

Electron-Transfer Properties of C₆₀ and *tert*-Butyl-C₆₀ RadicalShunichi Fukuzumi,^{*,†} Ikuo Nakanishi,[†] Tomoyoshi Suenobu,[†] and Karl M. Kadish^{*,‡}

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Abstract: The rate constants of electron transfer from C₆₀^{•-} and C₆₀²⁻ to electron acceptors such as allyl halides and manganese(III) dodecaphenylporphyrin are correlated with those from semiquinone radical anions and their derivatives; linear correlations are obtained between the logarithms of the rate constants and the oxidation potentials of C₆₀^{•-}, C₆₀²⁻, and semiquinone radical anions for different electron acceptors. Such correlations indicate that reorganization energies for the electron-transfer reactions of C₆₀^{•-} and C₆₀²⁻ are essentially the same as those of semiquinone radical anions. The self-exchange rate constants between *p*-benzoquinone and the semiquinone radical anion as well as between tetramethyl-*p*-benzoquinone and the semiquinone radical anion in benzonitrile are determined at various temperatures by analyzing line width variations of the ESR spectra. The fast-exchange rate constants and small activation enthalpies demonstrate the efficient electron-transfer properties of the *p*-benzoquinone/semiquinone radical anion, C₆₀/C₆₀^{•-}, and C₆₀^{•-}/C₆₀²⁻ systems. The self-exchange rate constant between *t*-BuC₆₀[•] and *t*-BuC₆₀⁻ is also determined by analyzing line width variations of the ESR spectra.

Introduction

Since C₆₀ is essentially spherical, it is an ideal molecule to examine the electron-transfer reactions involving C₆₀ in light of Marcus electron-transfer theory.¹ The first electron in the reduction of C₆₀ is added to a triply degenerate t_{1u} unoccupied molecular orbital and is highly delocalized.^{2,3} Thus, electron transfer to C₆₀ is expected to be highly efficient because of the minimal changes of structure and solvation associated with the electron-transfer reduction. The efficiency of electron transfer can be expressed by the self-exchange rates between C₆₀ and the radical anion (C₆₀^{•-}), which is the most fundamental property of electron-transfer reactions in solution. Line width variations of the ESR spectra of radical anions in the presence of various concentrations of the corresponding neutral compounds have usually been used to determine fast-exchange rate constants which are close to the diffusion limit.⁴ Unfortunately, this method cannot be applied to C₆₀^{•-} because of the absence of hyperfine structure in the ESR spectrum.⁵ For monoalkyl adduct radicals of the type RC₆₀[•], spin polarization and hyperconjugative effects give rise to resolvable hyperfine interactions from

R of RC₆₀[•].^{6–8} However, there has been no report on the electron-exchange reactions between RC₆₀ radicals and RC₆₀ anions.

Photoinduced electron transfer from various electron donors to the triplet excited states of C₆₀ and C₇₀ occurs efficiently and is associated with a small reorganization energy of electron transfer involving the excited states.^{9–14} Thus, the occurrence of fast electron transfer involving the excited states of fullerenes with a small intrinsic barrier of electron transfer has been well established. Guldi and Asmus¹⁵ have recently reported a Marcus inverted type dependence of the rate constants for electron-transfer oxidation of C₇₆ and C₇₈ with a series of arene radical cations produced upon radiolysis of the C₇₆/C₇₈–arene systems,

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from which a reorganization energy of 13.8 kcal mol⁻¹ is deduced in the electron-transfer oxidation reactions. Thus, the electron-transfer oxidation of C₇₆ and C₇₈ should also be fast with a small intrinsic barrier of the electron transfer.

With regard to the electron-transfer reduction of the C₆₀ ground state, however, it is still not clear whether the reduction is as efficient as the oxidation. For example, an extremely slow electron-transfer reaction of C₆₀ has been reported for the reaction from 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to C₆₀ in benzonitrile, which can be followed even by conventional vis-near-IR spectroscopy.¹⁶ In this case, however, it is not clear whether the generation of C₆₀^{•-} is directly related to the electron transfer from DBU to C₆₀ or if C₆₀^{•-} is the product of a secondary reaction. In contrast, Fawcett et al.¹⁷ have reported that electron transfer of C₆₀ is fast, as one would expect for a large spherical reactant, on the basis of the kinetics of the electroreduction of C₆₀ in the presence of tetrabutylammonium perchlorate in benzonitrile at ultramicroelectrodes by applying the ac admittance technique. The reported standard rate constant for the electroreduction of C₆₀ (0.3 cm s⁻¹) is comparable with that of ferricenium ion (0.2 cm s⁻¹).¹⁷ On the other hand, the self-exchange rate constant of ferrocene in acetonitrile is reported as 5.3 × 10⁶ M⁻¹ s⁻¹, which is far smaller than the diffusion limit.^{18,19}

Imahori et al. have recently reported a longer-lived charge-separated state of a zinc porphyrin-C₆₀ dyad system (350 ps) formed by the photoinduced electron transfer as compared to the corresponding porphyrin-linked *p*-benzoquinone system (<14 ps).²⁰ The decelerated back electron transfer from C₆₀^{•-} to the porphyrin π radical cation is explained by a smaller reorganization energy in C₆₀ as compared with that in *p*-benzoquinone, which leads to the slower back-electron-transfer rate for the zinc porphyrin-C₆₀ dyad system in the Marcus inverted region.²⁰ On the other hand, Guldi et al. has reported a much longer-lived charge-separated state of a ferrocene-C₆₀ dyad system (2.4 μs), where the back electron transfer is not in the Marcus inverted region.²¹ They have shown that the rates of back electron transfer in such types of donor-bridge-acceptor dyads are extremely sensitive to the flexibility of the bridge spacer.¹² Extensive efforts have continued to be made to design various covalently linked C₆₀-based donor-bridge-acceptor systems as artificial photosynthetic systems.²²⁻²⁶ Thus, a reliable determination of the reorganization energy of electron-transfer reduction of C₆₀ would be of significant interest.

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In this study we report the electron-transfer properties of C₆₀ and its radical anion, C₆₀^{•-}, in comparison with those of *p*-benzoquinone derivatives in benzonitrile. The self-exchange rate constants between *p*-benzoquinones and semiquinone radical anions in benzonitrile at various temperatures are directly determined by analyzing line width variations of the ESR spectra. The rate constants of electron transfer from C₆₀^{•-} and C₆₀²⁻ to four different electron acceptors (three allyl halides and manganese(III) dodecaphenylporphyrin) are compared with rate constants from four different semiquinone radical anions by plotting the logarithms of the rate constants vs the oxidation potentials of C₆₀^{•-}, C₆₀²⁻, and the semiquinone radical anions for different electron acceptors. Comparisons are made between the electron-transfer properties of C₆₀ and *p*-benzoquinone derivatives in benzonitrile which provide confirmative and quantitative information about the self-exchange rates of C₆₀/C₆₀^{•-} and C₆₀^{•-}/C₆₀²⁻ in solution. We also report a direct determination of the self-exchange rate constant between *t*-BuC₆₀ radical and *t*-BuC₆₀ anion by analyzing line width variations of the ESR spectra.}

Experimental Section

Materials. C₆₀ (>99.95% pure) was purchased from Science Laboratories Co., Ltd., Japan, and used as received. C₆₀ of 99.99% purity was obtained from Science Laboratories Co., and used for the spectral measurements. Dimeric *N*-benzylidihydronicotinamide, (BNA)₂, was prepared according to a procedure described in the literature.²⁷ Benzonitrile (PhCN) was purchased from Wako Pure Chemical Industries Ltd., Japan, and distilled over P₂O₅ according to standard procedures.²⁸ Allyl halides, naphthalene, and sodium were obtained commercially from Aldrich and Wako Pure Chemical Industries Ltd. in special grade. *tert*-Butyl iodide (*t*-BuI) from Wako Pure Chemical Industries Ltd. was distilled in the dark under a reduced pressure of 100 mmHg at 333 K. Manganese(III) dodecaphenylporphyrin chloride, Mn(DPP)Cl (DPP = the dianion of dodecaphenylporphyrin), was provided by Professor R. Guillard of the Université de Bourgogne and was synthesized using previously described procedures.²⁹ Tetrahydrofuran (THF) was dried by refluxing under nitrogen with sodium prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized from ethanol and dried under vacuum at 40 °C for at least 1 week

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prior to use. The sodium salt of the naphthalene radical anion (1.0 M in THF) was prepared by reduction of naphthalene (10 mmol) with sodium (10 mmol) under deaerated conditions in distilled THF at 298 K.

Electron-Transfer Kinetics of $C_{60}^{\bullet-}$ and C_{60}^{2-} . In a typical experiment for preparation of $C_{60}^{\bullet-}$ in solution, C_{60} (5.8 mg, 0.008 mmol) was dissolved in deaerated PhCN (50 mL), and (BNA)₂ (3.4 mg, 0.008 mmol) was added to the solution under an atmospheric pressure of argon. The solution was irradiated with a Xe lamp equipped with a UV-cutoff filter ($\lambda < 420$ nm) for 10 min. The quantitative conversion of C_{60} to $C_{60}^{\bullet-}$ was confirmed by the appearance of a diagnostic absorption band at 1080 nm.³⁰ This was used as a stock solution of $C_{60}^{\bullet-}$ for the kinetic measurements.

Rates of electron transfer from $C_{60}^{\bullet-}$ to the allyl halides in deaerated PhCN at 298 K were monitored by following a decrease in absorbance due to loss of $C_{60}^{\bullet-}$ ($\lambda_{\max} = 1080$ nm) under pseudo-first-order conditions where the allyl halide concentrations were maintained at more than 10-fold excess of the $C_{60}^{\bullet-}$ concentration (1.6×10^{-4} M). The vis-near-IR spectral changes during these reactions were followed with a Shimadzu UV-160A spectrophotometer which was thermostated at 298 K.

A stock solution of C_{60}^{2-} was prepared by reduction of C_{60} using naphthalene radical anion (2.4×10^{-1} M) in THF which was generated as described in the literature³¹ and added to a quartz cuvette (10 mm i.d.) containing a deaerated PhCN solution (3.0 mL) of C_{60} (2.8×10^{-4} M). The quantitative conversion of C_{60} to C_{60}^{2-} was confirmed by the diagnostic dianion absorption band at 955 nm.³⁰ Rates of electron transfer from C_{60}^{2-} to the allyl halides in benzonitrile at 298 K were monitored by following a decrease in absorbance due to loss of C_{60}^{2-} ($\lambda_{\max} = 955$ nm) under pseudo-first-order conditions, where the allyl halide concentrations were maintained at more than 10-fold excess of the C_{60}^{2-} concentration (1.0×10^{-4} M) as reported previously.^{32,33}

Semiquinone radical anions in benzonitrile were prepared by proportionation reactions of *p*-benzoquinone and its derivatives with the dianions obtained by deprotonation of the corresponding hydroquinones with tetrabutylammonium hydroxide.³⁴ Rates of electron transfer from the semiquinone radical anions to the allyl halides in deaerated PhCN at 298 K were monitored by following a decrease in absorbance due to the semiquinone radical anion ($\lambda_{\max} = 422$ nm) under pseudo-first-order conditions where the allyl halide concentrations were maintained at more than 10-fold excess of the semiquinone radical anion concentration (1.7×10^{-4} M).

Kinetic measurements for electron transfer from $C_{60}^{\bullet-}$ or the semiquinone radical anions to Mn(DPP)Cl were carried out using a Union RA-103 stopped-flow spectrophotometer in deaerated PhCN at 298 K. The rates of the electron transfer were followed by monitoring an increase in absorbance at 488 or 720 nm due to the reduced porphyrin product, [Mn(DPP)Cl]⁻, under second-order conditions where the initial concentrations of $C_{60}^{\bullet-}$ or the semiquinone radical anions and Mn(DPP)Cl were the same (2.1×10^{-4} M).

In each case, it was confirmed that the rate constants of electron transfer (k_{et}) derived from at least five independent measurements agreed within an experimental error of $\pm 5\%$. Pseudo-first-order or second-order rate constants were determined by a least-squares curve fit using an Apple Macintosh computer. The pseudo-first-order plots of $\ln(A_{\infty}$

– A) vs time and the second-order plots of $(A_{\infty} - A)^{-1}$ vs time (A_{∞} and A are the final absorbance and the absorbance at the reaction time, respectively) were linear for 3 or more half-lives with the correlation coefficient $\rho > 0.999$.

Fast electron-transfer reactions between $C_{60}^{\bullet-}$ and 2,6-dichloro-*p*-benzoquinone or semiquinone radical anion and C_{60} were monitored by following an increase or a decrease in absorbance due to the semiquinone radical anion with use of a Union RA-103 stopped-flow spectrophotometer. The detection limit of the pseudo-first-order rate constant was ca. 1000 s⁻¹.

ESR Measurements. Typically, an aliquot of a stock solution of the semiquinone radical anion (2.0×10^{-3} M) was added to an ESR tube containing a deaerated benzonitrile solution of various concentrations of *p*-benzoquinone (1.0×10^{-2} to 3.0×10^{-2} M) under an atmospheric pressure of Ar. The ESR spectra of the semiquinone radical anions were measured at various temperatures (-10 to $+80$ °C) with a JEOL X-band spectrometer (JES-REIXE). However, tetramethylsemiquinone radical anion was unstable in the presence of excess tetramethyl-*p*-benzoquinone, and the ESR measurements were then only performed at temperatures lower than 25 °C using an attached VT (variable temperature) apparatus. The ESR spectra were recorded under non saturating microwave power conditions. The magnitude of modulation was chosen to optimize the resolution and the signal-to-noise (S/N) ratio of the observed spectra, when the maximum slope line width (ΔH_{msl}) of the ESR signals was unchanged with the larger modulation. The ΔH_{msl} values of the semiquinone radical anions were determined just after addition of the semiquinone radical anion to a deaerated benzonitrile solution containing various concentrations of the *p*-benzoquinone, since the values become smaller after prolonged times. The *g* values and the hyperfine coupling constants were calibrated with a Mn²⁺ marker.

In a typical experiment for the ESR measurements of *t*-BuC₆₀[•], 25 μ L of *tert*-butyl iodide was added to 350 mL of a saturated benzonitrile/benzene (1:7 v/v) solution of C_{60} (2.0×10^{-3} M) and *t*-BuC₆₀⁻ in a 3 mm quartz tube under an atmospheric pressure of Ar. The *t*-BuC₆₀⁻ solution was prepared by the reaction of C_{60}^{2-} with *t*-BuI in benzonitrile/benzene (1:7 v/v) according to the procedure reported previously.³³ The ESR samples containing *t*-BuI, C_{60} , and *t*-BuC₆₀⁻ were then irradiated in the cavity of the ESR spectrometer with the focused light of a 1000 W high-pressure Hg lamp through an aqueous filter.

Theoretical Calculations. Theoretical studies were performed using the PM3 molecular orbital method.³⁵ The calculations were performed by using the MOL-MOLIS program Version 2.8 by Daikin Industries, Ltd. Final geometries and energetics were obtained by optimizing the total molecular energy with respect to all structural variables. The geometries of the radicals were optimized using the unrestricted Hartree-Fock (UHF) formalism. The ΔH_f values of the radicals were calculated with the UHF-optimized structures using the half-electron (HE) method with the restricted Hartree-Fock (RHF) formalism.³⁶ The reorganization energies of the inner coordination spheres (λ_i) associated with the structural change of *p*-benzoquinones upon the electron-transfer reduction were calculated as the difference in ΔH_f of the radical anions with the same structures as the neutral forms and ΔH_f with the optimized structures using the UHF formalism.

Results and Discussion

Electron Transfer between C_{60} and Semiquinone Radical Anion. Since the one-electron oxidation potential of semiquinone radical anion (-0.50 V vs SCE)³⁷ is slightly more negative than the one-electron reduction potential of C_{60} (-0.43 V vs SCE),³⁸ electron transfer from the semiquinone radical anion to C_{60} (eq 1) is expected to occur thermodynamically. In fact, the addition of semiquinone radical anion to a deaerated

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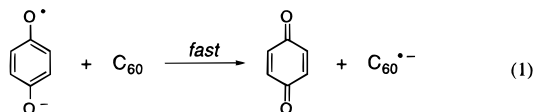
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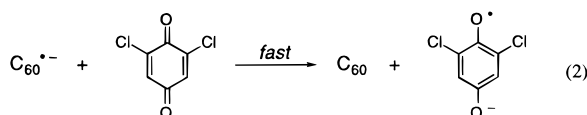
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PhCN solution results in the facile formation of $C_{60}^{\bullet-}$ ($\lambda_{\text{max}} = 1080$ nm), accompanied by the disappearance of the semiquinone radical anion ($\lambda_{\text{max}} = 422$ nm). The rate of electron transfer is so rapid as to fall outside the stopped-flow range even with small concentrations (ca. 1.0×10^{-5} M). Judging from the detection limit of the stopped-flow technique, the rate constant of electron transfer must be larger than ca. 1×10^8 $\text{M}^{-1} \text{s}^{-1}$. Thus, the electron-transfer reduction of C_{60} , even with a slightly negative free energy change of the electron transfer (-1.6 kcal mol^{-1}), should be too fast to be determined directly.

When a *p*-benzoquinone derivative with electron-withdrawing substituents, such as 2,6-dichloro-*p*-benzoquinone, is used instead of *p*-benzoquinone, the direction of electron transfer reverses so that C_{60} is not reduced by 2,6-dichlorosemiquinone radical anion but electron transfer from $C_{60}^{\bullet-}$ ($E_{\text{ox}}^{\circ} = -0.43$ V) to 2,6-dichloro-*p*-benzoquinone ($E_{\text{red}}^{\circ} = -0.18$ V)³⁷ occurs rapidly (eq 2). In this case the rate constant of electron transfer is also beyond the detection limit of a stopped-flow technique, i.e., larger than 1×10^8 $\text{M}^{-1} \text{s}^{-1}$.



Comparison of Electron-Transfer Rates of $C_{60}^{\bullet-}$, C_{60}^{2-} , and Semiquinone Radical Anions. Since the rate of electron transfer from $C_{60}^{\bullet-}$ to *p*-benzoquinone is too fast to be determined by the stopped-flow technique (vide supra), electron acceptors which have large reorganization energies such as allyl halides and manganese(III) dodecaphenylporphyrin, Mn(DPP)-Cl,³⁹ were chosen to examine the rates of electron-transfer reactions of $C_{60}^{\bullet-}$ in comparison with those of the semiquinone radical anion. We have recently reported that the reactions of C_{60}^{2-} with allyl halides proceed via an electron transfer from C_{60}^{2-} to allyl halides, and the rate constants for these reactions were compared with those for electron transfer from tetramethyl-*p*-benzoquinone dianion to a series of allyl halides.³³ A similar comparison can be made between $C_{60}^{\bullet-}$ and semiquinone radical anions in their reactions with allyl halides and Mn(DPP)Cl. Thus, a determination of the rates of electron transfer from $C_{60}^{\bullet-}$ to allyl halides or Mn(DPP)Cl combined with the rates of electron transfer from semiquinone radical anions to the same oxidants provides an excellent opportunity to compare the electron-transfer properties between C_{60} and *p*-benzoquinones.

The rates of electron transfer from $C_{60}^{\bullet-}$ to allyl halides (RX) were determined by monitoring the decrease in the $C_{60}^{\bullet-}$ absorbance at 1080 nm as shown in Figure 1. The rates obey pseudo-first-order kinetics under experimental conditions where the RX concentration is greater than a 10-fold excess of the $C_{60}^{\bullet-}$ concentration (inset in Figure 1). The pseudo-first-order rate constants increase proportionally with the RX concentration as shown in Figure 2, where the second-order rate constants of electron transfer (k_{et}) in eq 3 are obtained from the slope of the plots. The k_{et} values of $C_{60}^{\bullet-}$ are listed in Table 1.

Similarly, the rates of electron transfer from semiquinone radical anion ($Q^{\bullet-}$) to RX were determined by monitoring a

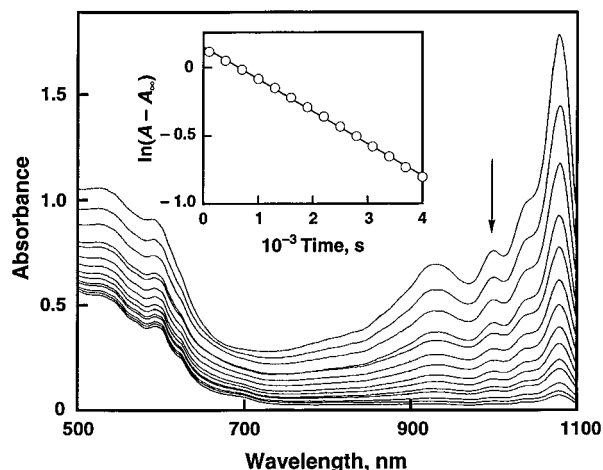


Figure 1. Spectral changes observed during the electron-transfer reaction from $C_{60}^{\bullet-}$ (1.6×10^{-4} M) to $\text{Me}_2\text{C}=\text{CHCH}_2\text{Br}$ (1.5×10^{-2} M) in deaerated PhCN at 298 K. Interval: 300 s. Inset: first-order plot based on the absorption change at 1000 nm (see the arrow).

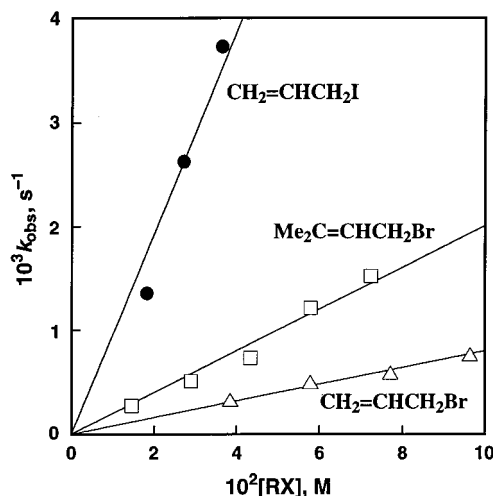
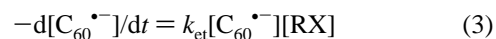


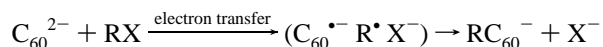
Figure 2. k_{obs} vs [RX] for electron transfer from $C_{60}^{\bullet-}$ to RX in deaerated PhCN at 298 K.



decrease in the $Q^{\bullet-}$ absorbance at 422 nm. The second-order rate constants of electron transfer (k_{et}) could also be obtained from the slope in the linear plots of the pseudo-first-order rate constants vs [RX]. The k_{et} values of tetramethylsemiquinone radical anion and 2,6-dimethylsemiquinone radical anion, as well as the unsubstituted semiquinone radical anion, were determined by this method, and these values are also listed in Table 1.

When $C_{60}^{\bullet-}$ is replaced by C_{60}^{2-} , the electron transfer from C_{60}^{2-} to RX becomes much faster than that from $C_{60}^{\bullet-}$ to RX.³³ This is consistent with the more negative oxidation potential of C_{60}^{2-} in benzonitrile ($E_{\text{ox}}^{\circ} = -0.87$ V) as compared to $C_{60}^{\bullet-}$ in the same solvent (-0.43 V).³³ The electron transfer from C_{60}^{2-} to RX is followed by a coupling of the resulting radicals ($C_{60}^{\bullet-}$ and R^{\bullet}) to yield $\text{RC}_{60}^{\bullet-}$ (Scheme 1).³³

Scheme 1



The rates of electron transfer from C_{60}^{2-} to the same allyl halides employed for the electron-transfer reactions of $C_{60}^{\bullet-}$ and the semiquinone radical anions were determined by

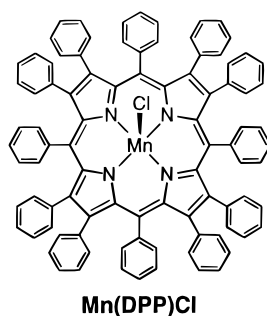
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Table 1. Electron-Transfer Rate Constants k_{et} from $C_{60}^{\bullet-}$, C_{60}^{2-} , Semiquinone Radical Anion ($Q^{\bullet-}$), Methylsemiquinone Radical Anion ($MeQ^{\bullet-}$), 2,6-Dimethylsemiquinone Radical Anion ($Me_2Q^{\bullet-}$), and Tetramethylsemiquinone Radical Anion ($Me_4Q^{\bullet-}$) to Various Oxidants in Deaerated PhCN at 298 K

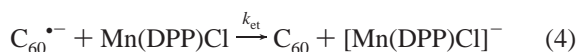
oxidant	$k_{et}(C_{60}^{\bullet-})$ ($M^{-1} s^{-1}$)	$k_{et}(Q^{\bullet-})$ ($M^{-1} s^{-1}$)	$k_{et}(MeQ^{\bullet-})$ ($M^{-1} s^{-1}$)	$k_{et}(Me_2Q^{\bullet-})$ ($M^{-1} s^{-1}$)	$k_{et}(Me_4Q^{\bullet-})$ ($M^{-1} s^{-1}$)	$k_{et}(C_{60}^{2-})$ ($M^{-1} s^{-1}$)
$Me_2C=CHCH_2Br$	2.0×10^{-2}	6.5×10^{-1}		2.5	1.9×10	3.2×10
$CH_2=CHCH_2I$	9.7×10^{-2}	5.1×10^{-1}		1.7	5.5×10	5.0×10
$CH_2=CHCH_2Br$	8.1×10^{-3}	2.8×10^{-2}		3.2×10^{-1}	1.5	2.2
$Mn(DPP)Cl$	7.0×10^3	1.3×10^4	4.1×10^4	4.7×10^5	too fast	too fast

monitoring either the decrease in C_{60}^{2-} absorbance or the increase in RC_{60}^- absorbance.³³ The second-order rate constants of electron transfer (k_{et}) were determined from slopes of the plots of the pseudo-first-order rate constants vs $[RX]$.³³ The k_{et} values of C_{60}^{2-} are also listed in Table 1.

Electron transfer from $C_{60}^{\bullet-}$ to $Mn(DPP)Cl$ is energetically feasible judging from the more negative oxidation potential of $C_{60}^{\bullet-}$ ($E^{\circ}_{ox} = -0.43$ V) as compared to the reduction potential



of $Mn(DPP)Cl$ ($E^{\circ}_{red} = -0.36$ V)^{29a} (eq 4). The rate of electron transfer from $C_{60}^{\bullet-}$ to $Mn(DPP)Cl$ was determined by monitoring the increase in the $[Mn(DPP)Cl]^-$ absorbance at 488 or 720 nm. The rate obeys second-order kinetics under experimental



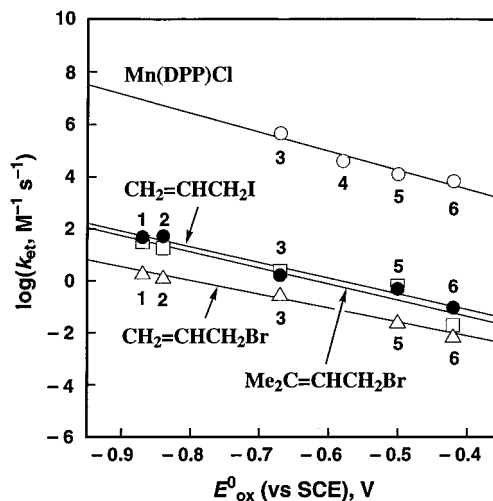
conditions where the initial concentrations of $C_{60}^{\bullet-}$ and $Mn(DPP)Cl$ are the same. The rate constant of electron transfer (k_{et}) from $C_{60}^{\bullet-}$ to $Mn(DPP)Cl$ was determined from the second-order plot as listed in Table 1. The k_{et} values for electron transfer from the semiquinone radical anions to $Mn(DPP)Cl$ were determined in the same manner, and these values are also listed in Table 1. The electron transfer from C_{60}^{2-} or $Me_4Q^{\bullet-}$ to $Mn(DPP)Cl$ is too fast to be followed with a stopped-flow technique.

Figure 3 shows a comparison of the k_{et} values of C_{60}^{2-} , semiquinone radical anions, and $C_{60}^{\bullet-}$ in the electron-transfer reactions with three different allyl halides ($CH_2=CHCH_2I$, $Me_2C=CHCH_2Br$, and $CH_2=CHCH_2Br$) and $Mn(DPP)Cl$ as plots of $\log k_{et}$ vs the E°_{ox} values of the electron donors. A linear correlation is seen for each electron acceptor, including C_{60}^{2-} , the four investigated semiquinone radical anions, and $C_{60}^{\bullet-}$.

According to the Marcus electron-transfer theory, the electron-transfer rate constant from an electron donor to an acceptor (k_{et}) is expressed in terms of the self-exchange rate constant of an electron donor (k_{11}) and an electron acceptor (k_{22}) and the equilibrium constant of electron transfer (K_{et}) as given by eq 5,

$$\log k_{et} = [\log(k_{11}k_{22}K_{et}) + (\log K_{et})^2 / \{4 \log(k_{11}k_{22}/Z^2)\}] / 2 \quad (5)$$

where Z is the collision frequency, taken as $1 \times 10^{11} M^{-1} s^{-1}$.¹ Since $\log K_{et} = -F(E^{\circ}_{ox} - E^{\circ}_{red}) / 2.3RT$, eq 5 can be expressed

**Figure 3.** Dependence of $\log k_{et}$ on E°_{ox} of the reductants (1, C_{60}^{2-} ; 2, $Me_4Q^{\bullet-}$; 3, $Me_2Q^{\bullet-}$; 4, $MeQ^{\bullet-}$; 5, $Q^{\bullet-}$; 6, $C_{60}^{\bullet-}$) for electron transfer from the reductants to different electron acceptors in deaerated PhCN at 298 K.

as a function of E°_{ox} by eq 6, where a and b are given by eqs 7 and 8, respectively.

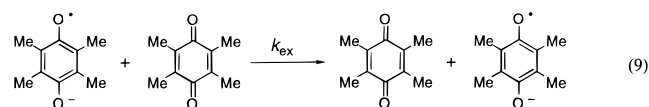
$$\log k_{et} = a + bE^{\circ}_{ox} \quad (6)$$

$$a = [\log(k_{11}k_{22}) + FE^{\circ}_{red} / (2.3RT) + (F/2.3RT)^2 (E^{\circ}_{red})^2 / \{4 \log(k_{11}k_{22}/Z^2)\}] / 2 \quad (7)$$

$$b = (-F/2.3RT) [1 + (F/2.3RT)(2E^{\circ}_{red} - E^{\circ}_{ox}) / \{4 \log(k_{11}k_{22}/Z^2)\}] / 2 \quad (8)$$

For each plot in Figure 3, k_{22} (allyl halides and $Mn(DPP)Cl$) and E°_{red} are constant. There will then be a linear correlation between $\log k_{et}$ and E°_{ox} within a limited variation in E°_{ox} , provided that k_{11} is constant. Thus, the linear correlations observed in Figure 3 indicate clearly that the self-exchange rate constants k_{11} are essentially the same among C_{60}^{2-} , $C_{60}^{\bullet-}$, and the semiquinone radical anions.

Reorganization Energies for Electron Exchange between *p*-Benzoquinones and the Semiquinone Radical Anions. To determine the self-exchange rate constant between $Me_4Q^{\bullet-}$ and Me_4Q (eq 9), the ESR spectra of $Me_4Q^{\bullet-}$ were measured in the



presence of various concentrations of Me_4Q in benzonitrile. The ESR spectrum of $Me_4Q^{\bullet-}$ consists of 13 lines having the binomial intensity distribution appropriate for 12 equivalent protons interacting with a single unpaired electron, $a(12H) = 1.9$ G. The maximum slope line width (ΔH_{msl}) of each line increases linearly with an increase in the concentration of Me_4Q

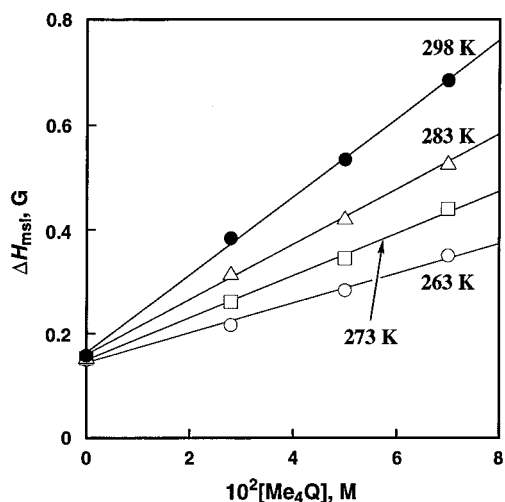


Figure 4. ΔH_{msl} vs $[\text{Me}_4\text{Q}]$ for the ESR spectra of $\text{Me}_4\text{Q}^{\bullet-}$ in deaerated PhCN at 298 (●), 283 (△), 273 (□), and 263 (○) K.

Table 2. Rate Constants (k_{ex}) and the Reorganization Energies (λ) for Electron Exchange between $\text{Me}_4\text{Q}^{\bullet-}$ and Me_4Q in Deaerated PhCN

T (K)	$10^{-8}k_{\text{ex}}$ ($\text{M}^{-1} \text{s}^{-1}$)	λ (kcal mol ⁻¹)	T (K)	$10^{-8}k_{\text{ex}}$ ($\text{M}^{-1} \text{s}^{-1}$)	λ (kcal mol ⁻¹)
263	0.48	16.0	283	0.84	15.9
273	0.70	15.8	298	1.24	15.9

Table 3. Rate Constants (k_{ex}) and the Reorganization Energies (λ) for Electron Exchange between $\text{Q}^{\bullet-}$ and Q in Deaerated PhCN

T (K)	$10^{-8}k_{\text{ex}}$ ($\text{M}^{-1} \text{s}^{-1}$)	λ (kcal mol ⁻¹)	T (K)	$10^{-8}k_{\text{ex}}$ ($\text{M}^{-1} \text{s}^{-1}$)	λ (kcal mol ⁻¹)
263	0.44	16.1	323	1.26	17.1
298	0.81	16.9	353	1.94	17.5

as shown in Figure 4. The rate constants (k_{ex}) of the electron exchange reactions between $\text{Me}_4\text{Q}^{\bullet-}$ and Me_4Q (eq 9) were determined using eq 10, where ΔH_{msl} and $\Delta H_{\text{msl}}^{\circ}$ are the

$$k_{\text{ex}} = (1.52 \times 10^7)(\Delta H_{\text{msl}} - \Delta H_{\text{msl}}^{\circ}) / \{(1 - P_i)[\text{Me}_4\text{Q}]\} \quad (10)$$

maximum slope line widths of the ESR spectra in the presence and absence of Me_4Q , respectively, and P_i is a statistical factor.⁴ The k_{ex} values for the electron exchange between $\text{Q}^{\bullet-}$ and Q were also determined in a similar manner, and the k_{ex} values of $\text{Me}_4\text{Q}^{\bullet-}$ and $\text{Q}^{\bullet-}$ are listed in Tables 2 and 3, respectively. The reorganization energies (λ) of the electron-transfer reactions are obtained from the k_{ex} values using eq 11 ($Z = 10^{11} \text{M}^{-1} \text{s}^{-1}$),¹ and these λ values are also listed in Tables 2 and 3.

$$k_{\text{ex}} = Z \exp(-\lambda/4RT) \quad (11)$$

No significant difference in the k_{ex} or λ values is observed depending on the presence of methyl substituents on the quinone. The λ value of the $\text{Q}^{\bullet-}/\text{Q}$ system in benzonitrile at 298 K (16.9 kcal mol⁻¹) determined in this study is larger than the value reported in DMF (13.1 kcal mol⁻¹)⁴⁰ but smaller than the value in DMF/H₂O (9:1; 17.7 kcal mol⁻¹).⁴⁰ Since the larger λ value in DMF/H₂O is ascribed to the larger solvation of $\text{Q}^{\bullet-}$ in the presence of H₂O,⁴⁰ the solvation of $\text{Q}^{\bullet-}$ in benzonitrile may be slightly smaller than that in DMF/H₂O (9:1).

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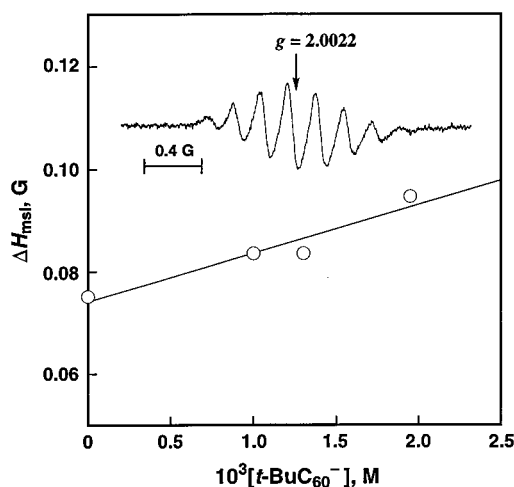


Figure 5. ΔH_{msl} vs $[\text{t-BuC}_{60}^{\bullet-}]$ for the ESR spectra of $\text{t-BuC}_{60}^{\bullet-}$. Inset: ESR spectrum of $\text{t-BuC}_{60}^{\bullet-}$ produced by UV irradiation of C_{60} and t-BuI in deaerated benzonitrile/benzene (1:7 v/v) at 298 K.

Radical anions may exist in solution as free ions, ion pairs, or a mixture of both depending on the nature of the solvent and the counterions.⁴¹ The k_{ex} values for free radical ions of aromatic hydrocarbons such as naphthalene and anthracene are on the order of $10^9 \text{M}^{-1} \text{s}^{-1}$,⁴² but those for tight ion pairs range between 5×10^6 and $1 \times 10^7 \text{M}^{-1} \text{s}^{-1}$.⁴³ Since the k_{ex} values in Tables 2 and 3 are on the order of $10^8 \text{M}^{-1} \text{s}^{-1}$, the NMe_4^+ counterion used in this study may not form an ion pair with the semiquinone radical anions in benzonitrile.

Arrhenius plots of $\log k_{\text{ex}}$ vs $1/T$ give the activation enthalpy (ΔH^\ddagger) and activation entropy (ΔS^\ddagger). The ΔH^\ddagger values for $\text{Me}_4\text{Q}^{\bullet-}$ and $\text{Q}^{\bullet-}$ were determined as 4.1 and 3.0 kcal mol⁻¹, respectively. These values are about the same as the $\lambda/4$ values in Tables 2 and 3. The ΔS^\ddagger values for $\text{Me}_4\text{Q}^{\bullet-}$ and $\text{Q}^{\bullet-}$ were determined as 0.6 and $-3.9 \text{ cal K}^{-1} \text{ mol}^{-1}$, respectively. Such small ΔS^\ddagger values, which are close to zero, are consistent with adiabatic outer-sphere electron-transfer reactions.¹

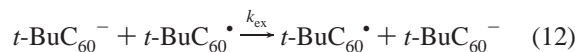
The reorganization energy for the one-electron reduction of Q was evaluated theoretically by using semiempirical PM3 MO calculations. The difference between the ΔH_f (heat of formation) of $\text{Q}^{\bullet-}$ with the same structure as Q and ΔH_f with the optimized structure of $\text{Q}^{\bullet-}$ can be regarded as the reorganization energy of the inner coordination spheres (λ_i) associated with the structural change upon the electron-transfer reduction of Q in the gas phase. The λ_i value thus obtained is 4.9 kcal mol⁻¹. The corresponding λ_i value for the one-electron reduction of C_{60} is calculated as 0.001 kcal mol⁻¹, but this value may not be valid because of the large spin contamination of $\text{C}_{60}^{\bullet-}$. Then, the difference between ΔH_f of C_{60}^{2-} with the same structure as C_{60} and ΔH_f with the optimized structure of C_{60}^{2-} is calculated as 4.3 kcal mol⁻¹, which corresponds to the λ_i value of the two-electron reduction of C_{60} . The λ_i value for the one-electron reduction of C_{60} may be smaller than the value for the two-electron reduction. Thus, the small λ_i values as compared with the observed λ values which include the solvent reorganization energy indicate that solvent reorganization plays a major role in determining the intrinsic barrier of the electron-transfer reduction of Q and C_{60} .

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Electron Exchange between $t\text{-BuC}_{60}^-$ and $t\text{-BuC}_{60}^\bullet$. An ESR spectrum of the *tert*-butyl- C_{60} radical adduct, $t\text{-BuC}_{60}^\bullet$, was obtained by a photochemical method^{6–8} involving UV irradiation of a saturated benzonitrile/benzene (1:7 v/v) solution containing C_{60} and $t\text{-BuI}$. The spectrum consists of 10 lines having the binomial intensity distribution appropriate for nine equivalent protons interacting with a single unpaired electron, $a(9\text{H}) = 0.17$ G as shown in the inset of Figure 5. When $t\text{-BuC}_{60}^-$, prepared by the reaction of C_{60}^{2-} with $t\text{-BuI}$,³³ was added to a benzonitrile/benzene (1:7 v/v) solution of C_{60} and $t\text{-BuI}$, the UV irradiation gave the same ESR signal as the signal without $t\text{-BuC}_{60}^-$, but the maximum slope line width (ΔH_{msl}) of each line increased linearly with an increase in the concentration of $t\text{-BuC}_{60}^-$ as shown in Figure 5. The rate constant (k_{ex}) of the electron exchange reaction between $t\text{-BuC}_{60}^-$ and $t\text{-BuC}_{60}^\bullet$ (eq 12) was determined as $1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 298 K using



eq 10. The corresponding λ value is $14.8 \text{ kcal mol}^{-1}$. It is interesting to note that this value is close to the value of $13.8 \text{ kcal mol}^{-1}$ for the one-electron oxidation of C_{60} by arene radical cations.¹⁵

Summary and Conclusions

Rates of electron transfer from C_{60}^{2-} or $\text{C}_{60}^{\bullet-}$ to allyl halides and $\text{Mn}(\text{DPP})\text{Cl}$ are compared with rates of electron transfer from semiquinone radical anions to the same allyl halides and $\text{Mn}(\text{DPP})\text{Cl}$, revealing that reorganization energies for the electron exchange of $\text{C}_{60}^{\bullet-}/\text{C}_{60}^{2-}$ and $\text{C}_{60}/\text{C}_{60}^{\bullet-}$ are essentially the same as those of $\text{Q}/\text{Q}^{\bullet-}$ and $\text{Me}_4\text{Q}/\text{Me}_4\text{Q}^{\bullet-}$, which were directly determined as $16\text{--}17 \text{ kcal mol}^{-1}$ by analyzing line width variations of the ESR spectra. The rate constant of self-exchange between $t\text{-BuC}_{60}^\bullet$ and $t\text{-BuC}_{60}^-$ was also determined as $1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 298 K, and this value is comparable with the self-exchange rate constants involving $\text{Q}/\text{Q}^{\bullet-}$ and $\text{Me}_4\text{Q}/\text{Me}_4\text{Q}^{\bullet-}$. Thus, the efficiency of electron transfer for the redox pairs of $\text{C}_{60}^{\bullet-}/\text{C}_{60}^{2-}$, $\text{C}_{60}/\text{C}_{60}^{\bullet-}$, and $t\text{-BuC}_{60}^\bullet/t\text{-BuC}_{60}^-$ has been clarified quantitatively for the first time in this study.

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