Driving Force Dependence of Intermolecular Electron-Transfer Reactions of Fullerenes

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Abstract: Pulse-radiolytic studies were performed to determine the rate constants of *inter*molecular electron transfer (k_{et}) from fullerenes (C_{60}, C_{76}, and C_{78}) to a series of arene radical cations in dichloromethane. The one-electron oxidation potentials of the employed arenes—corresponding to the one-electron reduction potentials of arene π-radical cations—were determined in dichloromethane to evaluate the driving forces of electron-transfer oxidation of fullerenes with arene π-radical cations. The driving force dependence of log k_{et} shows a pronounced decrease towards the highly exothermic region, representing the first definitive confirmation of the existence of the Marcus *inverted* region in a truly *inter*molecular electron transfer. Electron-transfer reduction of fullerenes with anthracene radical anion was also examined by laser flash photolysis in benzonitrile. The anthracene radical anion was produced by photoinduced electron transfer from 10,10′-dimethyl-9,9′,10,10′-tetrahydro-9,9′-biacridine [$(AcrH)_2$] to the singlet excited state of anthracene in benzonitrile. The rate constants of electron transfer (k_{et}) from anthracene radical anion to C_{60}, C_{70}, and a C_{60} derivative were determined from the decay of anthracene radical anion in the presence of various concentrations of the fullerene. Importantly, a significant decrease in the k_{et} value was observed at large driving forces (1.50 eV) as compared to the diffusion-limited value seen at smaller driving forces (0.96 eV). In conclusion, our study presents clear evidence for the Marcus *inverted* region in both the electron-transfer reduction and oxidation of fullerenes.

Keywords: electron transfer · fullerenes · Marcus inverted region · photochemistry · time-resolved spectroscopy

Introduction

The most important prediction of the Marcus theory of electron transfer (ET) is that the ET rate is expected to decrease as the ET driving force ($-\Delta G^0_{et} < \lambda$) increases in the strongly exergonic region.[1] The reorganization energy (λ) is the energy required to structurally reorganize the donors, acceptors, and their solvation spheres upon ET. The strongly exergonic regime is generally referred to as the Marcus inverted region, which has now been well-established in a number of donor–acceptor systems, in which covalent linkages ensure fixed distances.[2–6] However, for second-order *inter*molecular ET processes of electron donors and acceptors at diffusional encounters, definitive evidence for the inverted region is almost nonexistent,[6] although the inverted effect has been well-established for the first-order back-electron-transfer process in the radical ion pair produced by intermolecular ET reactions.[7] Normally, these *inter*molecular ET reactions follow the Rehm–Weller behavior, such that the ET rate increases with an increase in driving force, reaches a diffusion-limit, and remains unchanged no matter how exergonic ET might become.[8, 9] Gopidas and co-workers have recently reported the driving force dependence of electron transfer in a series of hydrogen-bonded donor–acceptor systems. When the donor–acceptor ensemble is assembled through hydrogen-bonding interactions diffusion is prevented and *intra*molecular ET in the Marcus behavior is observed.[10] In contrast, when diffusion is allowed in *inter*molecular ET, the Rehm–Weller behavior is observed.[10] Thus, the failure to observe the Marcus inverted region in *inter*molecular ET is attributed to diffusion processes, which, in turn, prevent the observation of the inverted region. As is well known, this is the main reason why some twenty-five

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years elapsed before the Marcus inverted region was confirmed for ET reactions in which the diffusion processes were avoided.

As far as second-order *inter*molecular ET reactions involving diffusion processes are concerned, however, there have so far been only a few reports on observations of the inverted region.[11] However, the claim was questioned later.[12] The Marcus inverted region should be discerned for those ET reactions with small λ and large driving force. These criteria are unequivocally given for *inter*molecular ET reactions involving fullerenes, which have small reorganization energies due to their highly delocalized π-electron systems.[13, 14] In fact, pulse-radiolytic studies, focusing on *inter*molecular charge-shift dynamics between fullerenes and a series of radiolytically generated arene π-radical cations, revealed a tendency of an decrease in the ET rate as the difference in the respective arene and fullerene ionization potentials increases.[15] This seems to be the most promising scenario for observing the Marcus inverted region for *inter*molecular ET reactions. However, definitive evidence for the inverted region has yet to be reported from the $-\Delta G^0_{et}$ values, determined experimentally from the redox potentials in solution, instead of from the values extrapolated from the difference in their ionization potentials. This is now reported herein, and the λ values of ET reactions between fullerenes and arene π-radical cations are determined based on the parabolic dependence of the ET rates on $-\Delta G^0_{et}$.

The one-electron oxidation potentials of arenes, which correspond to the one-electron reduction potentials of arene π-radical cations in dichloromethane were determined by using the second harmonic ac voltammetry. These values together with the known values of fullerenes (C_{76} and C_{78}) employed in this study provide the firm experimental values of the driving force of electron transfer between fullerenes and arene π-radical cations. The driving-force dependence of electron transfer between fullerenes and anthracene radical anion is also reported, exhibiting the Marcus inverted region for *inter*molecular ET reactions.

Results and Discussion

One-electron oxidation potentials of arenes: Slow scan cyclic voltammograms of arenes exhibit an anodic wave with a current maximum, but, most importantly, the complementary cathodic peak, as expected for a reversible redox couple, was not seen due to the instability of the generated radical cations. When the scan rate is increased above 100 V s^{-1} by using a microelectrode (see Experimental Section), a reversible redox couple is observed as shown in Figure 1a, in which a fast scan voltammogram of 9,10-dibromoanthrane in CH_2Cl_2 is given as an example. The second-harmonic alternating current voltammograms (SHACV) of various arenes were also measured in CH_2Cl_2 at 298 K. The SHACV method provides a superior approach to directly establishing the one-electron redox potentials in the presence of a follow-up chemical reaction, relative to the better-known dc and fundamental harmonic ac methods (see Experimental Section). A typical example of the signals of arenes are shown in Figure 1b.

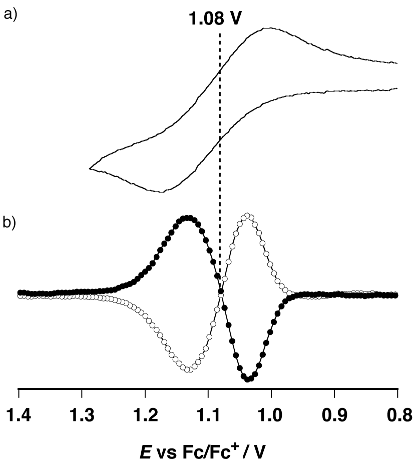

Figure 1. a) Cyclic voltammogram of 9,10-dibromoanthracene (1.0×10^{-2} M) in deaerated CH_2Cl_2 containing nBu$_4$NClO$_4$ (0.10 M) with a gold microelectrode (i.d. 100 μm) at 298 K; sweep rate 100 V s^{-1}; b) Second harmonic ac voltammogram of 9,10-dibromoanthracene (5.0×10^{-3} M) in deaerated CH_2Cl_2 containing nBu$_4$NClO$_4$ (0.10 M) with a gold electrode at 298 K; sweep rate 4.0 mV s^{-1}.

Importantly, symmetrical traces at phase angles differing by 90° are obtained around the intersection with the dc potential axis. The one-electron oxidation potential E^0_{ox} (vs Ag/0.01 M AgNO$_3$) are readily given as the intersection value, which agrees with the value obtained by the fast scan cyclic voltammogram. The E^0_{ox} values were converted to those in reference to the ferrocene/ferrocenium couple (Fc/Fc$^+$) by using ferrocene as an internal standard. The E^0_{ox} values of arenes studied in the present work were determined by the SHACV method and they are listed in Table 1, together with their ionization potentials (IP).

A linear correlation is obtained between E^0_{ox} of arenes in CH_2Cl_2 and IP with a correlation coefficient (ρ) of 0.914 [Eq. (1)], as shown in Figure 2:

$$E^0_{ox}\ (\text{arenes in } CH_2Cl_2) = -2.03 + 0.46\,\text{IP} \qquad \rho = 0.914 \qquad (1)$$

The significantly smaller slope (0.46) than unity may result from the decrease in the solvation energies of the radical cations with decreasing IP as the electron becomes more delocalized. Thus, even the relative IP values cannot be used as the measure of the electron donor ability of arenes in solution. Now that the E^0_{ox} values of arenes in CH_2Cl_2 have been determined, the driving force of electron transfer from fullerenes (C_{60}, C_{76}, and C_{78}) to arene radical cations ($-\Delta G^0_{et}$) can be obtained from the known E^0_{ox} values of fullerenes in CH_2Cl_2,[16, 17] by using [Eq. (2)]:

$$-\Delta G^0_{et} = e[E^0_{ox}(\text{arenes}) - E^0_{ox}(\text{fullerenes})] \qquad (2)$$

in which e is the elementary charge and E^0_{ox} of arenes correspond to the one-electron reduction potential (E^0_{red}) of arene radical cations.

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Table 1. Ionization potentials (IP), one-electron oxidation potentials (E^0_{ox}) and rate constants (k_{et}) for electron transfer from C_{76} (D_2), C_{78} (D_3) and C_{60} to various arene$^{\bullet+}$ in CH_2Cl_2 at 298 K.

Entry	Compound	IP [eV]	E^0_{ox} [V][a]	k_{et} [$M^{-1}s^{-1}$] C_{76}	 C_{78}	 C_{60}
1	*p*-xylene	8.80	1.47	7.1×10^9		
2	mesitylene	8.87	1.47	3.4×10^9	2.3×10^9	
3	1,2,4-trimethylbenzene	8.69	1.49	7.9×10^9	8.6×10^9	
4	durene	8.20	1.35	6.6×10^9	6.9×10^9	
5	naphthalene	8.15	1.26	8.9×10^9	9.3×10^9	2.5×10^9[b]
6	*m*-terphenyl	8.01	1.39	1.1×10^{10}	1.5×10^{10}	3.8×10^9[b]
7	biphenyl	7.89	1.33	2.0×10^{10}	2.5×10^{10}	7.9×10^9[b]
8	hexamethylbenzene	7.90	1.20	2.1×10^{10}	2.5×10^{10}	
9	triphenylene	7.86	1.26	2.9×10^{10}	2.3×10^{10}	
10	phenanthrene	7.85	1.22	3.0×10^{10}	2.5×10^{10}	
11	fluorene	7.78	1.13	3.2×10^{10}	2.9×10^{10}	
12	9-anthraldehyde	7.69	1.18	2.9×10^{10}	3.0×10^{10}	
13	chrysene	7.59	1.13	4.5×10^{10}	4.2×10^{10}	
14	9,10-dibromoanthracene	7.58	1.09	2.8×10^{10}	2.7×10^{10}	
15	anthracene	7.45	0.94	1.5×10^{10}	1.7×10^{10}	
16	pyrene	7.41	0.85	1.0×10^{10}	1.1×10^{10}	
17	coronene	7.29	0.82	3.6×10^9		
18	9-anthracenemethanol	7.21	0.75	7.8×10^8	2.0×10^9	

[a] Versus Fc/Fc$^+$. [b] Taken from reference [19].

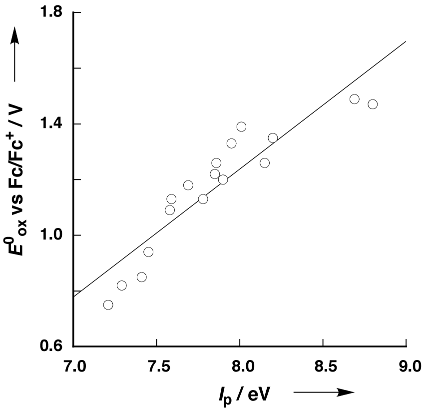


Figure 2. Plot of one-electron oxidation potentials of arenes in CH_2Cl_2 (E^0_{ox} vs Fc/Fc$^+$) versus the corresponding ionization potentials.

Electron-transfer oxidation of fullerenes: Pulse radiolysis of chlorinated hydrocarbons such as CH_2Cl_2, in the presence of arenes and fullerenes, was performed to study electron-transfer oxidation of fullerenes with arene radical cations, which can be generated by the oxidation of arenes with $CH_2Cl_2^{\bullet+}$. The primary ionization of CH_2Cl_2 results in formation of solvated electrons and $CH_2Cl_2^{\bullet+}$ [Eq. (3)].[18] The solvated electrons are scavenged efficiently by CH_2Cl_2 and, therefore, do not interfere with the oxidation process. In contrast, $CH_2Cl_2^{\bullet+}$ is reduced by the arene, present in 10^{-2} M concentrations, to produce accordingly the arene radical cation [Eq. (4)].[18] The addition of C_{60} in variable concentrations to the arene/CH_2Cl_2 system results in an electron transfer from C_{60} to the arene radical cation to produce $C_{60}^{\bullet+}$ [Eq. (5)].[19] This species is readily detected by its diagnostic near IR band at 980 nm.[20–22]

$$CH_2Cl_2 \rightarrow CH_2Cl_2^{\bullet+} + e_s^- \tag{3}$$

$$\text{arene} + CH_2Cl_2^{\bullet+} \rightarrow \text{arene}^{\bullet+} + CH_2Cl_2 \tag{4}$$

$$\text{fullerene} + \text{arene}^{\bullet+} \xrightarrow{k_{et}} \text{fullerene}^{\bullet+} + \text{arene} \tag{5}$$

The arene radical cation decays obeying first-order kinetics, and the first-order decay rate constant increases with increasing C_{60} concentration. The rate constants of electron transfer (k_{et}) from C_{60} to radical cations of naphthalene, *m*-terphenyl, and biphenyl were determined from the slope of the linear plots of the first-order decay rate constants versus C_{60} concentration, as 2.5×10^9, 3.8×10^9, and $7.9 \times 10^9 M^{-1}s^{-1}$, respectively.[19] The driving forces of these electron-transfer reactions ($-\Delta G^0_{et}$) are obtained from Equation (2) and are 0.02, -0.13, and -0.07 eV, respectively. Thus, the electron-transfer oxidation of fullerene with these arene radical cations is slightly endergonic or exergonic.

The substantially lower one-electron oxidation potentials of D_2-C_{76} ($E^0_{ox} = 0.84$ V vs Fc/Fc$^+$)[16] and D_3-C_{78} ($E^0_{ox} = 0.74$ V vs Fc/Fc$^+$)[16] relative to that of C_{60} ($E^0_{ox} = 1.32$ V vs Fc/Fc$^+$)[17] enable us to study highly exergonic electron-transfer oxidation of fullerenes. As in the case of C_{60}, the addition of C_{76} or C_{78} to the arene/CH_2Cl_2 system results in electron transfer from arene radical cation to C_{76} or C_{78} to produce the fullerene radical cations, $C_{76}^{\bullet+}$ and $C_{78}^{\bullet+}$ [Eq. (5)]. Differential absorption spectra recorded upon pulse radiolysis for the C_{76}-containing solutions exhibit the formation of a transient with a distinct maximum at 960 nm, accompanied by additional absorptions at 550 and 770 nm and shoulder at 1050 nm as shown in Figure 3a. These absorption bands agree with those reported for the isolated radical cation hexabromocarborane salt $[C_{76}]^{\bullet+}[CB_{11}H_6Br_6]^-$.[23] Similar near IR bands are observed for the electron-transfer oxidation of C_{78} with arene radical cations, showing a distinct band around 980 nm, although the overall intensity is weaker than that of $C_{76}^{\bullet+}$. In each case, the decay of the arene radical cation, monitored at the absorption bands of arene radical cations in the visible region (330–480 nm depending on the type of arene radical cations), obeys first-order kinetics, and the first-order decay rate constant increases linearly with increasing fullerene concentration. Importantly, we were able to confirm that the decay of the arene radical cation is an excellent match to the growth of the fullerene radical cation absorption as shown in Figure 3b. Thus, the *inter*molecular electron transfer rate constant (k_{et}) was obtained from the slope of linear plot of the first-order decay rate constant versus fullerene concentration. The results are summarized in Table 1.

The driving-force dependence of k_{et} for electron-transfer oxidation of C_{60}, C_{76}, and C_{78} with a series of arene radical cations is shown in Figure 4, which reveals a striking parabolic dependence including the Marcus *inverted* region, that is, a decrease of the rate constants with increasing the driving force. The log k_{et} value increases with increasing the driving force to reach a diffusion-limited value and then decreases

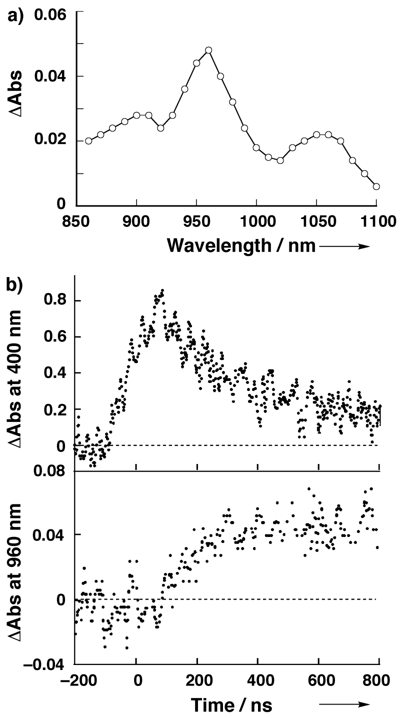


Figure 3. a) Transient absorption spectrum for $C_{76}^{\bullet +}$ observed upon *inter*molecular electron transfer from C_{76} (7.0×10^{-5} M) to chrysene radical cation formed in the radiolysis of chrysene (1.0×10^{-2} M) in CH_2Cl_2; b) Decay of crysene radical cation, accompanied by appearance of $C_{76}^{\bullet +}$.

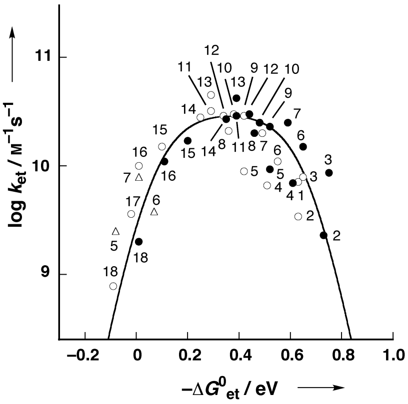


Figure 4. Plot of log k_{et} versus $-\Delta G^0_{et}$ for electron transfer from C_{60} (△), C_{76} (○), and C_{78} (●) to arene radical cations in CH_2Cl_2. The solid line is drawn based on the Marcus theory of electron transfer [Eq. (6)].

with further increase in the driving force. The k_{et} value (2.3×10^9 M^{-1}s^{-1}) for a highly exergonic electron transfer from C_{78} to mesitylene radical cation ($-\Delta G^0_{et} = 0.73$ eV) is about 20 times smaller than the value (4.5×10^{10} M^{-1}s^{-1}) for a much less exergonic electron transfer from C_{76} to, for example, chrysene radical cation ($-\Delta G^0_{et} = 0.32$ eV). Such a pronounced decrease towards the highly exothermic region represents the first definitive confirmation of the existence of the Marcus *inverted* region in a truly bimolecular electron transfer.

The plateau in Figure 4 corresponds to the diffusion-limited region in which the rate of electron transfer is faster than the rate of diffusion. According to the Marcus theory of electron transfer, the observed rate constant of an *inter*molecular electron transfer is given as Equation (6):

$$\frac{1}{k_{et}} = \frac{1}{k_{diff}} + \frac{1}{Z\exp[-(\lambda/4)(1 + \Delta G^0_{et}/\lambda)^2/k_B T]} \tag{6}$$

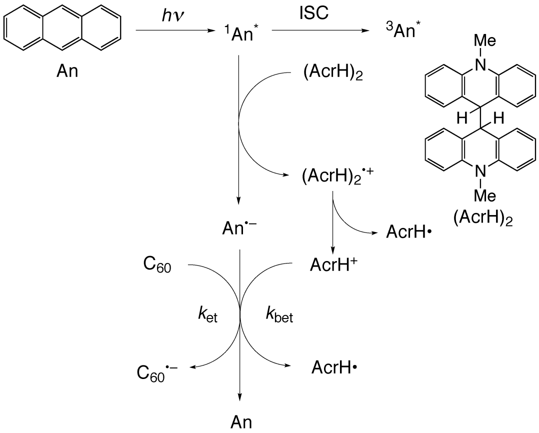
in which k_{diff} is the diffusion rate constant, Z is the collision frequency, which is taken as 1×10^{11} M^{-1}s^{-1}, λ is the reorganization energy of electron transfer, and k_B is the Boltzmann constant.[1] By fitting the data in Figure 4 with the Marcus equation for bimolecular ET reactions [Eq. (6)], an experimental value of 0.36 eV is deduced for the reorganization energy for electron-transfer oxidation of fullerenes (C_{60}, C_{76}, and C_{78}) in CH_2Cl_2.[24] The virtually same λ value is obtained from the k_{et} value at $\Delta G^0_{et} = 0$. Judging from the experimental error in determining k_{et} value (at most ±50%), the experimental error in λ is estimated as ±0.04 eV. The λ value (0.36 ± 0.04 eV) thus determined in this study is comparable to the λ value for electron self-exchange between 9-phenyl-10-methylacridinyl radical and the corresponding cation in CH_2Cl_2 (0.28 eV), which is the smallest value for bimolecular electron-transfer reactions ever reported.[9f, 25]

The reason why we obtained such a small λ value is twofold (vide infra). Firstly, the electron-transfer reactions that we have examined are those of a charge-shift type in CH_2Cl_2. CH_2Cl_2 is, however, less polar than typical polar solvents such as benzonitrile and acetonitrile. Electron-transfer reactions are normally performed in such polar solvents, in which the product ions of the electron transfer are subject to stabilization through strong solvation.[26] When cationic electron acceptors, such as arene radical cations, are employed together with a neutral electron donor (i.e., fullerene), the solvation before and after the electron transfer may be largely canceled out. Especially, when the free-energy change of electron transfer is expected to be independent of the solvent polarity. In addition, the solvent reorganization energy for the charge-shift-type electron-transfer reaction is known to decrease with decreasing solvent polarity.[9f, 27] Thus, the solvent reorganization energy for charge-shift-type electron transfer in a less polar solvent should be much smaller than that for charge-separation-type electron transfer in a more polar solvent.[9f] Secondly, the choice of the fullerenes as electron donors is important. The cationic charge of the radical cations is highly delocalized in the large, three-dimensional π system. Such delocalizations of positive charges result in minimal reorganization of, for instance, bonds and solvation upon electron transfer.[28] Arene radical cations, employed as electron acceptors, may also have small reorganization energies upon electron transfer due to the delocalized charge. It is important to note that the deduced reorganization energy from the driving force dependence of k_{et} is that of the average of the reorganization energy between arene radical cations and fullerenes. Strictly speaking the reorganization energy reveals some variation, depending on the type of arene and/or fullerene. Somewhat scattered points in Figure 4 may in fact evolve from a slight variation of the reorganization energies, especially those for arenes.

Nonetheless, uniformly small reorganization energies for electron-transfer reactions from fullerenes to arene radical cations, regardless of the large variation of the redox potentials, has made it possible for the first time to observe the Marcus inverted region clearly for *inter*molecular electron-transfer reactions, which are normally masked by the diffusion process.

Electron-transfer reduction of fullerenes: Electron-transfer reduction of C_{60} with metalloporphyrin π-radical anions has previously been studied by radiolysis in a solvent mixture that contained 65 vol % 2-propanol, 25 vol % toluene and 10 vol % acetone.[19] This solvent mixture was chosen to achieve optimal solubility for both the porphyrins and C_{60}, and this solvent mixture has been demonstrated to be very suitable for the radiolytic reduction of both C_{60} and the porphyrin.[29] The rate constants for electron transfer from various metalloporphyrin π-radical anions to C_{60} are found to be diffusion-limited in the range of $2-3 \times 10^9 \, \text{M}^{-1}\text{s}^{-1}$, despite the fact that the electron transfer is highly exergonic. The largest driving force is 0.96 eV for electron transfer from $[Zn(TPP)]^{\bullet -}$ (TPP^{2-} = tetraphenylporphyrin dianion) to $C_{60.}$ However, there was no indication of slowing down of the electron transfer rate with the larger driving force. In this case, the reorganization energy of electron transfer in this polar solvent mixture is still too large to observe the Marcus inverted region at the driving force of 0.96 eV. Thus, we examined electron-transfer reduction of C_{60} with the anthracene radical anion, which is a much stronger reductant than metalloporphyrin π-radical anions (vide infra).

The anthracene radical anion is produced by a photoinduced electron transfer evolving from 10,10′-dimethyl-9,9′,10,10′-tetrahydro-9,9′-biacridine [$(AcrH)_2$] to the singlet excited state of anthracene ($^1An^*$; * denotes the excited state) in benzonitrile (PhCN) as summarized in Scheme 1. The singlet excited state of anthracene ($^1An^*$) is known to be efficiently converted to the triplet excited state by a fast intersystem crossing.[29] Upon laser excitation at 355 nm of a solution of An (1.0×10^{-4} M) in PhCN, a transient triplet–triplet (T–T) absorption spectrum is observed with λ_{max} = 430 nm. The T–T absorbance decays obeying second-order kinetics due to T–T annihilation with a diffusion-limited rate.[30] Importantly, the addition of $(AcrH)_2$ (1.0×10^{-4} M) to a solution of An in PhCN results in electron transfer from $(AcrH)_2$ to $^1An^*$ to produce $(AcrH)_2^{\bullet +}$ and $An^{\bullet -}$ (Scheme 1). Comparing the one-electron oxidation potential of $(AcrH)_2$ (E^0_{ox} vs SCE = 0.59 V)[31] with the one-electron reduction potential of $^1An^*$ (E^0_{red} vs SCE = 1.38 V) and $^3An^*$ (E^0_{red} vs SCE = -0.08 V),[32] electron transfer from $(AcrH)_2$ to $^1An^*$ is highly exergonic, whereas electron transfer from $(AcrH)_2$ to $^3An^*$ is highly endergonic. In fact, the fluorescence of An was efficiently quenched by $(AcrH)_2$ with a diffusion-limited rate constant ($3.0 \times 10^9 \, \text{M}^{-1}\text{s}^{-1}$) in PhCN (see Experimental Section). Since there is no absorption due to $(AcrH)_2$ at 355 nm, no contribution of any electron transfer from $^1(AcrH)_2^*$ to An should be present in the formation of $An^{\bullet -}$. The C–C bond of $(AcrH)_2^{\bullet +}$ is known to be cleaved rapidly to produce 10-methylacridinyl radical ($AcrH^{\bullet}$) and 10-methylacridinium ion ($AcrH^+$).[33] Finally, the formation of $AcrH^{\bullet}$ and $An^{\bullet -}$ in a photoinduced electron transfer from $(AcrH)_2$ to $^1An^*$ is confirmed by the transient absorption spectroscopy, as shown in Figure 5. The absorption bands at 360 and 470 nm are assigned to $An^{\bullet -}$, matching those of reported values.[34] The T–T absorption of $^3An^*$ is also seen at 430 nm, since only a small portion of $^1An^*$ is quenched by electron transfer from $(AcrH)_2$ under the present experimental conditions ($[(AcrH)_2] = 1.0 \times 10^{-4}$ M) in competition with the facile intersystem crossing to $^3An^*$ (Scheme 1). The absorption band at 530 nm in Figure 5 is attributed to $AcrH^{\bullet}$, which is known to have the absorption maximum at 530 nm.[9f, 35]



Scheme 1.

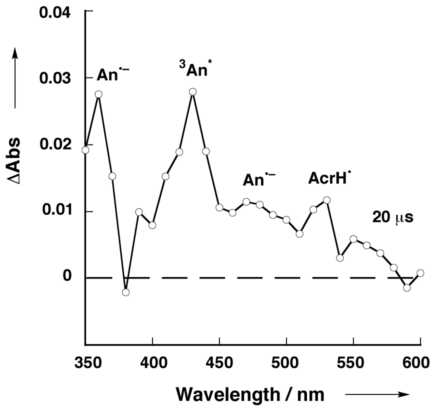


Figure 5. Transient absorption spectrum observed in photoinduced electron transfer from $(AcrH)_2$ (1.0×10^{-4} M) to anthracene (1.0×10^{-4} M) at 20 μs after laser excitation at 355 nm in deaerated PhCN at 298 K.

The absorption band at 360 nm due to $An^{\bullet -}$ decays obeying second-order kinetics (Figure 6). The second-order plot of $[An^{\bullet -}]$ obtained from the absorbance at 360 nm by using the ε value in the literature[34] gives a linear line (see inset of Figure 6). The second-order decay rate constant is determined from the slope as $3.0 \times 10^9 \, \text{M}^{-1}\text{s}^{-1}$, which is nearly the same as the diffusion-limited value in PhCN.[36, 37] Judging from the one-electron oxidation potential of $An^{\bullet -}$, which is equivalent to the one-electron reduction potential of An (E^0_{red} vs SCE = -1.93 V) and the one-electron reduction potential of $AcrH^+$ (E^0_{red} vs SCE = -0.46 V),[38] the back electron transfer from $An^{\bullet -}$ to $AcrH^+$ is highly exergonic ($-\Delta G^0_{et}$ = 1.47 eV) and the

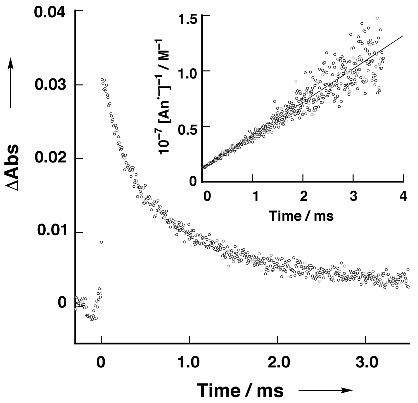


Figure 6. Kinetic trace for decay of anthracene radical anion ($\lambda = 360$ nm) in photoinduced electron transfer from anthracene radical anion to C_{60} (4.0×10^{-5} M) in deaerated PhCN at 298 K. Inset: The second-order plot of $[An^{\bullet-}]$ (see text).

*inter*molecular reaction should occur at the diffusion-limited rate (Scheme 1).[39, 40]

The addition of C_{60} (4.0×10^{-5} M) to the $(AcrH)_2$–An system, results in a significant acceleration of the $An^{\bullet-}$ decay.[41] Moreover, the decay kinetics change from a pure second-order to a pseudo-first-order process. The pseudo-first-order decay rate constant increases linearly with increasing C_{60} concentration as shown in Figure 7 (open circle). This

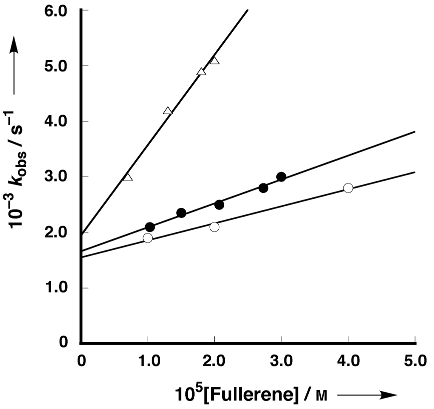


Figure 7. Plot of the pseudo-first-order rate constant (k_{et}) versus $[C_{60}]$ (○), $[C_{70}]$ (●), and $[1,4\text{-}t\mathrm{Bu}(PhCH_2)C_{60}]$ (△), for the decay of anthracene radical anion in the presence of C_{60}.

indicates that electron transfer from $An^{\bullet-}$ to C_{60}, which is present in large excess, occurs in competition with the *inter*molecular back electron transfer from $An^{\bullet-}$ to $AcrH^+$, the initial concentration of which is the same as $An^{\bullet-}$ (Scheme 1). The second-order rate constant of electron transfer (k_{et}) from $An^{\bullet-}$ to C_{60} is determined from the slope of the linear plot in Figure 7 (open circle) as $3.2 \times 10^7\,\mathrm{M^{-1}s^{-1}}$. Similarly, the k_{et} values, as listed in Table 2, were determined for electron transfer from $An^{\bullet-}$ to C_{70} (closed circle) and 1-*tert*-butyl-4-benzyl-1,4-dihydro[60]fullerene [1,4-*t*Bu-$(PhCH_2)C_{60}$] (open triangle). On the other hand, we determined the driving force of electron transfer from $An^{\bullet-}$ to the fullerenes from the E^0_{red} value of An and the fullerene in PhCN (see Table 2). Notably, the k_{et} values for the highly exergonic electron transfer are much smaller than the diffusion-limited value. It should be noted that this relationship is in a sharp contrast with the case of electron transfer from the metalloporphyrin π-radical anions to C_{60} in a polar solvent mixture (Table 2), in which the electron transfer is essentially diffusion-limited with driving forces up to −0.92 eV (vide supra).[18, 42] Virtually the same diffusion-limited values [$(2.1-3.4) \times 10^9\,\mathrm{M^{-1}s^{-1}}$] have previously been reported for bimolecular rate constants involving electron transfer from NADH analogues to the triplet excited state of C_{60} in PhCN. Here the driving forces were in the range of 0.43–0.88 eV (Table 2).[36, 43] Also a similar value ($2.5 \times 10^9\,\mathrm{M^{-1}s^{-1}}$) has been reported for electron transfer from a C_{60} radical anion to *p*-chloranil in PhCN, for which a driving force of 0.40 eV was given (Table 2).[44]

Table 2. Free-energy change ($-\Delta G^0_{et}$) and rate constants (k_{et}) for intermolecular electron-transfer reaction in PhCN.

Entry	Donor	Acceptor	$-\Delta G^0_{et}$ [eV][a]	k_{et} [$\mathrm{M^{-1}s^{-1}}$]	Ref.
1	anthracene$^{\bullet-}$	C_{60}	1.50	3.2×10^7	this study
2	anthracene$^{\bullet-}$	C_{70}	1.50	4.3×10^7	this study
3	anthracene$^{\bullet-}$	1,4-*t*Bu$(PhCH_2)C_{60}$	1.38	1.6×10^8	this study
4	$ZnTPP^{\bullet-}$	C_{60}	0.96	2.6×10^9	[b]
5	$(BNA)_2^-$	$^3C_{60}^*$	0.88	3.4×10^9	[c]
6	$(BNA)_2^-$	$^3C_{70}^*$	0.85	3.3×10^9	[d]
7	$GaTPP^{\bullet-}$	C_{60}	0.69	2.2×10^9	[b]
8	$InTPP^{\bullet-}$	C_{60}	0.61	2.6×10^9	[b]
9	BNAH	$^3C_{60}$	0.57	2.9×10^9	[c]
10	$GeTPP^{\bullet-}$	C_{60}	0.56	2.2×10^9	[b]
11	BNAH	$^3C_{70}^*$	0.54	3.0×10^9	[d]
12	*t*BuBNAH	$^3C_{60}^*$	0.43	2.1×10^9	[c]
13	*t*BuBNAH	$^3C_{70}^*$	0.40	2.3×10^9	[d]
14	$C_{60}^{\bullet-}$	*p*-chloranil	0.40	2.5×10^9	[e]
15	*t*PrBNAH	$^3C_{70}^*$	0.39	2.5×10^9	[d]
14	*t*Bu$C_{60}^{\bullet-}$	*t*Bu$C_{60}^{\bullet-}$	0.00	1.9×10^8	[f]

[a] The driving force of electron transfer is obtained for the E^0_{ox} value of the donors and the E^0_{red} value of acceptors; $-\Delta G^0_{et} = e(E^0_{ox} - E^0_{red})$. [b] Taken from reference [19]. [c] Taken from reference [36]. [d] Taken from reference [43]. [e] Taken from reference [44]. [f] Taken from reference [14].

In conclusion, the significant deviation in k_{et} values, at large driving forces (1.50 eV), from the diffusion-limited value, which was seen at much smaller driving forces (0.40 eV), is clear manifestation of the Marcus inverted region. When the driving force is further reduced to zero, that is, the electron self-exchange reaction of C_{60}, the rate constant ($1.9 \times 10^8\,\mathrm{M^{-1}s^{-1}}$) also becomes significantly smaller than the diffusion-limited value (Table 2).[14] Such driving-force dependence of the rate constants ($\log k_{et}$) for electron-transfer reactions of fullerenes in PhCN is shown in Figure 8, combined with the reported data of electron-transfer reactions from the different π-radical anions (i.e., metalloporphyrins and anthracene) to C_{60}, since the diffusion-limited value in all these solvents is nearly the same.

By fitting the data in Figure 8 with the Marcus equation for *inter*molecular ET reactions [Eq. (6)], the average λ value for electron-transfer reduction of fullerenes is determined as 0.72 eV.[45] Interestingly, this λ value agrees well with the reported λ value (0.73 eV) for electron transfer from $C_{60}^{\bullet-}$ to various electron acceptors in PhCN.[14] It is also interesting to note that the λ value for *inter*molecular electron-transfer reduction of C_{60} (Figure 8) is comparable to the λ value

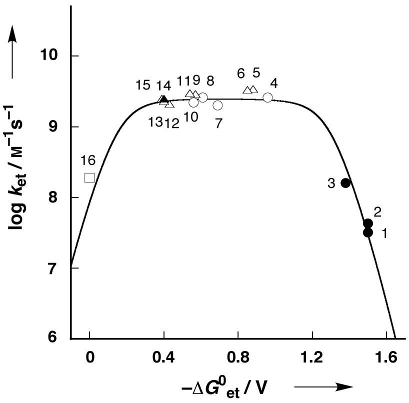


Figure 8. Plot of log k_{et} versus $-\Delta G^0_{et}$ for electron transfer from anthracene radical anion to C_{60}, C_{70}, and 1,4-tBu($PhCH_2$)C_{60} in PhCN (●), electron transfer from $C_{60}^{\bullet -}$ to p-chloranil in PhCN (▲),[37] electron transfer from NADH analogs to $^3C_{60}$* and $^3C_{70}$* in PhCN (△),[36,43] electron self-exchange between tBu$C_{60}^{\bullet}$ and tBuC_{60}^{-} in PhCN/toluene (□),[14] and electron transfer from metalloporphyrin π-radical anions to C_{60} (○) in propanol/toluene/acetone.[16] The solid line is drawn based on the Marcus theory of electron transfer [Eq. (6)].

(0.66 eV) determined previously for *intra*molecular electron transfer from the C_{60} radical anion to the zinc–porphyrin π-radical cation moiety in covalently linked zinc–porphyrin/C_{60} dyads in PhCN.[5a] The larger λ value for electron-transfer reduction of C_{60} in PhCN than the λ value for electron-transfer oxidation of fullerenes in CH_2Cl_2 (0.36 eV) may result from the larger solvent reorganization in the more polar solvent. Such a difference in the λ value based on solvent dependence may largely come from the change in the λ value of the arene part rather than the fullerene part, since the reorganization energy of the fullerne part is rather insensitive to the solvent.[4a, 46] In fact, the λ value of photoinduced electron transfer from a series of aromatic compounds to acridinium ion has been reported to vary depending on the polarity of solvent from 0.88 eV (MeCN) to 0.53 eV (benzene).[47] In any case, the small reorganization energies for electron-transfer reactions of fullerenes relative to those of other smaller π systems have made it possible to observe unequivocally the Marcus inverted region for bimolecular electron-transfer reactions.

Experimental Section

Materials: Fullerene C_{60} was purchased from Kaesdorf (Geräte für Forschung und Industrie, München, Germany), fullerenes C_{70}, C_{76}, and C_{78} were purchased from Techno Carbo (France) and Science Laboratories Co. (Japan), and used as received. Separation of the C_{78} isomers was accomplished by HPLC on a buckyclutcher column leading to an overall purity of 99% relative to the other isomers. 1-*tert*-Butyl-4-benzyl-1,4-dihydro[60]fullerene [1,4-tBu($PhCH_2$)C_{60}] was prepared from C_{60}^{2-}, generated by electrochemical reduction with tBuI in deaerated benzonitrile at room temperature.[48] The solution was stirred for 1 h to give tBuC_{60}^{-}, after $PhCH_2Br$ was added to the reaction to give a major product along with unreacted C_{60} after evaporation of PhCN under evacuation. The reaction mixture was washed with MeCN, after which the brown solid was collected by centrifuguation, purified by HPLC on a buckyclutcher column.[48] Arenes were obtained commercially and purified by the standard method. 10,10′-Dimethyl-9,9′,10,10′-tetrahydro-9,9′-biacridine (($AcrH)_2$) was prepared from the reduction 10-methylacridinium perchlorate ($AcrH^+ClO_4^-$) with $Me_3SnSnMe_3$ in acetonitrile at 333 K, and purified by recrystallization from the mixture of acetonitrile and chloroform.[49] The alkyl halides were passed over alumina in order to separate them from the free halide ions. Dichloromethane (CH_2Cl_2) and benzonitrile (PhCN) were purchased from Wako Pure Chemical Industries (Japan) and distilled over P_2O_5 prior to use.

Pulse radiolysis: The pulse radiolysis experiments were performed by utilizing either 500 ns pulses of 1.55 MeV electrons or about 100 ns pulses of 3.8 eV electrons from two different Van de Graff accelerator facilities. Details of the equipment and the analysis of data have been described elsewhere.[50] Stock solutions of fullerene ($(0.5-5.0)\times 10^{-4}$ M) and arene (1.0×10^{-2} M) were freshly prepared for each set of experiments. First the intrinsic decay of the respective arene radical cation was monitored in the absence of any fullerene; then at least four different fullerene concentrations were added to the reaction mixture, with [fullerene] ≪ [arene]. This not only ensures that primary oxidation occurs with the arene, but it also allowed us to probe the intermolecular charge-shift between the one-electron oxidized arene and the fullerene. Therefore, all samples were irradiated after purging with N_2 or N_2O for ca. 30 min, which lead solely to the solvent radical cation induced oxidation of the arenes. The dose per pulse, determined by KSCN dosimetry, corresponded to a 4–24 μM radical concentration. All experiments were carried out at ambient temperature.

Electrochemical measurements: Electrochemical measurements were performed on a BAS 100B electrochemical analyzer in deaerated CH_2Cl_2 containing 0.10 M $n$$Bu_4N^+ClO_4^-$ (TBAP) as a supporting electrolyte at 298 K. The gold working electrode was polished with a BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/$AgNO_3$ (0.01M) reference electrode. The second-harmonic alternating current voltammetry (SHACV)[51] measurements of arenes were carried out with a BAS 100 W electrochemical analyzer in deaerated CH_2Cl_2 containing 0.10 M TBAP as a supporting electrolyte at 298 K. The E^0_{red} values (vs Ag/$AgNO_3$) were converted into those vs SCE by addition of 0.29 V.[52]

Laser flash photolysis: Nanosecond transient absorption measurements were carried out with an Nd:YAG laser (Continuum, SLII-10, 4–6 ns fwhm) at 355 nm with the power of 10 mJ as an excitation source. Photoinduced events were estimated by using a continuous Xe-lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu 2949) as a probe light and detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). The transient spectra were recorded with fresh solutions in each laser excitation. All experiments were performed at 298 K.

Fluorescence quenching: Quenching experiments of the fluorescence of anthracene were carried out on a Shimadzu spectrofluorophotometer (RF-5000). The excitation wavelength of anthracene was 422 nm in PhCN. The monitoring wavelength was corresponding to the maximum of the emission band at $\lambda_{max} = 435$ nm. Typically, a PhCN solution (3.0 cm^3) was deaerated by argon purging for 8 min prior to the measurements. Relative fluorescence intensities were measured for solutions of anthracene (1.0×10^{-5} M) in PhCN and ($AcrH)_2$ used as an electron donor quencher. There was no change in the shape, but there was a change in the intensity of the fluorescence peak by the addition of a quencher. The Stern–Volmer relationship, $I_0/I = K_{SV}[D]$, was obtained for the ratio of the emission intensities (I_0 and I and the intensities in the absence and presence of a quencher, respectively) and the quencher concentration [D]. The quenching rate constant of electron transfer was obtained from the Stern–Volmer constants K_{SV} and the fluorescence lifetime τ (5.3 ns).[32]

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(charge-recombination process) may be larger than that of a charge-shift type of electron transfer such as electron transfer from $An^{\bullet -}$ to C_{60}. This may be the reason why the bimolecular electron transfer rate is still diffusion-limited.

[40] When anthracene was replaced by 9,10-dicyanoanthracene, no radical anion of 9,10-dicyanoanthracene was formed due to the facile back electron transfer from the radical anion to $(AcrH)_2^{\bullet +}$ in the radical ion pair. In this case the driving force of back electron transfer (0.43 eV) is not large enough to slow down the rate of back electron transfer in the radical ion pair, allowing the escape of the radical anion from the cage. Thus, the choice of substrates to produce free radical anions in photoinduced electron transfer from $(AcrH)_2$ is rather limited.

[41] Under the present experimental conditions (Figure 7), the concentration of $An^{\bullet -}$ produced in photoinduced electron transfer from $(AcrH)_2$ to $^1An^*$ is rather low (ca. 10^{-7} M) so that the second-order decay of $An^{\bullet -}$ with $AcrH^+$ at the diffusion-limited rate constant (Figure 6) becomes much slower than the rate of electron transfer from $An^{\bullet -}$ to C_{60} which is in large excess to $An^{\bullet -}$.

[42] For the E^0_{ox} values of metalloporphyrin π-radical anions, see: a) F. D'Souza, M. E. Zandler, P. Tagliatesta, Z. Ou, J. Shao, E. Van Caemelbecke, K. M. Kadish, *Inorg. Chem.* **1998**, *37*, 4567; b) K. M. Kadish, J.-L. Cornillon, A. Coutsolelos, R. Guilard, *Inorg. Chem.* **1987**, *26*, 4167; c) K. M. Kadish, J.-L. Cornillon, P. Cocolios, A. Tabard, R. Guilard, *Inorg. Chem.* **1985**, *24*, 3645; d) R. Guilard, J.-M. Barbe, A. Boukhris, C. Lecomte, J. E. Anderson, Q. Xu, K. M. Kadish, *J. Chem. Soc. Dalton Trans.* **1988**, 1109.

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