Evaluation of Rate Constant for Electron Transfer from C_{60}-Anion Radical to Molecular Oxygen by Laser Flash Photolysis Method

Toshifumi Konishi, Mamoru Fujitsuka, and Osamu Ito*
Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai 980-8577

(Received November 19, 1999; CL-990988)

The rate constant for electron transfer from C_{60}-anion radical ($C_{60}^{\bullet -}$) to molecular oxygen was evaluated to be (3.7 ± 0.2) x 10^2 mol^{-1} dm^3 s^{-1} in benzonitrile by following the concentration of the $C_{60}^{\bullet -}$ by laser flash photolysis with a detector in the near-IR region for long time scale (> 0.1 s).

The importance of photoinduced electron transfer of fullerenes is well recognized in various electron transfer systems. In the photo-electric apparatus[1] and biological active systems[2,3] comprised of C_{60} and C_{60}-derivatives, the electron transfer from C_{60}-anion radical ($C_{60}^{\bullet -}$) to O_2 is an important process to consider, because the reduction of O_2 remarkably influences the overall reaction yields and generates the reactive super oxide anion ($O_2^{\bullet -}$). However, the rate constant has not been evaluated because of the difficulties in observing $C_{60}^{\bullet -}$ in the near-IR region in a few-seconds time-region. This rate of electron transfer is too fast to observe by the steady-state method, but absorption peak of $C_{60}^{\bullet -}$ is too longer wavelength to measure by the usual laser flash photolysis with photomultiplier tube system.

In the present study, we succeeded in the estimation of the rate constant by applying the long time-scale near-IR transient spectroscopy by using steady probe light and InGaAs-PIN photodiode module.[4] Tetrabutylammonium tetraphenylborate, $^{-}BPh_4(^{+}NBu_4)$ was employed as an electron donor which generates less reactive decomposition products immediately after one electron donation.[4,5]

Figure 1a shows the steady-state absorption spectra of benzonitrile mixture solution of C_{60} and $^{-}BPh_4(^{+}NBu_4)$, which exhibits an absorption at UV-region only ($\lambda_{ab} <$ 330 nm). After photo-excitation of C_{60} ($\lambda_{ex} >$ 410 nm) in the presence of $^{-}BPh_4$, the 1070 nm peak with shoulders in the region of 900 - 1100 nm is assigned to $C_{60}^{\bullet -}$ (Figure 1b),[6] which is persistent in the present system, because the electron donor decomposed sacrificially to less reactive triphenylboran and biphenyl by the following mechanism.[4,5]

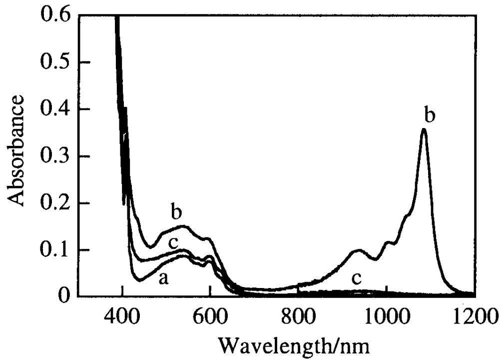


Figure 1. (a) Steady-state absorption spectrum of C_{60} (0.1 x 10^{-3} mol dm^{-3}) and $^{-}BPh_4$ (5 x 10^{-3} mol dm^{-3}), (b) after 450 s photo illumination of C_{60} with the visible light ($\lambda_{ex} >$ 410 nm) in deaerated benzonitrile, and (c) after addition of O_2.

$$C_{60} \xrightarrow[^{-}BPh_4]{h\nu} C_{60}^{\bullet -} + BPh_3 + 1/2\ Ph\text{-}Ph \quad (1)$$

When O_2 was introduced to the solution containing $C_{60}^{\bullet -}$, the absorption band of $C_{60}^{\bullet -}$ disappeared immediately, indicating that electron transfer from $C_{60}^{\bullet -}$ to O_2 takes place within a few seconds (Figure 1c), which is impossible to measure by the steady-absorption method.

The reaction was followed by laser flash photolysis as shown in Figure 2. From the observed transient absorption spectra after the excitation of C_{60} with the 532 nm laser light for 7 ns in the presence of $^{-}BPh_4$ in aerated benzonitrile, the triplet - triplet absorption of C_{60} ($^3C_{60}^*$) was confirmed initially;[7] with the decay of $^3C_{60}^*$, the transient absorption band of $C_{60}^{\bullet -}$ appeared with the peak at 1070 nm. This indicates that electron transfer occurs via $^3C_{60}^*$. When O_2 was added to this system, $^3C_{60}^*$ is consumed by both the electron-transfer process with $^{-}BPh_4$ and by the energy- transfer process to O_2. Since the both reactions are in competition, the formation of $C_{60}^{\bullet -}$ was observed when $k_{et}^{T}[^{-}BPh_4] >> k_{O_2}[O_2]$.

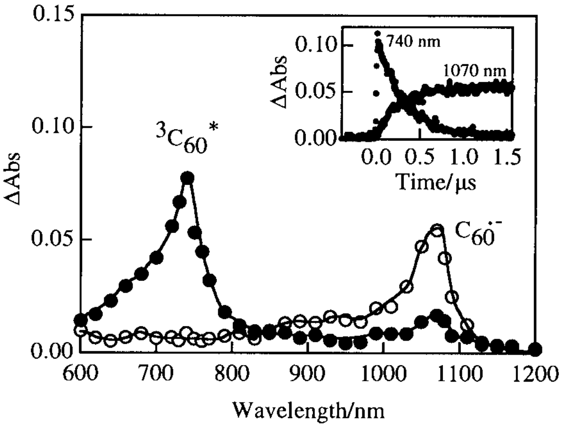
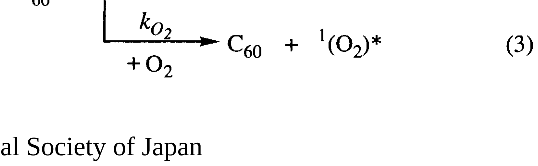


Figure 2. Transient absorption spectra obtained by the nano second laser light (532 nm) irradiation of C_{60} (0.1 x 10^{-3} mol dm^{-3}) in the presence of $^{-}BPh_4$ (20 x 10^{-3} mol dm^{-3}) in aerated benzonitrile. ● 100 ns, ○ 1 μs. Inset: Absorption-time profiles in short time scale.



$$^3C_{60}^* \xrightarrow[k_{et}^{T}]{+^{-}BPh_4} C_{60}^{\bullet -} + BPh_3 + 1/2\ Ph\text{-}Ph \quad (2)$$

$$^3C_{60}^* \xrightarrow[+O_2]{k_{O_2}} C_{60} + {}^1(O_2)^* \quad (3)$$

In the inserted time profile (Figure 2), the decay of $C_{60}^{\bullet-}$ was not observed in the time scale of micro second even in the presence of excess O_2 with respect to $C_{60}^{\bullet-}$.

The long time-scale observations of the time profiles of $C_{60}^{\bullet-}$ are shown in Figure 3. In deaerated solution, $C_{60}^{\bullet-}$ did not show appreciable decay for 1.5 s, which reasonably supports that the persistent $C_{60}^{\bullet-}$ is observed by the steady-state measurement as shown in Figure 1b. In aerated solution, $C_{60}^{\bullet-}$ begins decaying; with a decrease in the initial absorbance of $C_{60}^{\bullet-}$ due to the competitive reaction with k_{O2} $[O_2]$. The decay profile can be fitted with the first-order decay kinetic, yielding the first-order rate constant (k_{1st}); the half-life is ca. 0.75 s. In O_2-saturated solution, the decay rate increased, giving the large k_{1st}; the half-life is ca. 0.25 s. From the pseudo-first order plots (k_{1st} values against $[O_2]$, Inset of Figure 3),[8] the second-order rate constant for electron transfer from $C_{60}^{\bullet-}$ to O_2 (k_{et}^{O2}) was evaluated to be $(3.7 \pm 0.2) \times 10^2$ $mol^{-1}\,dm^3\,s^{-1}$.

This small k_{et}^{O2} reflects the reduction potentials (E_{red}) of C_{60} and O_2 ($E_{red}(C_{60}) = -0.92$ V, $E_{red}(O_2) = -1.2$ V (vs ferrocene/ferrocenium) in benzonitrile).[9] Electron transfer from $C_{60}^{\bullet-}$ to O_2 was revealed as the endothermic process ($\Delta G_{et} > 0$) by these electrochemical measurements.

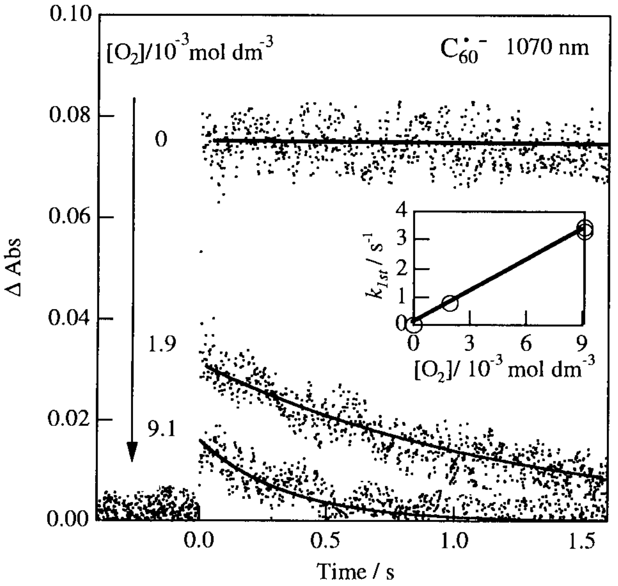


Figure 3. Time profiles of $C_{60}^{\bullet-}$ and calculated line in the long time-scale; (a) in deaerated solution ($[O_2] = 0$ mol dm^{-3}), (b) aerated solution ($[O_2] = 1.9 \times 10^{-3}$ mol dm^{-3}) and (c) O_2-saturated solution ($[O_2] = 9.1 \times 10^{-3}$ mol dm^{-3}). Inset: Pseudo-first order plots.

$$C_{60}^{\bullet-} + O_2 \xrightarrow{k_{et}^{O2}} C_{60} + O_2^{\bullet-} \qquad (4)$$

The formation of $O_2^{\bullet-}$ was proved by the ESR measurements in the presence of 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and by a successive electron transfer from $O_2^{\bullet-}$ to methylviologen yielding blue cation radical of methylviologen. When other electron donors such as triethanolamine were used in stead of $^{-}BPh_4$, persistent $C_{60}^{\bullet-}$ was similarly produced; however, in the presence of O_2, $C_{60}^{\bullet-}$ rapidly reacted with the decomposition products from the cation radical of triethanolamine.

Further study on the electron transfer processes of $C_{60}^{\bullet-}$ and O_2 in the aqueous systems is in progress, because of the importance in photobiology, which needs the water soluble C_{60} and a suitable electron donor.

References and Notes

1 H. Imahori, S. Ozawa, K. Ushida, M. Takahashi, T. Azuma, A. Ajavakom, T. Akiyama, M. Hasegawa, S. Taniguchi, T. Okada, and Y. Sakata, *Bull. Chem. Soc. Jpn.*, **72**, 485 (1999).

2 S. Fukuzumi, T. Suenobu, M. Patz, T. Hirasaka, S. Itoh, M. Fujitsuka, and O. Ito, *J. Am. Chem. Soc.*, **120**, 8060 (1998).

3 Y. Yamakoshi, S. Sueyoshi, K. Fukuhara, and N. Miyata, *J. Am. Chem. Soc.*, **120**, 12363 (1998).

4 T. Konishi, Y. Sasaki, M. Fujitsuka, Y. Toba, H. Moriyama, and O. Ito, *J. Chem. Soc., Perkin Trans. 2*, **1999**, 551.

5 T. Konishi, M. Fujitsuka, O. Ito, Y. Toba, and Y. Usui, *J. Phys. Chem. A*, **103**, 9938 (1999).

6 J. W. Arbogast, C. S. Foote, and M. Kao, *J. Am. Chem. Soc.*, **114**, 2277 (1992).

7 R. J. Sension, C. M. Phillips, A. Z. Szarka, W. J. Romanow, A. R. Macghie, J. P. McCauley, Jr., A. B. Smith III, and R. M. Hochstrasser, *J. Phys. Chem.*, **95**, 6075 (1991).

8 For the calculation of k_{et}^{O2}, the concentrations of O_2 in benzene and acetonitrile were employed (S. L. Murov, I. Carmichael, G. L. Hug, "Handbook of Photochemistry," Marcel Dekker, Inc., New York (1993), p.289).

9 The reduction half-wave potentials were measured by cyclic voltammetry with a scan rate of 0.1 V/s in dry benzonitrile at room temperature. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}).