Magnetic field effects on the decay rate of triplet biradical photogenerated from intramolecular electron transfer in fullerene-phenothiazine linked compounds

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Transient absorption spectra of fullerene-phenothiazine linked compounds indicated that the photoinduced intramolecular electron transfer occurred in benzonitrile, while not in benzene. In benzonitrile, the lifetime of a photogenerated biradical was very long, in spite of being around the top region in the Marcus theory. The lifetime of the biradical increased in the presence of magnetic fields. The magnetic field effects verified that the intramolecular electron transfer from phenothiazine to the triplet excited state of fullerene occurred. The long lifetime is most probably ascribed to spin multiplicities of the biradical.

Introduction

Recently, photochemical and photoelectrochemical properties of fullerene (C_{60}) have extensively been investigated.[1)] Photoinduced electron transfer reactions of a number of C_{60}-donor linked molecules have been reported.[1, 2)] However, in those papers, the intramolecular electron transfer on the singlet excited state ($^1C_{60}{}^*$) of C_{60} has been studied, in spite of very-high quantum yield for the triplet excited state ($^3C_{60}{}^*$) of C_{60}.

Magnetic field effects (MFEs) have been powerful for verifying the reaction mechanism *via* triplet intermediate states in photochemical reactions.[3)] The MFEs are expected to be observed, if the triplet biradical is obtained by photoinduced electron transfer in the C_{60}-donor linked compound.

In this paper, we have examined the photoinduced intramolecular electron transfer reactions of fullerene-phenothiazine linked compounds (**$C_{60}(n)$PH**) and the MFEs on the corresponding reverse electron transfer reactions in benzene and in benzonitrile, to verify the contribution of triplet biradicals to the electron transfer reactions.

Photoinduced intramolecular electron transfer reactions of $C_{60}(n)$PH[4,5)]

Transient absorption spectra of the three compounds (**C_{60}(ref)**, **C_{60}(10)PH**, and **C_{60}(12)PH**) (Fig. 1) were measured by laser excitation at 532 nm in benzene and in benzonitrile. In **C_{60}(ref)**, the broad absorption band around 700 nm was observed in both benzene and benzonitrile. In the case of **C_{60}(10)PH** and **C_{60}(12)PH**, broad absorption bands around 700 nm were also observed in benzene, corresponding well with that of **C_{60}(ref)**. Thus, these absorption bands are ascribed to the T_1-T_n absorption of the C_{60} moiety in these compounds. While, no appreciable absorption signals due to $PH^{\bullet +}$ and $C_{60}{}^{\bullet -}$ radicals were observed.

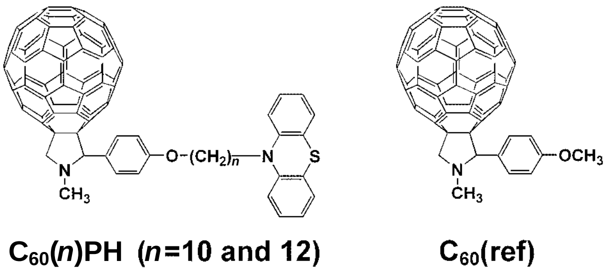

Fig. 1. Structural formulae for C_{60} derivatives used in this study.

In contrast, the T_1-T_n absorption band of the C_{60} moiety disappeared and the absorption bands due to $PH^{\bullet +}$ (λ_{max}, 520 nm) and $C_{60}{}^{\bullet -}$ ($\lambda > 600$ nm) radicals were observed in benzonitrile. Therefore, the photoinduced intramolecular electron transfer took place in benzonitrile (dielectric constant, $\varepsilon = 25.2$), while did not occur in benzene ($\varepsilon = 2.27$). These results are due to the solvent effect on the thermodynamic energies of the photogenerated biradical states. The photochemical properties of **C_{60}(10)PH** is summarized in Fig. 2, which indicates the relevant energy levels and kinetic pathways. These energy levels of the photogenerated biradical state, $C_{60}{}^{\bullet -}$-$PH^{\bullet +}$, in benzonitrile are estimated from difference pulse voltammetric measurements. Energy levels of $C_{60}{}^{\bullet -}$-$PH^{\bullet +}$ in benzene were also estimated by the using Weller's approach.[4, 5)] From Fig. 2, the intramolecular electron transfer from PH to $^1C_{60}{}^*$ or $^3C_{60}{}^*$ in **C_{60}(10)PH** is thermodynamically favorable in benzonitrile, but is unfavorable in benzene. Essentially the same result regarding the solvent effect on the energies of $C_{60}{}^{\bullet -}$-$PH^{\bullet +}$ was obtained in **C_{60}(12)PH**.

The energy barrier for the electron transfer can be estimated by using the Marcus theory. The Gibbs free energy changes for the charge separation from the $^1C_{60}{}^*$ or the $^3C_{60}{}^*$ to the biradical state ($-\Delta G_{CS}(S)$ or $-\Delta G_{CS}(T)$) are calculated to

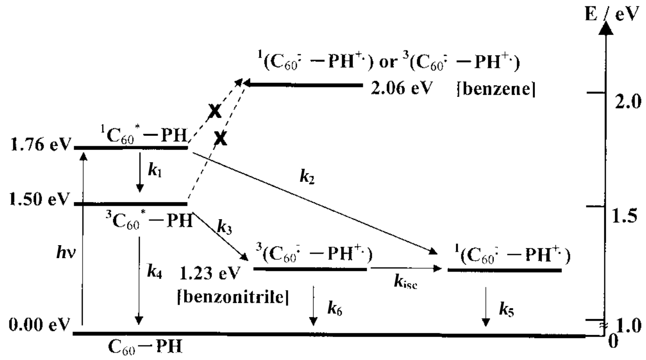

Fig. 2. Schematic energy levels of transient states of **C$_{60}$(10)PH** and the reaction scheme in benzonitrile.

be 0.53 or 0.27 eV for **C$_{60}$(10)PH**, and 0.52 or 0.26 eV for **C$_{60}$(12)PH**, respectively. They all fell in the normal region ($-\Delta G_{\mathrm{CS}} < \lambda = 1.15$ eV for **C$_{60}$(10)PH** and 1.19 eV for **C$_{60}$(12)PH**), where λ represents the reorganization energy. On the other hand, the energy changes for the charge recombination ($-\Delta G_{\mathrm{CR}} = 1.23$ eV for **C$_{60}$(10)PH** and 1.24 eV for **C$_{60}$(12)PH**) are rather close to the corresponding λ values ($\lambda = 1.15$ eV for **C$_{60}$(10)PH** and 1.19 eV for **C$_{60}$(12)PH**), and thus being around the top region in the reaction coordinate diagram. In **C$_{60}$(*n*)PH**, the long-lived photogenerated biradical, $\mathrm{C_{60}}\bullet^{-}$-$\mathrm{PH}\bullet^{+}$, is observed in benzonitrile, in spite of being around the top region in the Marcus theory. The reason is discussed below.

Magnetic field effects on the decay of photogenerated biradical of C$_{60}$(*n*)PH[4,5]

MFEs on the photoinduced electron transfer in **C$_{60}$(*n*)PH** were examined in benzonitrile or in benzene. In the case of **C$_{60}$(10)PH** the decay of transient absorption at 520 nm was retarded in the presence of the magnetic field. This strongly indicates that the reverse electron transfer occurs *via* the triplet state of biradical, ^{3}($\mathrm{C_{60}}\bullet^{-}$-$\mathrm{PH}\bullet^{+}$). The decay rate constant (k_{d}) as evaluated from the absorption decay at 520 nm decreased quickly with the increase of the magnetic field and reached a plateau region above ~ 0.2 T (Fig. 3). The decay rate of the biradical was reduced by 1.8 times on going from 0 to 1.0 T. The MFEs on k_{d} vaule for the biradical in **C$_{60}$(12)PH** were similar to those in **C$_{60}$(10)PH**.

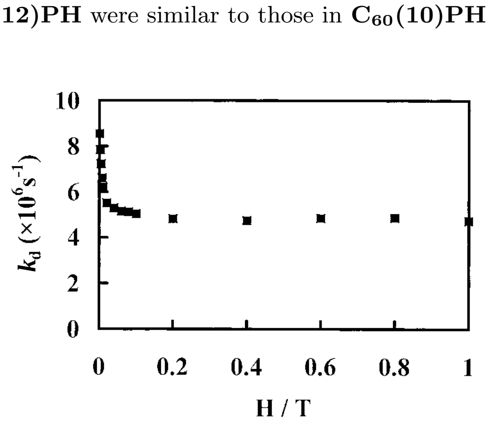

Fig. 3. MFEs on the decay rate constant (k_{d}) for the biradical of **C$_{60}$(10)PH**.

The MFE for the biradicals of **C$_{60}$(10)PH** and **C$_{60}$(12)PH** can be explained in terms of isotropic hyperfine coupling and spin-lattice relaxation mechanisms. At zero magnetic field, the decay constant (k_{d}) for the triplet biradical is controlled by the isotropic hyperfine-induced intersystem crossing (k_{isc} in Fig. 2), the reverse electron transfer from the singlet biradical (k_5), and spin-orbit (SO)-induced intersystem crossing to the ground state (k_6). The isotropic hyperfine-induced intersystem crossing process between T_{+1} and S (singlet) or T_{-1} and S states decreased due to the Zeeman splitting of the triplet sublevels (T_{+1}, T_0, and T_{-1}) in lower magnetic fields ($H <$ *ca.* 5 mT). In the medium magnetic field region (*ca.* 5 mT $< H <$ 0.2 T), the MFE on the k_{d}-value is most likely explained by spin-lattice relaxation in the three sublevels (T_{+1}, T_0, and T_{-1}) of the T state and the S state of the biradical. In higher magnetic fields (H > 0.2 T), the k_{d} value is governed by the magnetic-field-independent SO-induced intersystem crossing process, and thus the k_{d}-value becomes constant. Time-resolved electron paramagnetic resonance and fluorescence measurements also support the reaction mechanism described above.

MFEs on the decay of the radical pair of a C$_{60}$ cluster anion and a pyrene cation have been observed in a fluorinated micellar system.[6] The MFEs have been explained by the g-anisotropy-induced relaxation mechanism. MFEs on the decay of biradical have also been reported in a carotenoid-porphyrin-C$_{60}$ triad system at 77 K, but no MFEs were observed at 298 K.[7] Those MFEs are different from present case.

Among a number of C$_{60}$-donor linked compounds, some of them are known to show the novel properties that accelerate photoinduced charge separation and decelerate charge recombination in the electron transfer reactions.[1,2] Imahori *et al.* suggested that those interesting properties could be explained by the smaller reorganization energy of the C$_{60}$ moiety.[2] Paddon-Row *et al.* also suggested the contribution of the orbital symmetry effects arising from the special symmetry property of the C$_{60}$ π-system.[8] In this study, the long lifetime of the photogenerated biradical of **C$_{60}$(*n*)PH** in the absence of magnetic field cannot be explained by the Marcus theory as described above. On the basis of the MFEs in **C$_{60}$(*n*)PH**, such a long-lived charge-separated state is most likely ascribed to spin multiplicities in the photogenerated biradical, $\mathrm{C_{60}}\bullet^{-}$-$\mathrm{PH}\bullet^{+}$. In other words, the intersystem crossing process (k_{isc}) from the triplet to the singlet biradicals must become the rate-determining step in the decay of the photogenerated biradical *via* the charge recombination (reverse electron transfer) reaction, which results in the long-lived charge-separated state in spite of being around the top region in the Marcus theory.

On the contrary, no MFEs in the entire absorption spectral region were observed in benzene. The result is in good agreement with the fact that in benzene the biradical was not generated because the electron transfer from PH to ^{1}C$_{60}^*$ or ^{3}C$_{60}^*$ was endothermic.

Conclusion

Laser excitation of **C$_{60}$(*n*)PH** afforded the $\mathrm{T_1}$-$\mathrm{T_n}$ absorption spectra in benzene, while the $\mathrm{T_1}$-T_n absorption disappeared and the absorption due to the photogenerated biradical, $C_{60}{}^{\bullet -}$-$PH^{\bullet +}$, appeared in benzonitrile. The long-lived photogenerated biradical was observed in benzonitrile in spite that the charge separation process was located at the normal region while the charge recombination process around the top region in the Marcus theory. The MFEs on the decay rate of the biradical were observed. The MFEs strongly indicate that the photoinduced intramolecular electron transfer from PH to $^3C_{60}{}^*$ takes place and the long-lived photogenerated biradical is most probably ascribed to spin multiplicities. The present study provides an important insight for the design of the C_{60}-donor linked compound generating the long-lived photogenerated biradical state.

The present study was financially supported by the grants of KAWASAKI STEEL 21st Century and Shinkagakuhatten, and the Murata Science Foundations, and by the Grant-in-Aids for Scientific Research: Priority Area of “Electrochemistry of Ordered Interfaces” (No. 11118257), and Encouragement of Young Scientists (No. 12750737).

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