

Photoinduced Electron Transfer (PET) between C₆₀ and Amines in Micelle Solution —A Kinetic ESR Study

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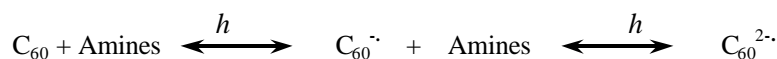
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Abstract: As indicated by kinetic ESR measurements, the key factor to affect electron recombination in the process of PET between C₆₀ and amines is the space between donor and C₆₀. To increase solubility of C₆₀ in water, it was incorporated into micelle of surfactants.

Keywords: C₆₀, ESR, photoinduced electron transfer (PET), micelle.

Fullerene chemistry has been one of the most exciting research subjects in the recent decade^{1,2}. However, the predominant hydrophobic character and the spherical carbon allotrope of C₆₀ hinder its solubility in an aqueous solution. In order to efficiently slow down charge recombination in the PET system containing C₆₀, water was selected as optimal polar media to stabilize charge separation state. Accordingly, solubility of fullerene in water had to be achieved by incorporating it into the hydrophobic cavity of several macromolecule hosts³⁻⁴ or micelle of surfactants⁵. Here, kinetics of electron recombination in the PET between both primary amines (PrNH₂, BuNH₂, HexNH₂, OctNH₂) and tertiary amines ((HOEt)₃N, Et₃N, Bu₃N) and C₆₀ were just systematically studied by means of ESR method in combination with the technique to increase solubility of C₆₀ in water upon the addition of some bipolar non-ionic Triton surfactants.

When micelle solution containing C₆₀ and amine donors was irradiated with YAG laser (532 nm), a single line ESR spectrum immediately appeared. Afterwards, another new single line peak became detectable at lower field position of the first peak while the irradiation period was continually extended. Two successively produced ESR signals can be respectively recognized as C₆₀^{•-} (g = 2.0000) and C₆₀^{2•-} (g = 2.0006) by comparing their g factors with the references in literature⁶. In other words, C₆₀^{2•-} and C₆₀^{•-} radicals can be photo-generated one after the other through two single electron transfer steps.



Half-life of C₆₀^{2•-} in photo-irradiated C₆₀/amines/Triton system are listed in **Table 1**. In the PET systems composed by either C₆₀/RNH₂ or C₆₀/R₃N, variation in half-life of C₆₀^{2•-} at different Triton micelle solution follows the order of:

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Triton X-114 < Triton X-100 < Triton X-405

The order is clearly related to the length of the corresponding Triton surfactant chain in micelle. The shorter the length of surfactant chain is, the shorter the half-life of C_{60}^{2-} dianion radicals is. Amine electron donors can be self-assemblingly embedded nearby the hydrophilic surface of surfactants in the micelle according to their hydrophilic characters⁷. Therefore, the distance between C_{60} molecule and amine donors is in accordance with the radius of the micelle. By this way, when Coulomb action and solvent effect are ignored, the rate of the electron recombination inside charge separation state could be proportional to the radius of the micelle.

Table 1 Half-life of C_{60}^{2-} in photo-irradiated C_{60} /amines/Triton system

Tritons	$t_{1/2}$ (S)	PrNH ₂	BuNH ₂	HexNH ₂	OctNH ₂	(HOEt) ₃ N	Et ₃ N	Bu ₃ N
Triton X-114		84.3	69.4	42.2	38.1	69.4	50.3	42.2
Triton X-100		91.1	74.8	51.7	40.8	72.1	54.4	45.1
Triton X-405		446.0	424.3	380.7	342.7	89.7	81.6	

Half-life of C_{60}^{2-} also exhibits distinct difference in the PET system containing same micelle solution but different amine donors. Extra comparison of data in the **Table 1** can further reveal that half-life of C_{60}^{2-} varies with various primary amine donors and tertiary amine donors in the following orders respectively:



The orders seem to correlate with hydrophobic behavior of the amines. Being more hydrophobic means that the amine donors can be more deeply embed inside micelle, and the longer distance between C_{60} and electron donors is, the more stable the charge separation state and the lower kinetic rate of the electron recombination are.

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References

1. T. Pradeep, *Current Sci.*, **1997**, 72 (2), 124.
2. W. Kratschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature*, **1990**, 347, 354.
3. C. Fraci, *Chem. In Australia*, **1997**, 12.
4. J. Sun, Y. Liu, D. W. Chen, Q. Y. Zhang, *J. Phys. Chem. Solid*, **2000**, 61 (7), 1149.
5. H. Hungerbuhler, D. M. Guldi, K.-D. Asmus, *J. Am. Chem. Soc.*, **1993**, 115, 3386.
6. V. Brezova, A. Stasko, P. Rapta, G. Domschke, A. Bartl, L. Dunsch, *J. Phys. Chem.*, **1995**, 99, 16234.
7. D. K. Lee, Y. Kim, Y. S. Kwon, Y. S. Kang, L. Kevan, *J. Phys. Chem.*, **1997**, 101, 5319.

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