-.[35,36] In fact, the subsequent trap of the photoproduct by CF_3COOH and $PhCH_2Br$ gave *t*-$BuC_{60}H$ and *t*-$Bu(PhCH_2)C_{60}$, respectively (Scheme 3, see Experimental Section), as reported for the reactions of *t*-BuC_{60}^- with electrophiles.[37] The isolated *t*-$Bu(PhCH_2)C_{60}$ has a broad absorption band at 447 nm, which is similar to that seen in the spectrum of 1,4-$(PhCH_2)_2C_{60}$, the X-ray structure of which has been disclosed recently.[38] The ^1H NMR spectrum of the isolated *t*-$BuC_{60}H$ agrees with that of 1,2-*t*-$BuC_{60}H$, which is readily distinguished from that of 1,4-*t*-$BuC_{60}H$ (see Experimental Section).[39,40] The *t*-BuC_{60}^- has so far been prepared by using a strong alkylating reagent, that is, *tert*-butyllithium in toluene.[37] Thus, the photochemical reaction (eq 7) provides a unique and new way to prepare *t*-BuC_{60}^- with use of *t*-BuBNAH, which is a mild alkylating reagent under neutral conditions.



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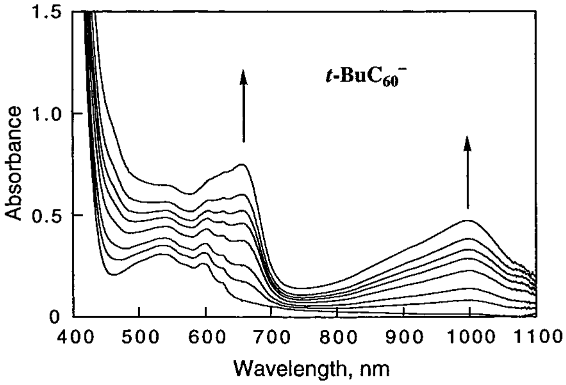
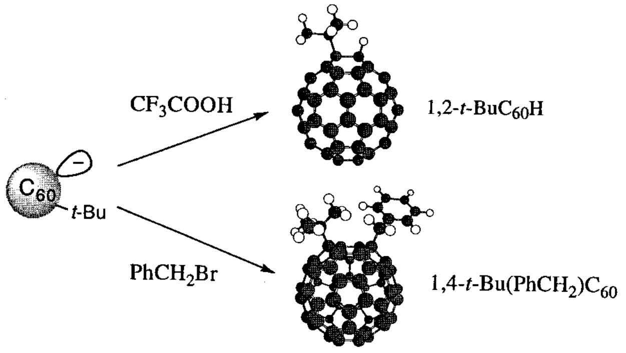


Figure 4. Electronic absorption spectra observed in the photochemical reaction of C_{60} (2.8×10^{-4} M) with *t*-BuBNAH (2.8×10^{-4} M) in deaerated PhCN under irradiation of visible light ($\lambda > 540$ nm) at 298 K.

Scheme 3



The quantum yields (Φ) for the photochemical formation of *t*-BuC_{60}^- were determined from an increase in absorbance due to *t*-BuC_{60}^- under irradiation by monochromatized light of λ = 546 nm. The Φ value for the photoreduction of C_{60} by *t*-BuBNAH in PhCN increases with an increase in the concentration of *t*-BuBNAH to reach a limiting value (Φ_∞) as in the

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[35] Fukuzumi, S.; Suenobu, T.; Hirasaka, T.; Gao, X.; Van Caemelbecke, E.; Kadish, K. M. In *Recent Advances in the Chemistry and Physics of Fullerenes*; Ruoff, R. S., Kadish, K. M., Eds.; Pennington: NJ, 1997; Vol. 4, pp 173−185.

[36] Kitagawa, T.; Tanaka, T.; Takata, Y.; Takeuchi, K.; Komatsu, K. *Tetrahedron* **1997**, *53*, 9965. Murata, Y.; Motoyama, K.; Komatsu, K.; Wan, T. S. M. *Tetrahedron* **1996**, *52*, 5077.

[37] Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 766. Kitagawa, T.; Tanaka, T.; Takata, Y.; Takeuchi, K. *J. Org. Chem.* **1995**, *60*, 1490. Tanaka, T.; Kitagawa, T.; Komatsu, K.; Takeuchi, K. *J. Am. Chem. Soc.* **1997**, *119*, 9313.

[38] Subramanian, R.; Kadish, K. M.; Vijayashree, M. N.; Gao, X.; Jones, M. T.; Miller, M. D.; Krause, K. L.; Suenobu, T.; Fukuzumi, S. *J. Phys. Chem.* **1996**, *100*, 16327.

[39] Banim, F.; Cardin, D. J.; Heath, P. *Chem. Commun.* **1997**, 25.

[40] The initial product of 1,4-*t*-$BuC_{60}H$ was rearranged to the 1,2-isomer during the isolation procedure to give the 1,2-isomer exclusively (see ref 39).

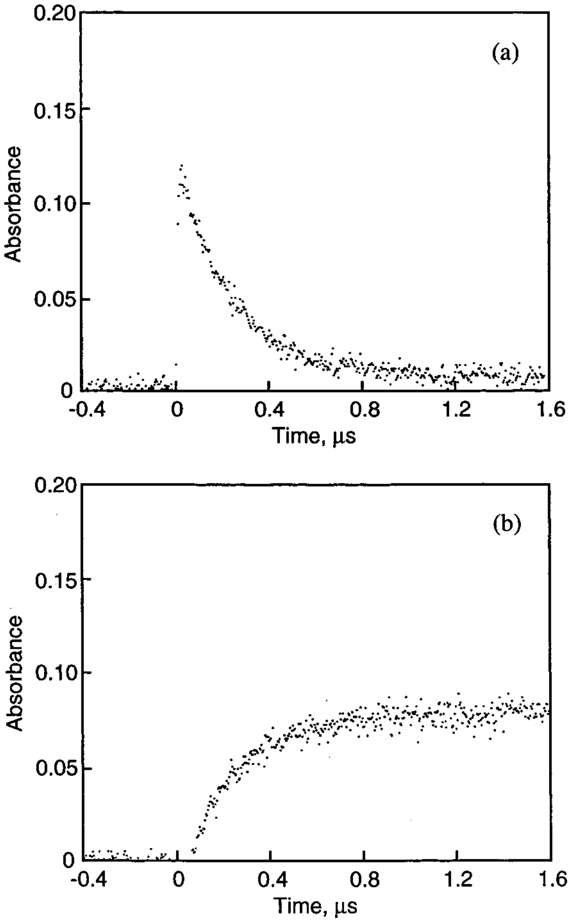


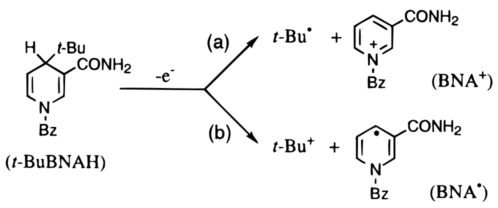
Figure 5. Decay of the absorbance at 740 nm due to $^3C_{60}$* (a) and the rise of the absorbance at 1080 nm due to $C_{60}^{\bullet-}$ (b) observed in the photoreduction of C_{60} (1.0×10^{-4} M) by *t*-BuBNAH (2.0×10^{-3} M) after laser excitation in deaerated PhCN at 295 K.

case of $(BNA)_2$ in Figure 2. The Φ_∞ value for *t*-BuBNAH is also listed in Table 1.

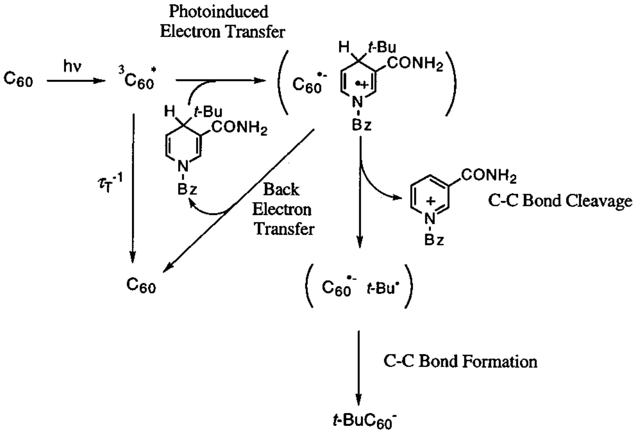
Although no one-electron reduction of C_{60} to $C_{60}^{\bullet-}$ occurs under a steady-state visible light irradiation (Figure 4), the formation of $C_{60}^{\bullet-}$ is detected as a reactive intermediate in the two-electron reduction of C_{60} by *t*-BuBNAH to *t*-BuC_{60}^- by the laser flash photolysis of a deaerated PhCN solution of C_{60} in the presence of *t*-BuBNAH. The decay of the absorbance at 740 nm due to $^3C_{60}$* obeys pseudo-first-order kinetics, coinciding with the rise of the absorbance at 1080 nm due to $C_{60}^{\bullet-}$ as shown in Figure 5. Thus, it is confirmed that the photochemical reaction of C_{60} with *t*-BuBNAH proceeds via photoinduced electron transfer from *t*-BuBNAH to $^3C_{60}$*. The rate constant for the reaction of $^3C_{60}$* with BNAH was determined as 2.1×10^9 M^{-1} s^{-1} as listed in Table 1.

We have previously reported that cleavage of the C(9)−C bond of the radical cation of an NADH analogue, 9-*tert*-butyl-10-methyl-9,10-dihydroacridine (AcrH(*t*-Bu)), occurs selectively rather than the cleavage of the C(9)−H bond in the electron-transfer oxidation of AcrH(*t*-Bu) by Fe^{3+} complexes.[30] Savéant et al. have also reported that the electrochemical oxidation of *t*-BuBNAH results in the selective C(4)−C bond cleavage of *t*-BuBNAH$^\bullet$.[41] Although there are two possible modes of the carbon−carbon bond cleavage in such reactions to generate (a) *t*-Bu$^\bullet$ and BNA^+ or (b) *t*-Bu^+ and BNA$^\bullet$ as shown in Scheme 4, the formation of *t*-Bu$^\bullet$ in the one-electron oxidation of *t*-BuBNAH has recently been confirmed by applying a rapid-mixing flow electron spin resonance (ESR) technique.[42] Thus, the photoinduced electron transfer from *t*-BuBNAH to $^3C_{60}$* to give *t*-BuBNAH$^{\bullet+}$ and $C_{60}^{\bullet-}$ may be followed by the facile C(4)−C bond cleavage of *t*-BuBNAH$^{\bullet+}$, giving *t*-Bu$^\bullet$ that is coupled immediately with $C_{60}^{\bullet-}$ to yield the final product (*t*-BuC_{60}^-) in competition with the back electron transfer as shown in Scheme 5.

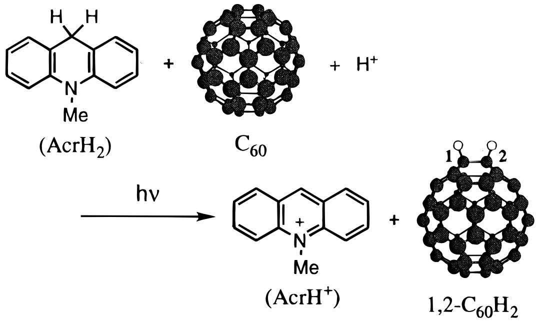
Scheme 4



Scheme 5



Selective Two-Electron Reduction of C_{60} to $C_{60}H_2$ via Photoinduced Electron Transfer. When another NADH analogue, 10-methyl-9,10-dihydroacridine ($AcrH_2$), is employed in the photochemical reaction with C_{60}, the selective two-electron reduction of C_{60} to $C_{60}H_2$ is attained accompanied by the two-electron oxidation of $AcrH_2$ to $AcrH^+$ in the presence of trifluoroacetic acid (eq 8). Irradiation of a solution of C_{60} (10.1 mg, 0.014 mmol) in deaerated PhCN (50 mL), 10-methyl-9,10-dihydroacridine ($AcrH_2$, 2.7 mg, 0.014 mmol), and CF_3COOH (0.014 mmol) with a Xe lamp (λ > 540 nm) equipped with a O-54 cut filter for 30 min resulted in the formation of 1,2-$C_{60}H_2$ exclusively in 70% yield (see Experimental Section). In the dark, however, no reaction has occurred



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(41) Anne, A.; Moiroux, J.; Savéant, J.-M. *J. Am. Chem.* Soc. **1993**, *115*, 10224.

(42) In the presence of O_2, *t*-Bu$^\bullet$ can be trapped efficiently by O_2 to yield *tert*-butylperoxyl radical (*t*-BuOO$^\bullet$), the formation of which, upon the oxidation of *t*-BuBNAH (5.0×10^{-4} M) by $[Fe(phen)_3]^{3+}$ (5.0×10^{-4} M) in aerated MeCN, was confirmed by the ESR spectrum (g = 2.016) with a rapid mixing flow apparatus; see ref 23.

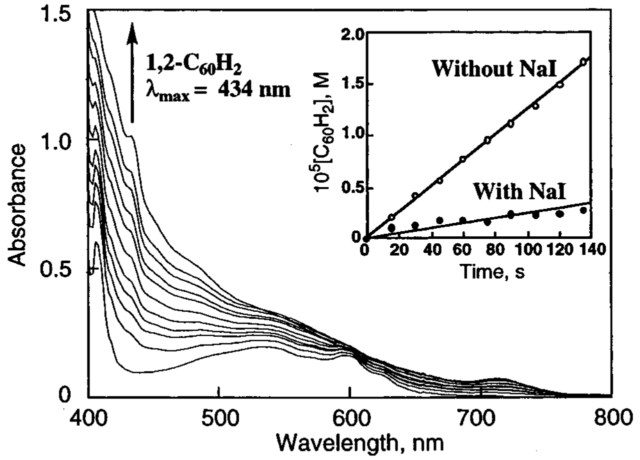

Figure 6. Electronic absorption spectra observed in the photoreduction of C_{60} (2.8×10^{-4} M) by $AcrH_2$ (2.8×10^{-4} M) in the presence of CF_3COOH (5.6×10^{-4} M) under irradiation of visible light ($\lambda > 540$ nm) in deaerated PhCN at 298 K. The inset shows the time dependence of the concentration of $C_{60}H_2$ in the absence and presence of NaI (1.9×10^{-2} M).

even at high temperatures (e.g., 373 K). No appreciable amounts of polyadducts were obtained even after the prolonged irradiation time under the present experimental conditions. The ^1H NMR signal at δ 5.91 (s, 2H) of 1,2-$C_{60}H_2$ (in C_6D_6) agrees well with that reported previously.[19] Irradiation of the absorption band of C_{60} in PhCN solution containing $AcrH_2$ and CF_3COOH results in an increase in the absorbances at $\lambda_{max} =$ 434 and 714 nm, which is known as a fingerprint of the 1,2-monoadduct such as 1,2-$C_{60}H_2$ resulting from 1,2-addition to a 6−6 bond.[1] A typical example of the electronic absorption spectra observed in the photoreduction of C_{60} by $AcrH_2$ in the presence of CF_3COOH in deaerated PhCN is shown in Figure 4. When the photoreduction of C_{60} is carried out in the presence of NaI, which is a well-known triplet quencher,[43] the reaction is strongly inhibited by NaI as shown in the inset in Figure 6.

The quantum yields (Φ) for the photoreduction of C_{60} by $AcrH_2$ were determined from an increase in absorbance due to 1,2-$C_{60}H_2$ under irradiation of monochromatized light of $\lambda =$ 546 nm. The Φ value increases with an increase in the concentration of $AcrH_2$ to reach a limiting value (Φ_∞) as shown in Figure 7a. When $AcrH_2$ is replaced by the dideuterated compound ($AcrD_2$), the deuterium isotope effect is observed for the limiting quantum yield ($\Phi^\infty{}_H/\Phi^\infty{}_D = 1.2$); compare Figure 7a with Figure 7b. The effect of CF_3COOH on the quantum yields was also examined as shown in Figure 8, where the quantum yield is constant with variation of the CF_3COOH concentration.

The transient absorption spectra of the radical ion pair ($AcrH_2{}^{\bullet+}C_{60}{}^{\bullet-}$) in the visible and near-IR regions are observed by the laser flash photolysis of a deaerated PhCN solution of C_{60} in the presence of $AcrH_2$ and CF_3COOH with 532 nm laser light as shown in Figure 9. The absorption band at 640 nm in the visible region agrees with that reported for $AcrH_2{}^{\bullet+}$ observed as a transient spectrum in the electron-transfer oxidation of $AcrH_2$ by $Fe(phen)_3{}^{3+}$ (phen = 1,10-phenanthroline).[30] The decay of the absorbance at 740 nm due to $^3C_{60}{}^*$ obeys pseudo-first-order kinetics, coinciding with the rise of the absorbance at 640 nm due to $AcrH_2{}^{\bullet+}$ and the absorbance at 1080 nm due to $C_{60}{}^{\bullet-}$. The rate constant for formation of $C_{60}{}^{\bullet-}$ determined from the rise of the absorbance at 1080 nm (3.7×10^9 M^{-1} s^{-1}) agrees within experimental error with the k_q value determined from the quenching of $^3C_{60}{}^*$ by $AcrH_2$ (4.3×10^9 M^{-1} s^{-1} in Table 1). At the prolonged monitoring time (0−16 μs) the absorbance at 1080 nm due to $C_{60}{}^{\bullet-}$ decays gradually (ca. 10%). The addition of CF_3COOH (1.0×10^{-3} M) to the $AcrH_2$−C_{60} system resulted in no appreciable effect on the formation or decay rate of $C_{60}{}^{\bullet-}$.

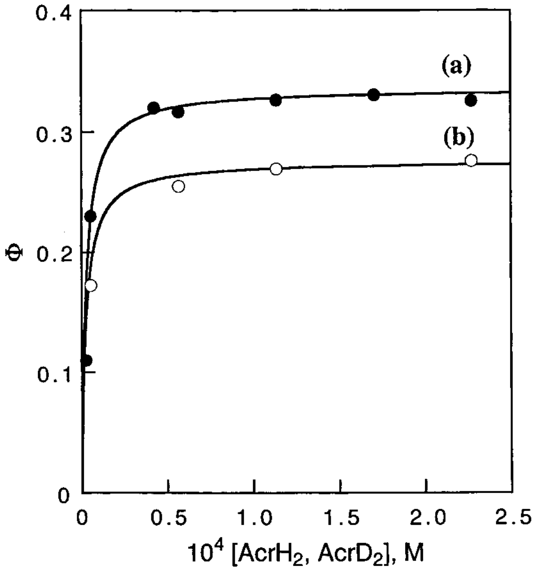

Figure 7. Dependence of the quantum yields on [$AcrH_2$] (a) and [$AcrD_2$] (b) for the photoreduction of C_{60} (2.8×10^{-4} M) by $AcrH_2$ and $AcrD_2$, respectively, in the presence of CF_3COOH (5.6×10^{-4} M) in PhCN at 298 K.

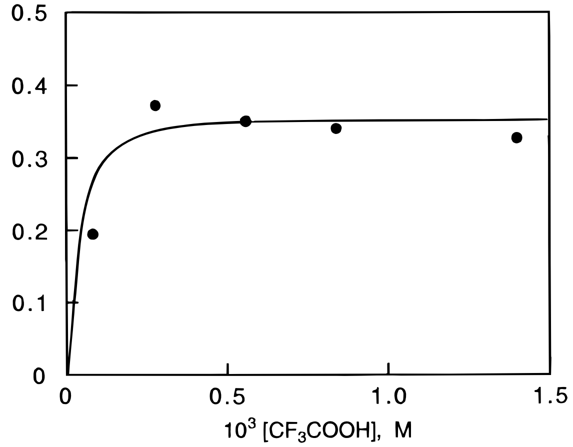

Figure 8. Dependence of the quantum yield on [CF_3COOH] in the photoreduction of C_{60} (2.8×10^{-4} M) by $AcrH_2$ (2.8×10^{-4} M) under irradiation of visible light ($\lambda = 546$ nm) in deaerated PhCN at 298 K.

When $AcrH_2$ was replaced by $AcrD_2$, essentially the same k_q value was obtained as for $AcrH_2$. Thus, there is no kinetic isotope effect on the quenching process. The rate constant of photoinduced electron transfer from $AcrH_2$ to $^3C_{60}{}^*$ (k_{et}) can also be evaluated from the $\Delta G^0{}_{et}$ and $\Delta G^{\ddagger}{}_0$ values[21] using eqs 4 and 5. The k_{et} value thus evaluated (4.3×10^9 M^{-1} s^{-1}) agrees with the k_q value (4.3×10^9 M^{-1} s^{-1}) listed in Table 1. The k_{et} value for $AcrH_2$ is the largest despite it having the least negative $\Delta G^0{}_{et}$ value. This results from it having the smallest $\Delta G^{\ddagger}{}_0$ value (2.6 kcal mol^{-1}).[21]

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(43) Fukuzumi, S.; Kuroda, S.; Tanaka, T. *J. Am. Chem. Soc.* **1985**, *107*, 3020.

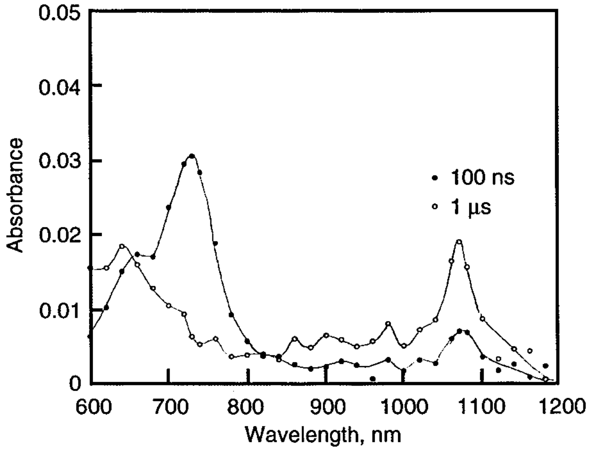
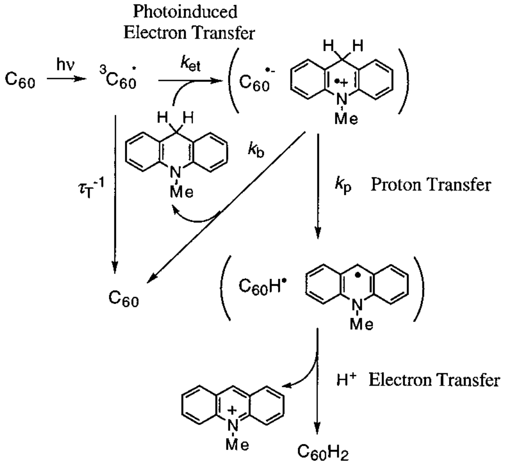


Figure 9. Transient absorption spectra observed in the photoreduction of C_{60} (1.0×10^{-4} M) by $AcrH_2$ (1.0×10^{-3} M) at 100 ns (●) and 1 μs (○) after laser excitation in deaerated PhCN at 295 K.

Scheme 6



The agreement between the k_{et} and k_q values together with the direct observation of the radical ion pair by the laser flash photolysis indicates that a photoinduced electron-transfer mechanism may also be applied to the photoreduction of C_{60} by $AcrH_2$ as shown in Scheme 6. The photoinduced electron transfer from $AcrH_2$ to $^3C_{60}^*$ (k_{et}) gives the radical ion pair ($AcrH_2^{•+}C_{60}^{•-}$) in competition with the decay to the ground state ($k_T = \tau_T^{-1}$). The pK_a of singly reduced C_{60} ($C_{60}H^•$) encapsulated in γ-cyclodextrin (γ-CD) and dissolved in water−propane-2-ol has recently been determined as 4.5 on the basis of a specific IR absorption band for $C_{60}^{•-}$−γ-CD.[44] On the other hand, the pK_a of $AcrH_2^{•+}$ in water has previously been determined as 2.0.[21,30] Thus, proton transfer from $AcrH_2^{•+}$ to $C_{60}^{•-}$ (k_H) is significantly exergonic,[45,46] and it may occur efficiently in the radical ion pair in competition with the back electron transfer to the reactant pair (k_b), to give $C_{60}H^•$, which is converted to 1,2-$C_{60}H_2$ by the fast electron transfer from $AcrH^•$ in the presence of CF_3COOH (Scheme 6).[47] Alternatively, $C_{60}^{•-}$ produced in the initial photoinduced electron transfer from $AcrH_2$ to C_{60} could be protonated by the acid, and hydrogen transfer from $AcrH_2^{•+}$ to $C_{60}H^•$ gives the final products. However, no increase in the quantum yield was observed with an increase in the CF_3COOH concentration. In fact, the first reduction potential of C_{60} has not been affected by the presence of CF_3COOH in PhCN (see Experimental Section). Thus, the protonation process may not be involved in the rate-determining step as shown in Scheme 6. The theoretical calculations suggest that 1,2-$C_{60}H_2$ is the most stable form among 23 different regioisomers,[48] and it is thereby obtained selectively in the photoreduction of C_{60} by $AcrH_2$.

By application of the steady-state approximation to the reactive species, $^3C_{60}^*$ and the radical ion pair in Scheme 6, the dependence of Φ on the donor concentration [$AcrH_2$] can be derived as given by eq 9, which agrees with the observed dependence of Φ on [$AcrH_2$] in Figure 7. The limiting quantum

$$\Phi = [k_p/(k_p + k_b)]k_{et}\tau_T[\mathrm{AcrH_2}]/(1 + k_{et}\tau_T[\mathrm{AcrH_2}]) \qquad (9)$$

yield Φ_∞ corresponds to $k_p/(k_p + k_b)$. The observed isotope effect in Φ_∞ (Figure 7) is thereby ascribed to the proton-transfer process from $AcrH_2^{•+}$ to $C_{60}^{•-}$. The small isotope effect is consistent with the Φ_∞ value being significantly smaller than unity, when the back electron transfer (k_b) may be much faster than the proton transfer (k_p), that is, $k_p \ll k_b$.

The Mechanistic Difference in One-Electron and Two-Electron Reduction of C_{60}. The one-electron reduction of C_{60} by $(BNA)_2$ (Scheme 1) and BNAH (Scheme 2) as well as the two-electron reduction by $AcrH_2$ (Scheme 6) proceeds via photoinduced electron transfer from the electron donor to $^3C_{60}^*$. In the case of $(BNA)_2$ in Scheme 1, the facile C−C bond cleavage of $(BNA)_2^{•+}$ to produce $BNA^•$ that can reduce C_{60} to $C_{60}^{•-}$ is responsible for the selective one-electron reduction of C_{60}. On the other hand, the C−C bond cleavage of *t*-$BuBNAH^{•+}$ to produce *t*-$Bu^•$ that cannot reduce C_{60} to $C_{60}^{•-}$ but instead is coupled with $C_{60}^{•-}$ to yield *t*-BuC_{60}^- (Scheme 5) is responsible for the selective two-electron reduction of C_{60} to *t*-BuC_{60}^-. In the case of $AcrH_2$ in Scheme 6, the strong acidity of $AcrH_2^{•+}$ causes a proton transfer from $AcrH_2^{•+}$ to $C_{60}^{•-}$ to produce a strong reductant−oxidant pair ($AcrH^•C_{60}H^•$) followed by the second electron transfer to yield two-electron reduction of C_{60} to 1,2-$C_{60}H_2$ in the presence of an acid. Since the pK_a value of $BNAH^{•+}$ (3.6)[21,49] is significantly larger than that of $AcrH_2^{•+}$ (2.0),[21,30] the proton transfer from $BNAH^{•+}$ to $C_{60}^{•-}$ may be much slower than that from $AcrH_2^{•+}$. In addition, $BNA^•$ produced by the deprotonation of $BNAH^{•+}$ is a much stronger one-electron reductant than $AcrH^•$, judging from the largely negative E^0_{ox} value of $BNA^•$ (−1.08 V)[21] as compared with that of $AcrH^•$ (−0.43 V).[21] In such a case, the deprotonation of $BNAH^{•+}$ may be followed by the fast electron transfer from $BNA^•$ to C_{60} to yield BNA^+ and $C_{60}^{•-}$ as shown in Scheme 2. Thus, the difference in the redox and acid−base properties of the radical cations produced in the photoinduced electron transfer may determine the subsequent reaction pathway, leading to the one-electron reduction or the two-electron reduction.

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(45) The pK_a value in an aprotic solvent is expected to be much larger than that in water because of the strong solvation of water to protons. The pK_a value of $AcrH_2^{•+}$ in acetonitrile is determined as in the range 6.8−8.1, depending on the H_2O concentration.[30] On the other hand, the pK_a value of $C_{60}H^•$ has been estimated as 9 (see ref 46). Thus, the proton transfer from $AcrH_2^{•+}$ to $C_{60}^{•-}$ in an aprotic solvent may also be significantly exergonic.

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(47) In the absence of CF_3COOH, 1,2-$C_{60}H_2$ (434 nm) was not formed, but instead a new broad absorption at 450 nm, which may be assigned to a radical adduct, appears in the photochemical reaction. However, the radical adduct remains to be characterized.

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Supporting Information Available: Experimental procedures of laser flash photolysis (2 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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