C_{60} Anion Radical Produced in γ-Irradiated C_{60} Powder at 77 K

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The C_{60} powder was γ-irradiated at 77 K. The ESR spectrum and the near infrared spectrum of the irradiated sample have revealed for the first time that C_{60} monoanion radical is produced in the C_{60} powder at 77 K.

The monoanion radicals of C_{60} have been generated by γ-radiolysis of organic solid solutions at 77 K[1,4-6] as well as electrochemical, photochemical methods and so on.[2,3,7] Of these studies, Hase and Miyatake[4,5] reported the ESR spectrum of the C_{60} monoanion radical produced radiolytically at 77 K and showed that ESR parameters of the anion radical were similar to those produced by other methods.

In this study, C_{60} powder was γ-irradiated at 77 K and the ESR measurements were carried out at 73 K. This is the first report of the radical species produced in γ-irradiated C_{60} powder at 77 K and will lead hereafter to various studies on the radical processes of C_{60} powder as well as C_{60} in solid solutions.

The pristine C_{60} powder of the purity claimed to be 99.98% was used. The sample tube containing the powder of ca. 20 mg was evacuated and filled with helium gas to attain efficient cooling in both γ-irradiation at 77 K and ESR measurements at 73 K. The powder dissolved in toluene was mixed with KBr and then pressed under a high pressure during evaporating toluene to form a disc sample for the near infrared (NIR) measurement.

The C_{60} powder samples were γ-irradiated at 77 K. The dose was 5 and 55 KGy for ESR and optical absorption measurements, respectively. In order to avoid the color centers in ESR quartz tube caused by irradiation, the measurement part of the tube was shielded by lead blocks during irradiation. After irradiation the powder sample was transferred from the irradiation part to the measurement part of the tube in liquid nitrogen.

The ESR measurements were carried out at 73 K by bubbling helium gas into the Dewar. The NIR spectrum was measured at 77 K.

The ESR spectrum of the pristine C_{60} powder before γ-irradiation was observed with the ESR parameters of g=2.002 and the linewidth ΔH_{pp}=0.13 mT, and is shown in Figure 1(A). The same spectrum has already been reported and tentatively attributed to the radical species that is produced by a photochemical reaction with oxygen in the course of C_{60} powder production.[8,9] After γ-irradiation at 77 K, there appeared a new signal with g=2.000 and ΔH_{pp}=0.07 mT. This is shown in Figure 1(B). This signal was not observed for the sample irradiated at room temperature. The signal that was observed at 77 K disappeared after annealing the irradiated sample at room temperature for 3 min.

The signal has the same g-value as that of the C_{60} monoanion radical in solid solutions.[4,5] This leads us to infer that the new signal is ascribed to C_{60} monoanion radical produced in the powder at 77 K. To confirm this, we measured the NIR spectrum of the irradiated disc sample at 77 K. This is shown in Figure 2. It is seen from Figure 2 that the absorption peak at 1080 nm with a satellite structure appears. The feature of this spectrum is close to that of C_{60} monoanion radical in solid solutions.[1,6] Based on these results we conclude that the C_{60} monoanion radical is produced in the C_{60} powder by γ-irradiation at 77 K.

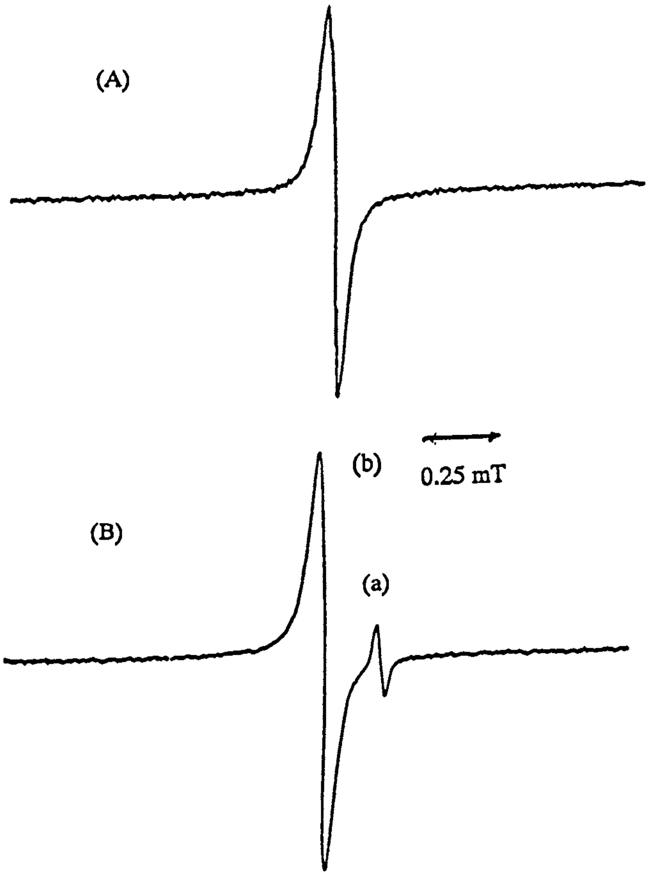

Figure 1. ESR spectra of the pristine C_{60} powder before (A) and after (B) γ-irradiation. The γ-irradiation was carried out at 77 K and the dose was 5 KGy. ESR measurements were carried out at 73 K. The ESR lines (a) and (b) are, respectively, attributed to the C_{60} monoanion radical and the radical species existing in the pristine C_{60} powder before irradiation.

The g-value, ΔH_{pp} and the optical absorption maximum (λ_{max}) of the C_{60} monoanion radical in the powder are listed in Table 1 together with those reported in solid solutions for comparison. It is seen from Table 1 that ΔH_{pp} of the monoanion radical in the powder is narrower than those in

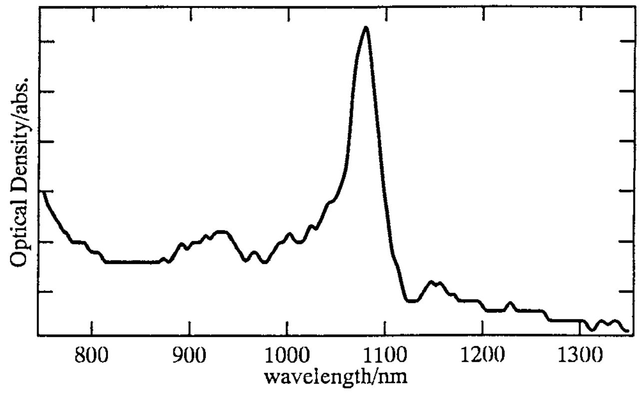

Figure 2. NIR spectrum of C_{60} powder after γ-irradiation. The disc sample of C_{60}/KBr of 1.5 mm in thickness was used. The γ-irradiation was carried out at 77 K and the dose was 55 KGy. NIR measurements were carried out at 77 K.

Table 1. Comparison of the g-value, the linewidth(ΔH_{pp}) of the ESR spectrum and the optical absorption maximum(λ_{max}) of the C_{60} monoanion radical produced by radiolysis in powder and 2-methyltetrahydrofuran (MTHF) and methylcyclohexane (MCH) solid solutions at 77 K

	g-value	ΔH_{pp}/mT	λ_{max}/nm
Powder sample[a]	2.0000	0.07	1080
MTHF solution	2.0002[b]	0.20[b]	1076[c]
MCH solution	2.0008[b]	0.20[b]	1076[c]

[a]This study. [b]Reference 5. [c]Reference 6.

solid solutions.[4,5] This implies that the C_{60} monoanion radical in the powder interacts with environments more weakly than in solid solutions. In the case of the C_{60} monoanion in the powder, the intramolecular spin relaxation is dominant. On the other hand, in the case of C_{60} monoanion radical in solid solutions the intermolecular relaxation processes mainly caused by interaction with protons of solvent molecules is involved, in addition to the intramolecular spin relaxation. Thus the narrowing occurred in the powder is convincing.

Next we have the question whether the C_{60} monoanion radical originates from the radical species which are present before γ-irradiation. However, it is improbable that the monoanion radical is produced by the electron attachment reaction between the pre-existing radical species and an excess electron, since the reaction would usually produce a nonparamagnetic species. If the C_{60} monoanion radical came from the radical species, the amount of the C_{60} monoanion radical produced after irradiation would approximate to the reduced amount of the radical species. The relative intensity of the ESR signal can be estimated by the product of the peak-to-peak height and the square of ΔH_{pp}. The result shows that the signal intensity of the radical species does not decrease after irradiation, in spite of the production of the monoanion radical, of which yield amounts to about 10% of the radical species. It follows that the monoanion radical does not originate from the radical species existing in the pristine C_{60} powder. However, the percentage of 10 may be same magnitude of the experimental error involved in ordinary ESR measurements. To clarify the origin of the C_{60} monoanion radical, we are trying to make further study by using more purified powder sample.

There still remain some questions such as the identification of the radical species existing in the pristine C_{60} powder and the formation mechanism of the C_{60} monoanion in the powder. In addition to these, the various studies on the radical processes of the C_{60} organoderivatives and host-guest compounds by radiolysis are in progress.

References and Notes

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