

ELECTRON TRANSFER REDUCTION OF FLUOROFULLERENES, C₆₀F₃₆ AND C₆₀F₁₈

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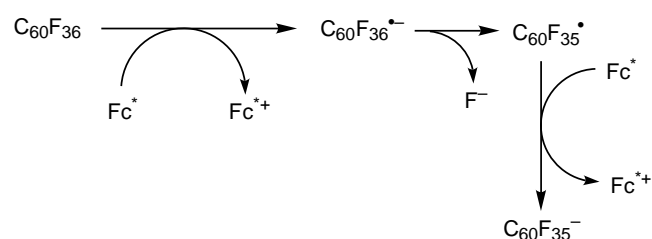
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Fluorofullerenes, C₆₀F₃₆ and C₆₀F₁₈, have unique structures identified by X-ray analyses, which have revealed the presence of three-four and one π -delocalized benzenoid rings, respectively.^{1,2} These fullerenes are strong oxidants as compared to C₆₀ due to strongly electron-deficient fluorines. Halogenated fullerenes such as C₆₀Cl₆, C₆₀Br₆ and C₆₀Br₈ are known to form charge-transfer complexes with organic donors and it is anticipated that increased electron withdrawal by the halogenated cage would increase electron-transfer reduction. We have recently reported electron transfer reduction mechanism and one-electron reduction potential of C₆₀F₁₈.³ However, the electron transfer reactivity of the stronger oxidant, C₆₀F₃₆, has yet to be reported.

We report herein the electron transfer reduction mechanism and the reactivity of the electron transfer reduction of three isomers of C₆₀F₃₆ (*T*, *C*₁ and *C*₃) in comparison with that of C₆₀F₁₈.

Upon mixing a dichloromethane (CH₂Cl₂) solution of C₆₀F₃₆ (*C*₃) with decamethylferrocene (Fc^{*}) at -80 °C, the new absorption band due to C₆₀F₃₆^{•-} appeared at 685 nm immediately, accompanied by the formation of Fc^{•+} at 790 nm. The absorbance at 685 nm disappeared gradually, accompanied by appearance of a new absorption band at 630 nm and further increase in absorbance at 790 nm. This indicates that an electron transfer from Fc^{*} to C₆₀F₃₆ is followed by defluorination from C₆₀F₃₆^{•-} to give C₆₀F₃₅^{•-}.



Scheme 1

which is further reduced by Fc^{*} to yield C₆₀F₃₅^{•-} (630 nm) as the final reduced product as shown in Scheme 1.

The electron-transfer reduction of C₆₀F₃₆ (*C*₃) was also achieved by photoinduced electron transfer from dimeric 1-benzyl-1,4-dihydronicotinamide [(BNA)₂] to C₆₀F₃₆ in PhCN. The (BNA)₂ is known to act as a unique electron donor to produce the radical anions of electron acceptors. Under photoirradiation of a benzonitrile (PhCN) solution of (BNA)₂ and C₆₀F₃₆, C₆₀F₃₆^{•-} is detected by ESR as shown in Figure 1. The *g* value of the isotropic ESR signal due to C₆₀F₃₆^{•-} is 2.0010 which is slightly larger than the *g* value of C₆₀F₁₈^{•-} (2.0005). The smaller *g* value being smaller than the free spin value (2.0023) is characteristic of the ESR spectra of C₆₀^{•-} and the functionalized C₆₀^{•-}. Hyperfine splitting due to fluorine atoms of C₆₀F₁₈^{•-} is observed in Figure 1. This indicates that the unpaired electron is delocalized on fluorine atoms in C₆₀F₃₆^{•-}. An electron is initially added on the fullerene π -electron system and then intramolecular electron transfer occurs to the antibonding C-F σ^* orbital, resulting in the cleavage of the C-F bond. Upon cutting off the light, the ESR signal disappears due to the C-F bond cleavage disappears.

The detailed comparison of the electron-transfer reactivities and the stabilities of the radical anions of three isomers of C₆₀F₃₆ with those of C₆₀F₁₈ will be reported.

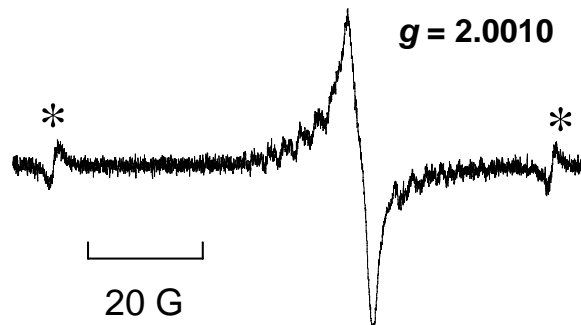


Figure 1. ESR spectrum of C₆₀F₃₆^{•-} (*C*₃) generated by photoinduced electron transfer from (BNA)₂ (1.0 × 10⁻³ M) to C₆₀F₃₆ (*C*₃, 2.5 × 10⁻⁴ M) with a high-pressure Hg lamp in deaerated PhCN at 278 K. * denotes an Mn²⁺ marker.

References

- [1] Hitchcock, P. B.; Taylor, R. *Chem. Commun.*, **2002**, 2078-2079; Avent, A. G.; Clare, B. W.; Hitchcock, P. B.; Kepert, D. L.; Taylor, R. *Chem. Commun.* **2002**, 2370-2371.
- [2] Neretin, I. S.; Lyssenko, K. A.; Antipin, M. Y.; Slovokhotov, Y. L.; Boltalina, O. V.; Troshin, P. A.; Lukonin, A. Y.; Sidorov, L. N.; Taylor, R. *Angew. Chem. Int. Ed.* **2002**, *39*, 3273-3276.
- [3] Ohkubo, K.; Taylor, R.; Boltalina, O. V.; Ogo, S.; Fukuzumi, S. *Chem. Commun.* **2002**, 1952-1953.