Bull. Chem. Soc. Jpn., ***69***, *2167—2171 (1996)*

Photoinduced Electron Transfer from Cyclic Organogermanium Compounds to C_{60} Studied by Laser Flash Photolysis

Osamu Ito,* Yoshiko Sasaki,† Akira Watanabe, and Kunio Mochida††

Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai 980-77

†Shokei Girl's High School, Hirose-machi, Aoba-ku, Sendai 980

††Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1, Mejiro, Tokyo 171

(Received February 13, 1996)

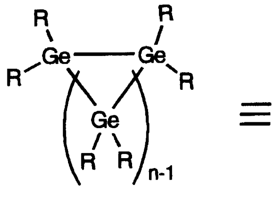
The electron transfer from cyclic organogermanium compounds to photo-excited C_{60} in benzonitrile solution has been investigated by the 532 nm-laser flash photolysis with observation of the transient absorption bands in the near-IR region. The transient absorption band of the C_{60} triplet state ($^{T}C_{60}{}^{*}$) appeared at 730 nm immediately after nanosecond laser exposure. With the decay of $^{T}C_{60}{}^{*}$, the absorption bands of the radical anion of C_{60} appeared at 1070 nm, showing that the electron transfer takes place from organogermanium compounds to $^{T}C_{60}{}^{*}$. The efficiencies and rates of the electron-transfer reactions vary with ring size of the germanium compounds.

It has been reported that photoexcited fullerenes act as good electron acceptors in the presence of electron donors such as aromatic amines and aliphatic amines.[1—8] In the case of C_{60} and C_{70}, the initial steps of the photoinduced electron-transfer reactions have been investigated by photochemical techniques such as transient absorption spectroscopy by measuring the quenching rates of the triplet states of C_{60} and C_{70} in the visible regions. By these methods, it was found that the electron transfer takes place via the triplet state of C_{60} ($^{T}C_{60}{}^{*}$) and C_{70} ($^{T}C_{70}{}^{*}$) in polar solvents.[4,5] In our previous papers, we reported that the observation of the transient absorption spectra in the near-IR region was useful to confirm the electron transfer of these fullerenes, because the absorption band of the anion radical of C_{60} ($C_{60}{}^{-\bullet}$) could be observed in this region.[9,10] From the rise of $C_{60}{}^{-\bullet}$, the participation of the singlet state or exciplex was confirmed in addition to the participation of $^{T}C_{60}{}^{*}$ to the electron transfer.

For polysilane and polygermane with degree of polymerization of 30—50 as donors,[11,12] we observed that photoinduced electron transfer took place producing their cation radicals and $C_{60}{}^{-\bullet}$. On the other hand, for the low-molecular-weight analogues such as disilane and digermane, the photoinduced electron transfer to C_{60} was not observed. In this report, we examine whether cyclic organogermanium compounds with low ionization potentials (IP's)[13—15] act as photoinduced electron donors with respect to C_{60} or not. The germanium compounds used in this study are shown in Scheme 1. We expected that the ringsize might affect the efficiency and rate of the electron transfer.

Experimental

C_{60} of 99.9% purity was obtained from Texas Fullerenes Corp. Cyclic organogermanium compounds shown in Scheme 1 were prepared in the manner described elsewhere.[16—18] The C_{60} and organogermanes were dissolved in benzonitrile. In the case of $(Ph_2Ge)_4$, benzene and benzonitrile solvent mixture [1/1 (volume ratio)] was used because of low solubility of $(Ph_2Ge)_4$ in benzonitrile. The solution was deaerated with Ar bubbling before measurements.



cyclo-$(R_2Ge)_n$
$n = 3, 4, 5, 6$
R; Me, *i*-Pr, Ph, and Mes
(Mes:2,4,6-trimethylphenyl)

Scheme 1.

The solution was excited by a Nd : YAG laser (Quanta-Ray, GCR-130, 6 ns fwhm) at 532 nm. A pulsed xenon flash lamp (Tokyo Instruments, XF80-60, 15 J, 60 ms fwhm) was used for the probe beam, which was detected with a Ge-APD module (Hamamatsu, C5331-SPL) after passing through the photochemical quartz vessel (10 mm × 10 mm) and a monochromator (Ritsu, MC-10N).[11] The output from Ge-APD was recorded with a digitizing oscilloscope (HP 54510B, 300 MHz). The steady-state UV-visible absorption spectra were recorded with a Hitachi U-3400 spectroscope. All experiments were done at 20 °C.

Results and Discussion

Figure 1 shows the transient absorption spectra in the near-IR region obtained by the laser flash photolysis of C_{60} with 532-nm light in the presence of *cyclo*-$[(i\text{-Pr})_2Ge]_4$ (0.01 $mol\,dm^{-3}$) in benzonitrile. The transient absorption band at 730 nm appearing immediately after laser exposure is attributed to the triplet–triplet absorption band of $^{T}C_{60}{}^{*}$.[19—22] With the decay of $^{T}C_{60}{}^{*}$, new absorption bands appeared in the region of 950—1200 nm. The absorption band at 1070

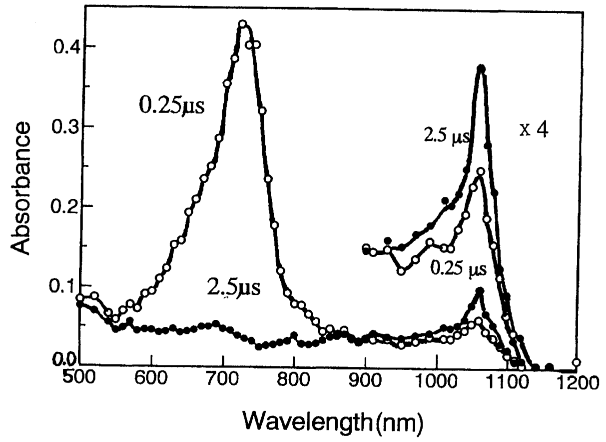


Fig. 1. Transient absorption spectra obtained by 532 nm-laser flash photolysis of C_{60} (2.5×10^{-4} mol dm^{-3}) in the presence of *cyclo*-[(*i*-Pr)$_2$Ge]$_4$ (10^{-2} mol dm^{-3}) in deaerated benzonitrile. (○) 0.25 μs, (●) 2.5 μs.

nm is characteristic of $C_{60}{}^{-\bullet}$.[9,10] The appreciable absorption band due to the cation radical of *cyclo*-[(*i*-Pr)$_2$Ge]$_4$ was not observed in the wavelength region in Fig. 1.

The observed time-profiles of the absorption bands are shown in Fig. 2. The decay of $^{T}C_{60}^{*}$ at 730 nm is accelerated in the presence of *cyclo*-[(*i*-Pr)$_2$Ge]$_4$ (0.01 mol dm^{-3}). The absorption intensity of $C_{60}{}^{-\bullet}$ at 1070 nm increases until about 1 μs accompanied by the decay of $^{T}C_{60}{}^{*}$. From these rises and decays, it is evident that $C_{60}{}^{-\bullet}$ is produced via $^{T}C_{60}{}^{*}$ which accepts the electron from *cyclo*-[(*i*-Pr)$_2$Ge]$_4$ as shown in Scheme 2. The rate constant (k_{fet}) of the forward electron- transfer reaction from *cyclo*-[(*i*-Pr)$_2$Ge]$_4$ to $^{T}C_{60}{}^{*}$ was evaluated from the rise-curve of $C_{60}{}^{-\bullet}$ to be 3.5×10^{8} mol^{-1} dm^{3} s^{-1}, which is in agreement with the value evaluated from the decay curve of $^{T}C_{60}{}^{*}$ (3.4×10^{8} mol^{-1} dm^{3} s^{-1}) within an estimation error of ±5%. In Scheme 2, the interaction of C_{60} with organogermanium compounds in the ground state was not taken into consideration, because no appreciable change was observed in the absorption bands of C_{60} on mixing with organogermanium compounds except *cyclo*-(Mes$_2$Ge)$_3$.

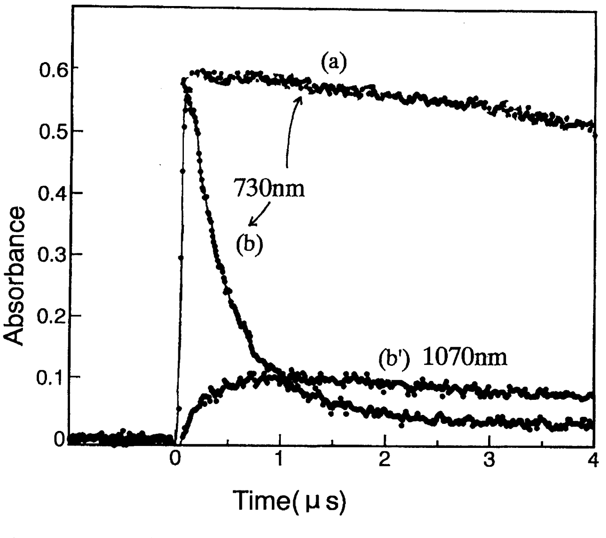
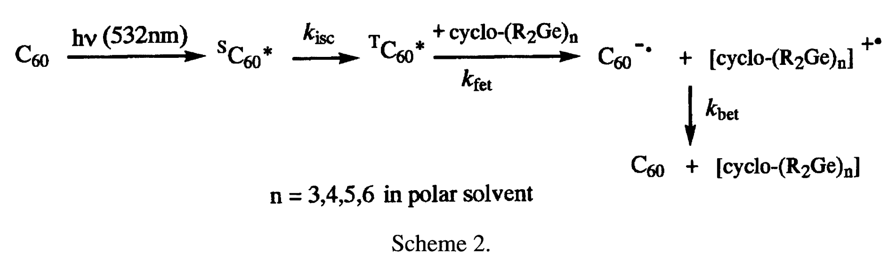


Fig. 2. The absorption intensity-time profiles obtained by 532 nm-laser flash photolysis of C_{60} (2.5×10^{-4} mol dm^{-3}) in deaerated benzonitrile. (a) In the absence and (b) in the presence of *cyclo*-[(*i*-Pr)$_2$Ge]$_4$ (10^{-2} mol dm^{-3}) at 730 nm and (b′) at 1070 nm.

For laser excitation of C_{60} in the presence of *cyclo*-(Me$_2$Ge)$_5$ or *cyclo*-(Me$_2$Ge)$_6$, $C_{60}{}^{-\bullet}$ appeared similarly with the decay of $^{T}C_{60}{}^{*}$ in benzonitrile. The k_{fet}'s evaluated from the decay rates of $^{T}C_{60}{}^{*}$ are summarized with the IP of germanium compounds in Table 1. The efficiencies of $C_{60}{}^{-\bullet}$ formation via $^{T}C_{60}{}^{*}$ were evaluated from the maximum concentration of $C_{60}{}^{-\bullet}$ and initial concentration of $^{T}C_{60}{}^{*}$ using observed absorbances and the reported molar extinction coefficients at 0.01 mol dm^{-3} of germanium compounds.[17,21,23,24] Since $[C_{60}{}^{-\bullet}]/[^{T}C_{60}{}^{*}]$ is dependent on the concentration of added germanium compounds, the efficiency of $C_{60}{}^{-\bullet}$ formation in Table 1 is not always same as the quantum yield for electron transfer via $^{T}C_{60}{}^{*}$. There was found a tendency for the efficiency of $C_{60}{}^{-\bullet}$ formation and the k_{fet} to decrease with Ge-ring size.

The back electron transfer rate was evaluated from the decay of $C_{60}{}^{-\bullet}$ after reaching the maximum intensity after the rise. The time-profile and the second-order plot for the decay of $C_{60}{}^{-\bullet}$ are shown in Fig. 3 for the reaction system of C_{60} and *cyclo*-[(*i*-Pr)$_2$Ge]$_4$. The slope of the second-order plot is referred to $k_{\text{bet}}/\varepsilon$, which was estimated to be 1.5×10^{6} cm^{-1} s^{-1}. On substituting the reported ε value at 1070 nm in a polar solvent (12000 mol^{-1} dm^{3} cm^{-1}),[23,24] the k_{bet} was calculated to be 1.8×10^{10} mol^{-1} dm^{3} s^{-1}. The k_{bet} thus evaluated was greater than the value calculated on assuming a diffusion-controlled limit (5×10^{9} mol^{-1} dm^{3} s^{-1}) by a factor of about 3. The deviation from the second-order decay kinetics as seen in insert of Fig. 3 indicates that other reactions may accompany the back electron transfer. In a later section, we will point out the adduct formation between $C_{60}{}^{-\bullet}$ and *cyclo*-[(*i*-Pr)$_2$Ge]$_4{}^{+\bullet}$ or its fragments.

In the case of *cyclo*-(Ph$_2$Ge)$_4$, because of its low solubility in benzonitrile, the photoinduced electron transfer reaction was examined in a mixed solvent of benzonitrile–benzene



Scheme 2.

Table 1. Efficiency of $C_{60}^{-\bullet}$ Formation by Photo-Induced Electron Transfer ($[C_{60}^{-\bullet}]/[^{T}C_{60}^{*}]$)$^{a)}$ and the Rate Constants for Forward (k_{fet} (via $^{T}C_{60}^{*}$)) and Backward Electron Transfer (k_{bet})$^{b)}$.

Ge-compounds$^{c)}$	IP$^{d)}$	Solvent$^{e)}$	$[C_{60}^{-\bullet}]$	k_{fet}	k_{bet}
	eV		$[^{T}C_{60}^{*}]$	mol^{-1} dm^{3} s^{-1}	mol^{-1} dm^{3} s^{-1}
c-[(Mes)$_2$Ge]$_3$	5.42	BN	(0.50)$^{f)}$	1.3×10^{9}	—$^{g)}$
c-[(i-Pr)$_2$Ge]$_4$	5.72	BN	0.23	3.4×10^{8}	$(1.8\times10^{10})^{h)}$
		BN : BZ (1 : 1)	0.14	2.0×10^{8}	$(3.6\times10^{10})^{h)}$
c-(Ph$_2$Ge)$_4$	5.80	BN : BZ (1 : 1)	0.10	1.9×10^{8}	—$^{g)}$
c-(Me$_2$Ge)$_5$	5.74	BN	0.10	4.3×10^{7}	2.2×10^{9}
c-(Me$_2$Ge)$_6$	5.85	BN	0.03	3.8×10^{7}	—$^{g)}$
Me–[Ph(Me)Ge]$_{32}$–Me	5.32	AN : BZ (1 : 1)	(0.30)$^{f)}$	2.3×10^{8}	—$^{i)}$

a) $[C_{60}^{-\bullet}]/[^{T}C_{60}^{*}]$ refers to $[C_{60}^{-\bullet}]_{max}/[^{T}C_{60}^{*}]_{initial}$ at [cyclic-(R$_2$Ge)$_n$]=10^{-2} mol dm^{-3} using the observed absorbances and ε values; ε of $^{T}C_{60}^{*}$ (16100 mol^{-1} dm^{3} cm^{-1}) and ε of $C_{60}^{-\bullet}$ (12100 mol^{-1} dm^{3} cm^{-1}).[17,21] $[C_{60}^{-\bullet}]/[^{T}C_{60}^{*}]$ is not same as quantum yield, because it depends on [cyclic-(R$_2$Ge)$_n$]. b) The k_{bet} values were calculated from k_{bet}/ε at 1070 nm. c) c-(R$_2$Ge)$_n$ refers to cyclic-(R$_2$Ge)$_n$. d) IP values are cited from Refs. 13 and 14. e) BN; benzonitrile, BZ; benzene, and AN; acetonitrile. f) For $cyclo$-[(Mes)$_2$Ge]$_3$, exciplex route is ca. 50% and triplet route is ca. 50%. For Me-[Ph(Me)Ge]$_{32}$–Me, the excited singlet route is 15% and triplet route is 85%.[12] g) The appreciable decay was not observed up to 20 μs. h) The reaction rates for other than back electron transfer reaction may be included. i) The absorption intensity of $C_{60}^{-\bullet}$ is too low to estimate k_{bet}/ε.

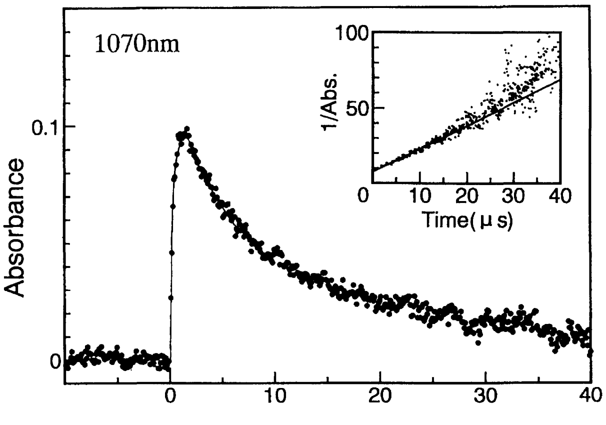


Fig. 3. Decay of the absorption band due to $C_{60}^{-\bullet}$ at 1070 nm in deaerated benzonitrile. Insert: The second-order plot for the decay of $C_{60}^{-\bullet}$.

(1 : 1 volume) having a permeability of 14.[25] To evaluate the solvent polarity effect, the photoinduced electron transfer of $cyclo$-[(i-Pr)$_2$Ge]$_4$ was examined in benzonitrile–benzene (1 : 1 volume), in which the k_{fet} was compatible with that in benzonitrile (Table 1). In the 4-member ring germanium compounds, the electron-transfer rates were not influenced much by solvent polarity with changing the permeability from 25.7 (benzonitrile) to 14 [benzonitrile-benzene (1 : 1 volume)]. The efficiency of the electron transfer, however, was slightly decreased in the less polar solvent (Table 1). In benzonitrile–benzene (1 : 1 volume), the k_{fet} for $cyclo$-(Ph$_2$Ge)$_4$ is similar to that of $cyclo$-[(i-Pr)$_2$Ge]$_4$. This implies that the phenyl substituents does not vary the electron-transfer rate compared with aliphatic groups such as isopropyl group.

For a cyclic germanium compound with a 3-member ring, $cyclo$-[(Mes)$_2$Ge]$_3$ was available as an electron donor.[16—18] When $cyclo$-[(Mes)$_2$Ge]$_3$ was mixed with C_{60} in benzonitrile solution, the characteristic purple solution of C_{60} changed into a faint brown solution, suggesting some interactions between C_{60} and $cyclo$-[(Mes)$_2$Ge]$_3$ in the ground state. The steady-state UV and visible spectra are shown in Fig. 4. The broadening of the absorption bands in the visible region and the absorption tail extending to near-IR region were observed on mixing them (Fig. 4B).

By laser flash photolysis of the solution containing C_{60} and $cyclo$-[(Mes)$_2$Ge]$_3$ with 532 nm, the characteristic transient absorption band due to $C_{60}^{-\bullet}$ appeared with the decay of the absorption band of $^{T}C_{60}^{*}$ at 730 nm as shown in Fig. 5.

The efficiency of the electron transfer evaluated by the relative intensity of the absorption band at 1070 nm to that at 730 nm for $cyclo$-[(Mes)$_2$Ge]$_3$ was the greatest among the organogermanium compounds examined in this study. The rise-time profile of $C_{60}^{-\bullet}$ seems to be two steps in Fig. 5; the initial fast rise and later slow rise. The initial fast electron transfer may take place via the exciplex that

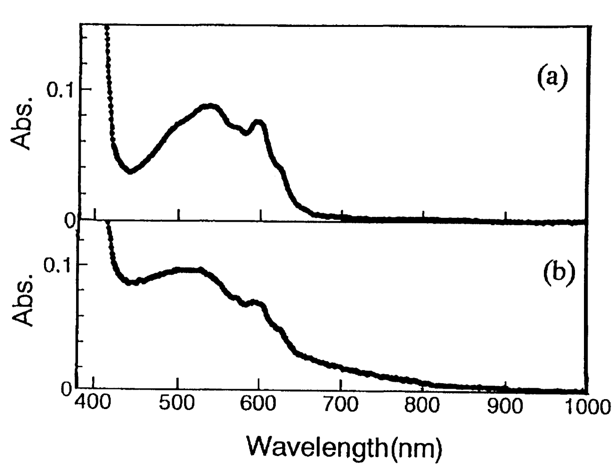


Fig. 4. Steady-state absorption spectra of (a) C_{60} (1.0×10^{-4} mol dm^{-3}), (b) C_{60} (1.0×10^{-4} mol dm^{-3}) and $cyclo$-[(Mes)$_2$Ge]$_3$ (2.5×10^{-3} mol dm^{-3}) before light-irradiation.

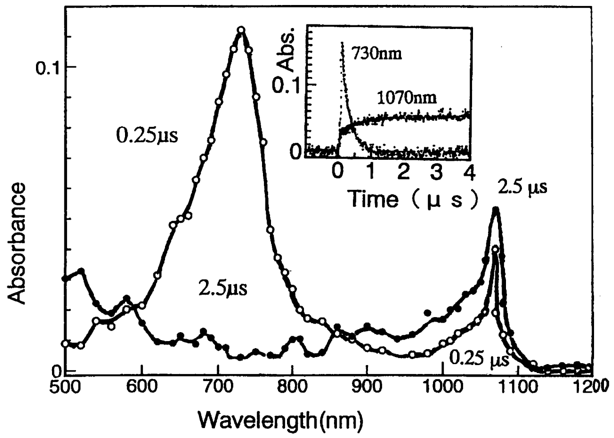


Fig. 5. Transient absorption spectra obtained by 532 nm-laser photolysis of C_{60} (2.5×10^{-4} mol dm^{-3}) and *cyclo*-[(Mes)$_2$Ge]$_3$ (2.5×10^{-3} mol dm^{-3}) in benzonitrile. (○) 0.25 μs, (●) 2.5 μs. Insert: Time profiles.

was formed by the excitation of the complex in the ground state (Scheme 3).[2,8] The latter slow electron transfer takes place via $^{T}C_{60}^{*}$, which is photoexcited from uncomplexed C_{60} (Scheme 2).

The decay rate of $^{T}C_{60}^{*}$ in the presence of *cyclo*-[(Mes)$_2$Ge]$_3$ was faster than other reaction systems such as *cyclo*-[(*i*-Pr)$_2$Ge]$_4$. The decay rate of $^{T}C_{60}^{*}$ by electron transfer with *cyclo*-[(Mes)$_2$Ge]$_3$ was compatible with the slow rise rate of $C_{60}^{-\bullet}$, although the initial rise curve of $C_{60}^{-\bullet}$ overlapped with the fast rise via exciplex. The k_{fet} evaluated from the decay rate of $^{T}C_{60}^{*}$ for *cyclo*-[(Mes)$_2$Ge]$_3$ was also the greatest among the k_{fet} evaluated in this study. By curve-resolving the rise curve of $C_{60}^{-\bullet}$, about a half of $C_{60}^{-\bullet}$ formation was attributed to the triplet route and the remaining half to the exciplex route in the case of *cyclo*-[(Mes)$_2$Ge]$_3$.

In Table 1, the efficiency of the $C_{60}^{-\bullet}$ formation vs. initial concentration of $^{T}C_{60}^{*}$ decreases with increase in the ring size, which is in accord with the increasing order of the IP values of the cyclic germanium compounds. The efficiency of the electron transfer increases with the increasing order of the k_{fet}. In the case of linear polygermane,[12] the photoinduced electron transfer takes place both via $^{S}C_{60}^{*}$ (probably exciplex) and via $^{T}C_{60}^{*}$; the former contribution is 15% and the later is 85% in a mixed solvent of acetonitrile and benzene (1 : 2 volume) with a permeability of about 14. For cyclic organogermanium compounds and polygermane, the IP value less than about 5.5 eV seems to be a criterion for the contribution of the singlet route or the exciplex route.

In the photoinduced electron-transfer reaction between C_{60} and *p*-phenylenediamine with low IP (6.8 eV),[26] the k_{fet} was evaluated to be about 5×10^{9} mol^{-1} dm^{3} s^{-1},[3] which is about 25 times greater than the observed k_{fet} for *cyclo*-[(*i*-Pr)$_2$Ge]$_4$. This suggests that the σ-electron donors such as cyclic germanium compounds and polygermane have different factors to control the electron-transfer rates and efficiency from that of aromatic π-donors. One of the factor is the bulkiness of the substituents along the σ-bond backbones, which hinders the penetration of the σ-electron to $^{T}C_{60}^{*}$.

The k_{bet}'s were not always estimated for all reaction systems, because of the difficulty in observing $C_{60}^{-\bullet}$-decay in the longer time scale than 50 μs in the near-IR region. The large k_{bet} from $C_{60}^{-\bullet}$ to *cyclo*-[(*i*-Pr)$_2$Ge]$_4^{+\bullet}$ may be attributed to the simultaneous side reactions, because this k_{bet} was greater than those of the $C_{60}^{-\bullet}$ and aromatic amine systems.[27,28] The stability of *cyclo*-[(*i*-Pr)$_2$Ge]$_4^{+\bullet}$ in polar solvents may be less than the aromatic amines.

After repeated laser photolysis of C_{60} in the presence of germanium compounds, the purple solution changed into a brown solution, indicating that reactions take place between them. One example is shown in Fig. 6, which indicates the appearance of new absorption bands at 425, 480, and 600 nm due to the new adduct formation.[29—31] The absorption region of the adduct is similar to C_{60}, suggesting that the π-system of C_{60} is not changed very much; this implies that one double bond or two double bonds of C_{60} served in the adduct formation. Because we used the photolysis light at 532 nm, which excites only C_{60}, it is certainly indicated that the adduct formation takes place after the electron transfer via the excited states of C_{60}. As successive reactions, it is considered either the direct coupling reaction occurs between $C_{60}^{-\bullet}$ and *cyclo*-[(*i*-Pr)$_2$Ge]$_4^{+\bullet}$ or the indirect coupling reaction occurs followed by the fragmentation reactions of *cyclo*-[(*i*-

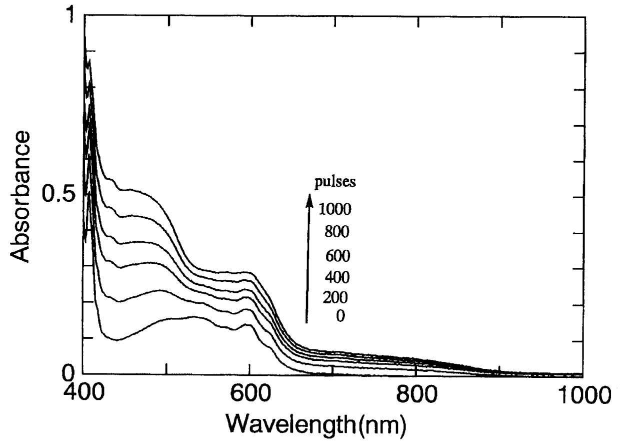
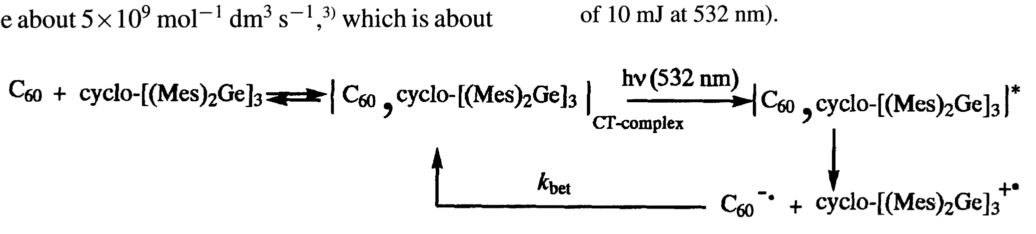


Fig. 6. Changes of absorption spectra of C_{60} (1.0×10^{-4} mol dm^{-3}) and *cyclo*-[(*i*-Pr)$_2$Ge]$_4$ (10^{-2} mol dm^{-3}) with irradiation (each spectrum is measured after 200 times-pulses of 10 mJ at 532 nm).



Scheme 3.

$Pr)_2Ge]_4^{+\bullet}$. Analysis of the structures of the products is in progress.

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