The C_{60}-Photosensitized Reduction of Methyl Viologen Through the Intermediary of O_2

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C_{60}-photosensitized reduction system of methyl viologen (1,1′-dimethyl-4,4′-bipyridinium) electron-mediated by O_2 in organic solvents was demonstrated. By steady-state photoirradiation of C_{60} in the presence of electron donors such as triethanolamine (2,2′,2″-nitrilotriethanol) and tetraphenylborate ($^-BPh_4$), the absorption-band of $C_{60}^{\bullet -}$ increased with irradiation time, and persisted for a long time. On introduction of O_2, followed by the irradiation, $C_{60}^{\bullet -}$ disappeared and superoxide anion ($O_2^{\bullet -}$) was generated. The photochemical reaction mechanisms were investigated by the transient-absorption method. The rate constant for electron transfer from $C_{60}^{\bullet -}$ to O_2 was estimated to be $(3.7 \pm 0.2) \times 10^2$ $mol^{-1}\ dm^3\ s^{-1}$. On addition of MV^{2+}, electron transfer from $O_2^{\bullet -}$ to MV^{2+} was observed in aprotic solvents such as benzonitrile, yielding blue methyl viologen cation radical ($MV^{\bullet +}$). By irradiation of the system of C_{60}/electron donor/O_2/MV^{2+}, $MV^{\bullet +}$ was also generated. In these systems, $MV^{\bullet +}$ accumulated and remained even in air-saturated solution for more than 1 h, because electron transfer from $O_2^{\bullet -}$ to MV^{2+} is an exothermic process in aprotic solvents.

O_2 usually interrupts the electron-sequences of the various photoredox systems. Therefore, the quantum yields for electron-transfer systems are changed significantly in the presence of O_2, and the superoxide anion ($O_2^{\bullet -}$) is generated, which possesses remarkable reactivities in chemical and biochemical systems.[1] For the photoinduced electron-transfer systems in solution, it is important to consider the redox properties of O_2 with radical-ion species generated during photoreaction.

On the other hand, the reduction systems of methyl viologen (1,1′-dimethyl-4,4′-bipyridinium; MV^{2+}) have been a subject of recent studies in photochemical and electrochemical fields, because MV^{2+} can play a vital role of electron-acceptor/carrier in chemical redox systems. These interesting properties have been investigated for the applications to photochemical cell,[2] optical memory devices and so on.[2,3] It has been believed that the reduction of MV^{2+} is hard to carry out in aerated solutions, because it was reported that methyl viologen cation radical ($MV^{\bullet +}$) is easy to be consumed by electron transfer to O_2.[4] This aspect seems to retard the applications of $MV^{\bullet +}$ to the many kinds of photo-electrochemical systems.

Recently, we have reported an efficient photoinduced electron-transfer system between the triplet state of C_{60} ($^3C_{60}^*$) and organo borates in solution, yielding a persistent anion radical of C_{60} ($C_{60}^{\bullet -}$).[5] For the construction and analysis of effective photochemical reactions, the utilization of C_{60} has some excellent advantages, because C_{60} shows high quantum yield for intersystem crossing,[6] high reduction potential,[7] long-living excited triplet state and radical anion,[5,8] and high extinction coefficients of excited triplet states[6a,8] and radical-ion species.[9] Some effective electron transfer systems have been designed by using C_{60} and C_{60}-derivatives.[10]

In the present paper, we report on a novel C_{60}-photosensitized reduction of MV^{2+} comprised of electron transfer from $O_2^{\bullet -}$ to MV^{2+}. Triethanolamine (2,2′,2″-nitrilotriethanol; TEOA) or tetraphenylborate ($^-BPh_4$) was used as an electron donor to the photoexcited C_{60}, producing $C_{60}^{\bullet -}$.[5,11] In the presence of photogenerated $O_2^{\bullet -}$, methyl viologen cation radical ($MV^{\bullet +}$) accumulates and remains for a long time even in aerated organic solvents. By observing the transient absorption spectra in the visible/near-IR region, the electron-transfer mechanism was examined.

Experimental

Materials. C_{60} was obtained from Term USA in a purity of > 99.5%. Tetrabutylammonium tetraphenylborate ($^-BPh_4$ ($^+NBu_4$)), triethanolamine (TEOA), 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), and tetrabutylammonium hexafluorophosphate were used as received. Methyl viologen hexafluorophosphate (MV^{2+} ($^-PF_6)_2$) was prepared by ion-exchange. Methyl viologen bis(butyltriphenylborate) (MV^{2+} ($^-BPh_3Bu)_2$) was prepared as described in our previous report;[12] $^-BPh_3Bu$ was used for MV^{2+}-dissolution to tetrahydrofuran (THF), which has less reactivity in the dark. Extra-pure grade benzonitrile (BN) and THF were used as solvents.

Steady-state Photolysis and Measurements. Steady-state photolysis was performed with visible light from a Xe–Hg arc lamp (150 W) equipped with a cut-off filter ($\lambda_{ex} > 410$ nm) in order to excite C_{60} selectively. In the addition experiments of MV^{2+} (described in a later section), BN or THF aerated solution of MV^{2+} (2×10^{-3} dm^3) was added to the photo-irradiated BN solution (2 ×

10^{-3} dm^3) containing C_{60} and electron donor. The steady-state UV-vis/NIR absorption spectra were measured with a JASCO V-570 spectrophotometer before and after photo-irradiation of solution. The ESR spectra were measured with a Varian E-4 EPR spectrometer after irradiation to BN solution. All experiments were carried out at 25 °C.

Laser-Flash Photolysis. Transient absorption spectra and the absorption-time profiles of transient species were measured by the selective excitation of C_{60} with 532 nm laser light. For the long timescale measurements, a steady probe light and an InGaAs-PIN photodiode module were applied. For the short time scale measurements, the apparatus details were described elsewhere.[12,13]

Electrochemical Measurements. The half-wave reduction potentials of C_{60}, MV^{2+} and O_2 were estimated by cyclic voltammetry with a scan rate of 100 mV s^{-1} in dry BN at room temperature. Platinum electrodes were employed as a working and a counter electrode. Tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}) was employed as the supporting electrolyte. A pseudo reference electrode (Ag/AgCl) was calibrated by the authentic potential of ferrocene in BN. The electrochemical measurements were carried out in the dark.

Results and Discussion

Photoinduced Reduction of C_{60} by Triethanolamine and $^-BPh_4$. TEOA and $^-BPh_4$ ($^+NBu_4$) showed absorption bands in shorter wavelength region ($\lambda_{ab} < 325$ nm) in BN. Absorption spectra of mixed solutions of C_{60} and electron donors are almost identical with the summation spectra of each compound, indicating no-interaction between C_{60} and electron donors in the ground state (spectrum a in Fig. 1).

By the steady-state photoirradiation of C_{60} in the presence of an electron donor ($^-BPh_4$ or TEOA) in deaerated BN, a new absorption band appeared with a peak at 1070 nm (spectrum b in Fig. 1), which can be attributed to $C_{60}^{\bullet -}$.[9] After irradiation, $C_{60}^{\bullet -}$ persisted for a long time (more than 5 h) in the deaerated solution, because back electron transfer was prevented by the decomposition of the electron–donor to less reactive species.

The photoreaction mechanism has been disclosed by laser flash photolysis. Photoinduced electron transfer between C_{60} and $^-BPh_4$ (or TEOA) occurs via the triplet excited state of C_{60} ($^3C_{60}^*$). The rate constants for electron transfer (k_{et}) were evaluated to be 3.1×10^7 mol^{-1} dm^3 s^{-1} ($^-BPh_4$) and 1.6×10^7 mol^{-1} dm^3 s^{-1} (TEOA). The efficiencies for electron transfer via $^3C_{60}^*$, which were evaluated from the ratio of $[C_{60}^{\bullet -}]/[^3C_{60}^*]$ at high concentration of electron donors, were reported as 0.88 ($^-BPh_4$) and 0.33 (TEOA) in deaerated BN.[5,11]

In the case of aerated systems, the transient absorption of $^3C_{60}^*$ at 740 nm also appeared (spectrum a in Fig. 2), although the absorption intensity was lower than that in the deaerated system. With the decay of $^3C_{60}^*$, new absorption bands appeared in the region of 1000–1100 nm, which can be attributed to $C_{60}^{\bullet -}$ (spectrum b in Fig. 2). As shown in the inset in Fig. 2, the decay profile of $^3C_{60}^*$ is a mirror image of the rise curve of $C_{60}^{\bullet -}$, indicating that $C_{60}^{\bullet -}$ is produced via $^3C_{60}^*$ (reaction (1) in Scheme 1). The contribution of the electron-transfer route via the excited singlet state of C_{60} ($^1C_{60}^*$) is negligibly small, because the rate constant for the intersystem crossing (k_{isc}) of $^1C_{60}^*$ is very large ($k_{isc} \approx 10^9$ s^{-1}).[6] In the O_2-containing system, the yield of $C_{60}^{\bullet -}$ was decreased, as shown in Fig. 3, because energy transfer from $^3C_{60}^*$ to O_2 occurs competitively with the reduction of C_{60} (reaction (2) in Scheme 1).

Electron Transfer from $C_{60}^{\bullet -}$ to O_2. In the steady-state measurements, the introduction of air (O_2-gas) to the solution containing $C_{60}^{\bullet -}$ led a complete disappearance of the absorption band of $C_{60}^{\bullet -}$ (spectrum c in Fig. 1), indicating that electron transfer from $C_{60}^{\bullet -}$ to O_2 takes place, yielding superoxide anion ($O_2^{\bullet -}$) by the mechanism shown in reaction (3). In spectrum c, the weak broad band of C_{60}-adduct-anions such as PhC_{60}^- appeared at 940 nm; this is generated by the fast addition reaction between $C_{60}^{\bullet -}$ and $Ph^\bullet$ within 30 µs after laser flash.[5] C_{60}-adduct-anions are less reactive toward O_2.[5]

For the estimation of the rate constant for electron transfer from $C_{60}^{\bullet -}$ to O_2, long timescale time-resolved measurements (> 0.1 s) were applied to the C_{60} / $^-BPh_4$ system in the near-IR

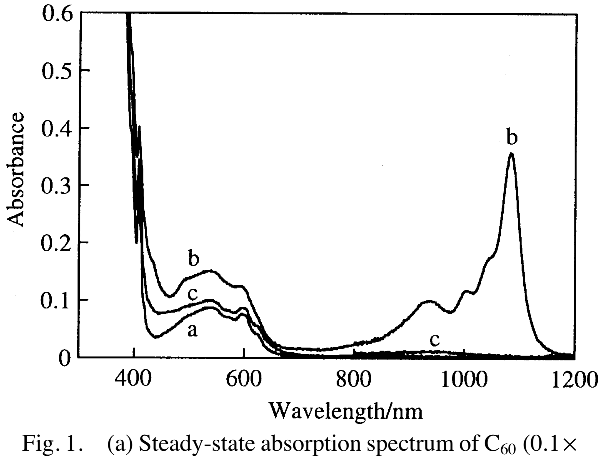


Fig. 1. (a) Steady-state absorption spectrum of C_{60} (0.1×10^{-3} mol dm^{-3}) and $^-BPh_4$ (5×10^{-3} mol dm^{-3}), (b) after 450 s photo illumination of C_{60} with the visible light ($\lambda_{ex} > 410$ nm) in deaerated BN, and (c) after introduction of air.

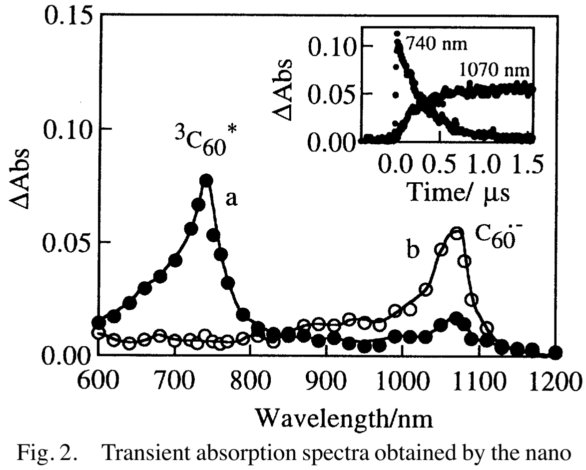
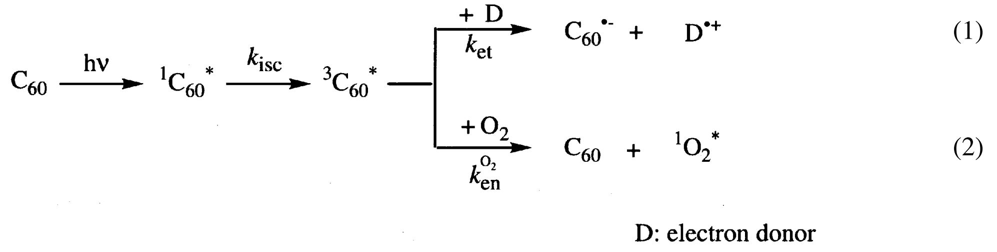


Fig. 2. Transient absorption spectra obtained by the nano second laser light (532 nm) irradiation of C_{60} (0.1×10^{-3} mol dm^{-3}) in the presence of $^-BPh_4$ (20×10^{-3} mol dm^{-3}) in aerated BN. (a) 100 ns (●), (b) 1 µs (○). Inset: absorption-time profiles in short timescale.



Scheme 1.

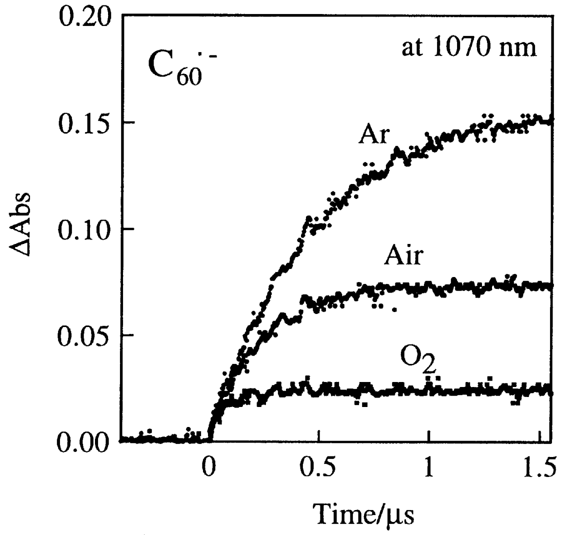


Fig. 3. Rise-time profiles of $C_{60}^{\bullet-}$ in 1.5 μs-timescale obtained by 532-nm laser flash in BN. (a) in deaerated solution, (b) in aerated solution, and (c) in O_2-saturated solution. $[C_{60}] = 0.1 \times 10^{-3}$ mol dm^{-3}, $[^{-}BPh_4] = 20 \times 10^{-3}$ mol dm^{-3}.

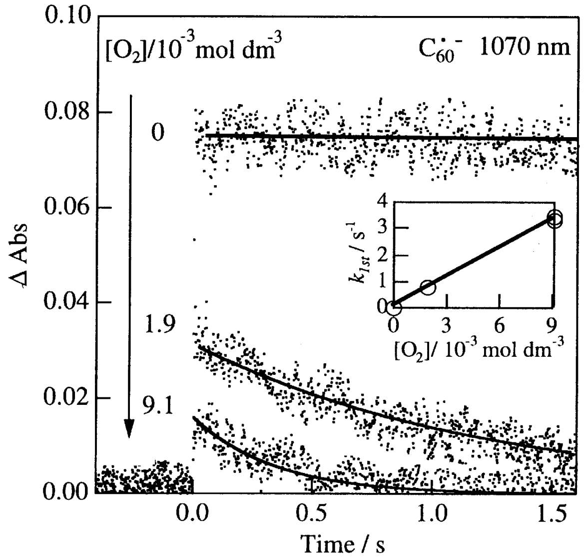


Fig. 4. Decay-time profiles of $C_{60}^{\bullet-}$ and calculated line in a sec-timescale; (a) in deaerated BN ($[O_2]$ = 0.0 mol dm^{-3}), (b) in aerated BN ($[O_2] = 1.9 \times 10^{-3}$ mol dm^{-3}), and (c) in O_2-saturated BN ($[O_2] = 9.1 \times 10^{-3}$ mol dm^{-3}). Inset: pseudo-first order plots.

region employing a steady-probe light and an InGaAs-PIN photodiode module.[14] In the deaerated solution, $C_{60}^{\bullet-}$ did not decay appreciably (profile a in Fig. 4), which reasonably supports the persistent $C_{60}^{\bullet-}$-formation by the steady-state photolysis (spectrum b in Fig. 1). In the aerated solution, on the other hand, $C_{60}^{\bullet-}$ began to decay; this can be fitted using the first-order rate constant (k_{1st}). In O_2-saturated solution, the decay rate increased, giving a larger k_{1st} value. From the pseudo-first order plots (k_{1st} values against $[O_2]$; inset of Fig. 4), the second-order rate constant for electron transfer from $C_{60}^{\bullet-}$ to O_2 ($k_{et}^{O_2}$) was evaluated to be $(3.7 \pm 0.2) \times 10^2$ mol^{-1} dm^3 s^{-1}. From the reduction potentials ($E_{red} = -0.92$ V for C_{60} and -1.2 V for O_2 vs ferrocene/ferrocenium in BN), electron transfer from $C_{60}^{\bullet-}$ to O_2 was revealed to be an endothermic process ($\Delta G_{et} > 0$), and this observation reasonably supports the small $k_{et}^{O_2}$ value.

From these findings, it was revealed that $C_{60}^{\bullet-}$ quantitatively provides an electron to O_2 in the presence of an excess O_2 with respect to $C_{60}^{\bullet-}$ within ca. 5 s in aerated solution. Because $^{-}BPh_4$ rapidly dissociates into phenyl radical (yielding mainly biphenyl) and triphenylboran immediately after electron donation,[5,12,15,16] the long timescale observation of electron transfer from $C_{60}^{\bullet-}$ to O_2 was realized. When TEOA was used as an electron donor, persistent $C_{60}^{\bullet-}$ was similarly observed by photolysis; however, in the presence of O_2, $C_{60}^{\bullet-}$ rapidly disappeared. This is probably due to the reaction with some reaction-products between O_2 and cation radical of TEOA.

Electron Transfer from $O_2^{\bullet-}$ to MV^{2+}. After irradiation of C_{60}/electron–donor/O_2, the pale purple solution turned colorless. The addition of MV^{2+} changed this solution to blue. The solution after mixing $O_2^{\bullet-}$ and MV^{2+} showed a new absorption band at 605 nm and a shoulder at 400 nm, which can be attributed to methyl viologen cation radical ($MV^{+\bullet}$; spectrum b in Fig. 5).[17] In this system, $MV^{\bullet+}$ lived for longer than 1 h. From this spectral-change, it was deduced that electron transfer from $O_2^{\bullet-}$ to MV^{2+} occurs in BN as shown in reaction (4).

The efficiency for electron transfer from $O_2^{\bullet-}$ to MV^{2+} ($\Phi_{et}^{O_2\text{-}MV}$) can be calculated from the corresponding initial concentration of $C_{60}^{\bullet-}$ and the maximum concentration of $MV^{\bullet+}$ (spectrum b in Fig. 5); the values of $\Phi_{et}^{O_2\text{-}MV}$ were estimated to be 0.14 (in BN) and 0.24 (in BN/THF 1 : 1 mixed solution), indicating that less polar solvents are favorable for large $\Phi_{et}^{O_2\text{-}MV}$ values. Solvents may affect both the rate constants for electron

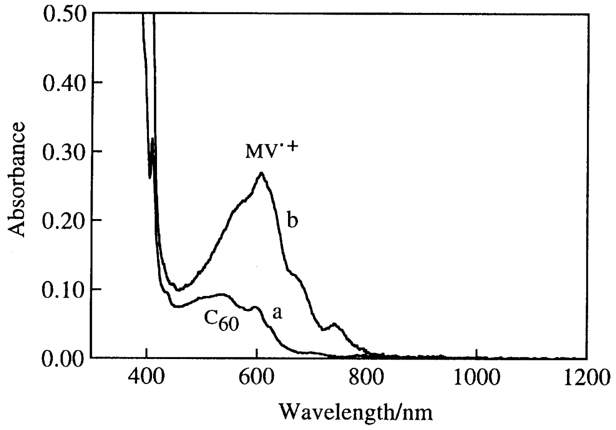


Fig. 5. Spectral-change of steady absorption after addition of air and MV^{2+} in the presence of $C_{60}^{\bullet-}$, (a) after introduction of air to the irradiated BN solution. (b) after addition of MV^{2+} THF solution (multiplied by 2). $C_{60}^{\bullet-}$ was formed by steady-state photolysis of C_{60}/TEOA deaerated BN solution. $[C_{60}] = 0.1 \times 10^{-3}$ mol dm^{-3}, [TEOA] = 5×10^{-3} mol dm^{-3}, $[MV^{2+}] = 0.2 \times 10^{-3}$ mol dm^{-3}, $[O_2] = 1.9 \times 10^{-3}$ mol dm^{-3}.

transfer from $O_2^{\bullet-}$ to MV^{2+} ($k_{et}^{O_2\text{-}MV}$) by changes such as solvent polarity and by other consumption reactions of $O_2^{\bullet-}$.

The electron transfer process (4) was confirmed to be an exothermic process ($\Delta G_{et} < 0$), because the reduction potential of MV^{2+} was estimated as −0.82 V (vs ferrocene/ferrocenium) in BN. This finding supports the observation of $MV^{\bullet+}$ obtained by steady-state photolysis even in the presence of O_2 (spectrum b in Fig. 5). From the Rehm and Weller relationship, the $k_{et}^{O_2\text{-}MV}$ value would be anticipated to be of the order of 10^9 (mol^{-1} dm^3 s^{-1}).[18]

In aqueous and other protic solutions, however, $MV^{\bullet+}$ can be consumed easily with O_2 (in the aerated protic solution, the lifetime of $MV^{\bullet+}$ is less than 1 s). For such reasons, it seemed plausible that electron transfer from $MV^{\bullet+}$ to O_2 is an exothermic process ($\Delta G_{et} < 0$) in protic solutions. The reduction potentials of O_2 and MV^{2+} are extremely affected by solvents.[2,4a] The electron-transfer processes between $O_2^{\bullet-}$ and MV^{2+} are summarized as Scheme 2. From the observation of long living $MV^{\bullet+}$ in aprotic solvents, it can be deduced that the equilibrium (5) lies quite far to the right. In the protic solvents, on the other hand, the equilibrium (5) lies to the left, and the consumption of $O_2^{\bullet-}$ occurs by some mechanisms such as protonation, as proposed in reaction (6).[19]

Thus, it is presumed that $MV^{\bullet+}$ is consumed together with $O_2^{\bullet-}$-consumption by the addition of some protic solvents to the aerated aprotic solutions. In other words, the $MV^{\bullet+}$-consumption may proceed by the decomposition of superoxide anion and by following re-balance of the equilibrium (5) to the left.

In fact, the addition of water or methanol (1 mol dm^{-3}) to the BN solution results in the gradual decrease of $MV^{\bullet+}$, and the lifetime of $MV^{\bullet+}$ remarkably decreases to ca. 10 min (at 25 °C), as shown in Fig. 6. In the absence of O_2, on the other hand, the addition of water or methanol does not influence the lifetime of $MV^{\bullet+}$. These reaction pathways in aprotic solutions can be described as an energy diagram (Fig. 7).

$$C_{60}^{\bullet-} + O_2 \xrightarrow{k_{et}^{O_2}} C_{60} + O_2^{\bullet-} \qquad (3)$$

$$MV^{2+} + O_2^{\bullet-} \xrightarrow[\Phi_{et}^{O_2\text{-}MV}]{k_{et}^{O_2\text{-}MV}} MV^{\bullet+} + O_2 \qquad (4)$$

$$MV^{2+} + O_2^{\bullet-} \rightleftharpoons MV^{\bullet+} + O_2 \qquad (5)$$

$$O_2^{\bullet-} + \text{R-OH} \longrightarrow \text{decompose} \qquad (6)$$

R-OH: protic solvent

Scheme 2.

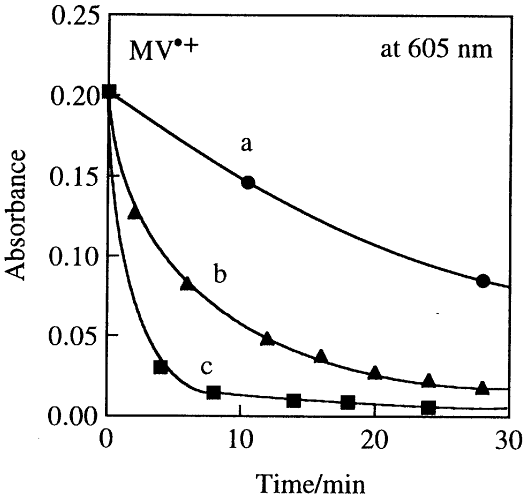


Fig. 6. Decay-time profiles of $MV^{\bullet+}$ in aerated THF/BN (1 : 1) solution; (a) in the absence of additive, (b) in the presence of methanol (1 mol dm^{-3}), and (c) in the presence of water (1 mol dm^{-3}).

To confirm the formation of each radical species in BN, the ESR-measurements were carried out. Figure 8a shows the ESR spectrum corresponding to the absorption spectrum b in Fig. 1, which can be identified as $C_{60}^{\bullet-}$. Figure 8b corresponding to the absorption spectrum c in Fig. 1 can be identified as a mixed spectrum of $O_2^{\bullet-}$–DMPO and $^{\bullet}CH_3$–DMPO adducts (DMPO and dimethyl sulfoxide were added to the solution as spin trap reagents).[20] And, Fig. 8c corresponding to the absorption spectrum b in Fig. 5 can be identified as $MV^{\bullet+}$.[21] From these observations, it can be reasonably concluded that the electron-transfer process from $O_2^{\bullet-}$ to MV^{2+} occurs, yielding long-living

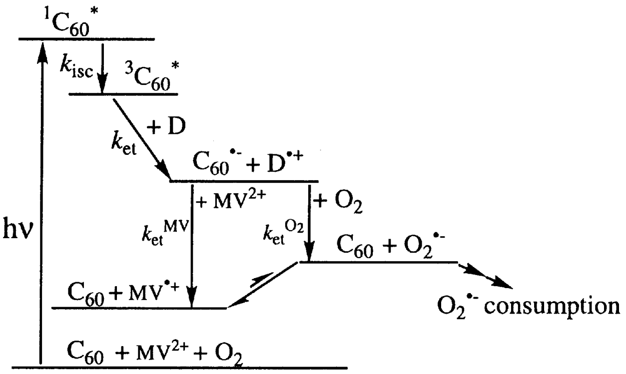


Fig. 7. Schematic energy diagram of MV^{2+}-photoreduction system.

$MV^{\bullet+}$ in aprotic solvents such as BN and BN/THF.

The overall quantum yield (Φ_{total}) for the C_{60}-sensitized $MV^{\bullet+}$-formation through the intermediary of O_2 can be found by multiplying the yields of the four steps:[22] the quantum yield for the intersystem crossing of $^1C_{60}^*$ ($\Phi_{isc} = 1.0$), the quantum yield for the reduction of C_{60} via the triplet route (Φ_{et}; 0.88 ($^-BPh_4$), 0.33 (TEOA)), the yield for electron transfer from $C_{60}^{\bullet-}$ to O_2 ($\Phi_{et}^{O_2} = 1.0$), and the yield for electron transfer from $O_2^{\bullet-}$ to MV^{2+} ($\Phi_{et}^{O_2\text{-}MV} = 0.14$ in BN, and 0.24 in BN/THF). Thus, the Φ_{total} values in BN were estimated to be 0.12 for $^-BPh_4$ and 0.05 for TEOA. In BN/THF, the Φ_{total} values were estimated to be 0.21 for $^-BPh_4$, and 0.08 for TEOA. The rate constants and efficiencies for electron transfer are summarized in Table 1.

Steady-State Photolysis of C_{60}/Electron–donor/MV^{2+}/O_2 System. By the irradiation of C_{60} in the presence of TEOA (or $^-BPh_4$) and MV^{2+} in aerated solution, $MV^{\bullet+}$ was also generated and remained for a long time. From these facts, two pathways of electron transfer leading to the $MV^{\bullet+}$-formation from $C_{60}^{\bullet-}$ can be considered kinetically as shown in Scheme 3: one is the electron transfer through the intermediary of O_2 (reaction (7)), and another is direct electron transfer from $C_{60}^{\bullet-}$ to MV^{2+} (reaction (8)). Because of the large second-order rate constant for electron transfer from $C_{60}^{\bullet-}$ to MV^{2+} ($k_{et}^{MV} = 2.8 \times 10^9$ $mol^{-1}\ dm^3\ s^{-1}$ in BN), the direct electron transfer from $C_{60}^{\bullet-}$ to

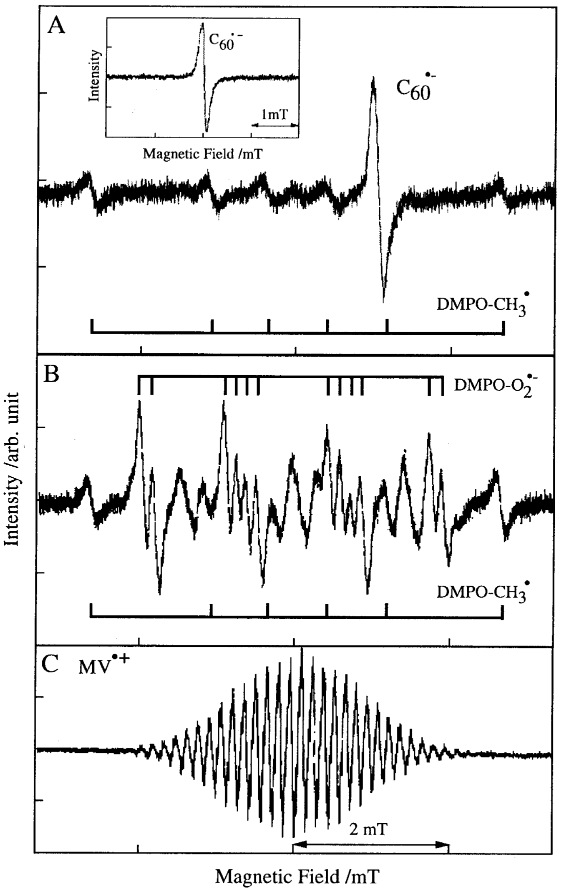


Fig. 8. ESR-measurements in BN; (A) after irradiation of deaerated C_{60}/TEOA/DMPO/dimethyl sulfoxide system; Inset: after irradiation of deaerated C_{60}/TEOA system, (B) after introduction of air and DMPO/dimethyl sulfoxide to the irradiated C_{60}/TEOA system, (C) after addition of air and MV^{2+} to the irradiated C_{60}/TEOA deaerated system. $[C_{60}] = 0.1 \times 10^{-3}\ mol\,dm^{-3}$, $[TEOA] = 10 \times 10^{-3}\ mol\,dm^{-3}$, $[MV^{2+}] = 0.2 \times 10^{-3}\ mol\,dm^{-3}$, $[DMPO] = 1\ mol\,dm^{-3}$, [dimethyl sulfoxide] $= 1\ mol\,dm^{-3}$.

Table 1. Summary of Kinetical Measurements

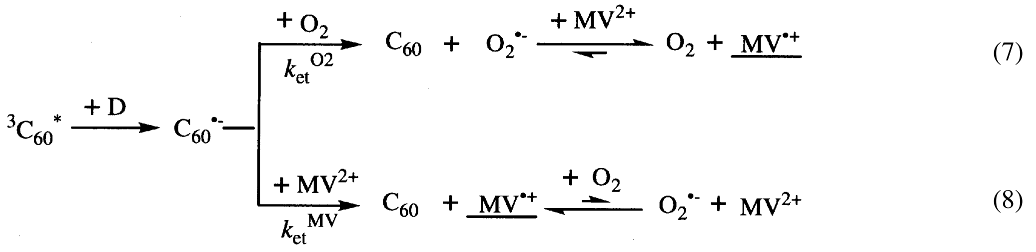
i) Second-order rate constants for electron transfer in BN ($mol^{-1}\ dm^3\ s^{-1}$)

Electron donor	k_{et}	k_{et}^{MV}	$k_{et}^{O_2}$	$k_{et}^{O_2-MV}$
$^-BPh_4$	3.1×10^7 a)	2.8×10^9 c)	3.7×10^2	$> 10^9$
TEOA	1.6×10^7 b)	2.8×10^9 c)	3.7×10^2	$> 10^9$

ii) Efficiencies for each electron transfer process

Electron donor	Solvent	Φ_{et}	Φ_{et}^{MV}	$\Phi_{et}^{O_2}$	$\Phi_{et}^{O_2-MV}$	Φ_{total}
$^-BPh_4$	BN	0.88 a,d)	1.0 c)	1.0	0.14	0.12
$^-BPh_4$	BN/THF	(0.88)	(1.0)	(1.0)	0.24	0.21
TEOA	BN	0.33 b)	1.0 c)	1.0	0.14	0.05
TEOA	BN/THF	(0.33)	(1.0)	(1.0)	0.24	0.08

a) Ref. 5. b) Ref. 11. c) Ref. 12. d) Efficiency for RC_{60}^--formation is quite low.



Underline refers to long-living radical-ion species.

Scheme 3.

MV^{2+} (reaction (8)) is a favorable path in BN. The proportion of reaction (7) to each of the consumption paths of $C_{60}{}^{\bullet -}$ in Scheme 3 depends on the relative concentration of O_2 to MV^{2+} and on the solvent polarity, which remarkably changes the reduction potentials of O_2 and MV^{2+} (the relative value of $k_{et}{}^{O_2}$ to $k_{et}{}^{MV}$ is also changed). Each electron transfer mechanism (7 or 8) leads to the effective accumulation of $MV^{\bullet +}$, because the equilibrium (5) lies so far to the right in BN. In this case, the total quantum yield (Φ_{total}) for the $MV^{\bullet +}$-formation via reaction (7) and (8) is mainly affected by the efficiency of the $C_{60}{}^{\bullet -}$-formation, as shown in reaction (1).

Concluding Remarks. A photoreduction system of MV^{2+} in the presence of O_2 was designed via electron transfer between $^3C_{60}{}^*$ and electron donors. By the photoirradiation of C_{60} in the presence of the electron donors, persistent $C_{60}{}^{\bullet -}$ was generated, which can reduce O_2 molecule by the slow single electron transfer, yielding $O_2{}^{\bullet -}$. In the presence of MV^{2+}, electron transfer from $O_2{}^{\bullet -}$ to MV^{2+} occurs, generating long-living $MV^{\bullet +}$ for more than 1 h even in aerated solution. In the aprotic solvents, $MV^{\bullet +}$ is thermodynamically stable. $MV^{\bullet +}$ is consumed by O_2 in the presence of excess protic solvents. We revealed that MV^{2+} is an effective electron acceptor even in the aerated solvents in the absence of protic solvents.

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