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# Photoinduced electron-transfer reaction between $C_{60}$ and cyclic silicon compounds

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## Abstract

Electron transfer from cyclic silicon compounds to photo-excited $C_{60}$ in polar solvents has been investigated by laser photolysis with observation of the transient absorption bands in the near-IR region. For three-, four- and five-membered cyclic silicon compounds in benzonitrile, the rise of the radical anion of $C_{60}$ [$C_{60}^{\bullet -}$] was observed with the rapid decay of the triplet state of $C_{60}$ [$^3C_{60}^*$], indicating that electron transfer takes place via $^3C_{60}^*$. The rate constant ($k_{et}$) and quantum yield ($\Phi_{et}$) of electron transfer decrease with an increase in the number of silicon units. The $k_{et}$ and $\Phi_{et}$ values of the cyclic silicon compounds are smaller than those of the corresponding cyclic germanium compounds; an especially prominent difference was observed for four-membered cyclic compounds. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Cyclic organosilicon compounds; $C_{60}$; Photoinduced electron transfer

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## 1. Introduction

It has been reported that photoexcited fullerenes such as $C_{60}$ and $C_{70}$ act as good electron acceptors in the presence of electron donors such as aromatic amines [1–7]. As electron donors, various organometallic compounds have also been employed; some of them form an adduct with $C_{60}$ after photoinduced electron transfer [8–10]. For three-membered cyclic silicon compounds, photo-adduct formation was reported for various fullerenes [8,11]. In the case of $C_{60}$, the initial steps of the photoinduced electron-transfer processes have been investigated by photochemical techniques such as transient absorption spectroscopy, by measuring the rise and decay of the radical anion of $C_{60}$ ($C_{60}^{\bullet -}$) in the near-IR region [1–7], in addition to the observation of quenching rates of the triplet states of $C_{60}$ ($^3C_{60}^*$) in the visible region [10b]. By these methods, it was found that the efficiency of electron transfer via $^3C_{60}^*$ increases with solvent polarity [12,13].

In our previous paper, we reported that the observation of the transient absorption spectra in the near-IR region was useful to confirm electron transfer to $^3C_{60}^*$ from cyclic germanium compounds [14]. Compared with the germanium compounds, it has been pointed out that the silicon compounds are poor electron donors, i.e. polysilane is a weaker electron donor than polygermane for $^3C_{60}^*$ [15,16]. In the present report, we examine whether or not cyclic silicon compounds act as electron donors with respect to $^3C_{60}^*$. The cyclic silicon compounds used in this study are shown in Scheme 1. We expect that the ring size might affect the efficiency and rate of electron transfer.

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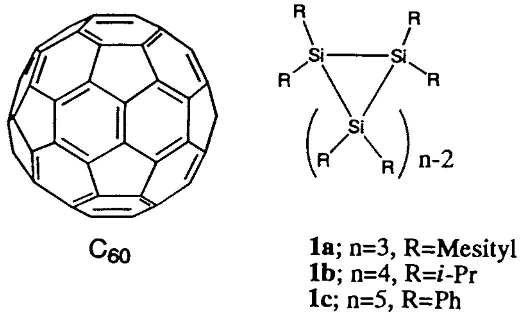


Scheme 1.

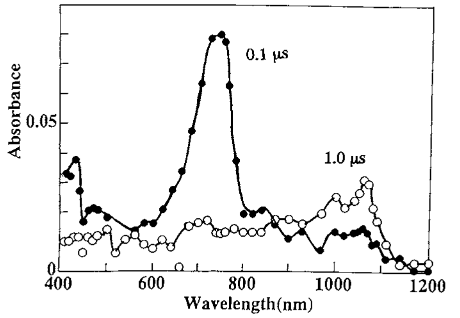


Fig. 1. Transient absorption spectra obtained by laser flash photolysis (532 nm) of $C_{60}$ ($0.15 \times 10^{-3}$ mol dm$^{-3}$) in the presence of *cyclo*-$(Mes_2Si)_3$ (**1a**; $5.0 \times 10^{-3}$ mol dm$^{-3}$) in deaerated benzonitrile.

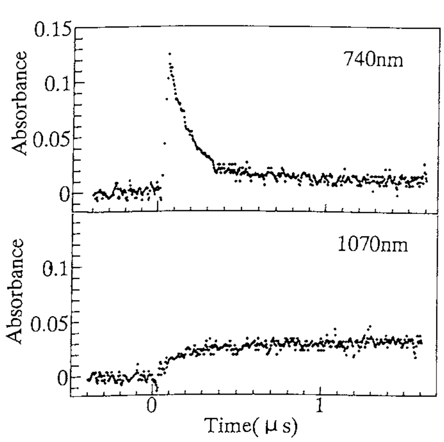
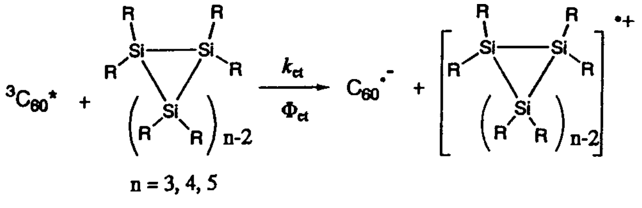


Fig. 2. Time profiles at 740 and 1070 nm for transient species obtained under the conditions shown in Fig. 1.



Scheme 2.

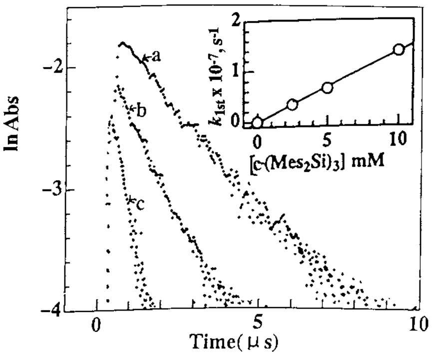


Fig. 3. First-order plots for decay at 740 nm. [**1a**; *cyclo*-$(Mes_2Si)_3$]; (a) 2.5, (b) 5.0, and (c) $10.0 \times 10^{-3}$ mol dm$^{-3}$. Inset: pseudo-first-order plot.

## 2. Results and discussion

Fig. 1 shows the transient absorption spectra in the visible and near-IR regions obtained by laser (532 nm) flash photolysis of $C_{60}$ in the presence of a cyclic trisilane **1a** ($5.0 \times 10^{-3}$ mol dm$^{-3}$) in benzonitrile. The transient absorption band at 740 nm appearing immediately (0.1 μs) after laser exposure is attributed to the triplet–triplet absorption band of $^3C_{60}^*$ [1–7]. With the decay of $^3C_{60}^*$, new absorption bands appeared in the region 950–1100 nm. This absorption band with a maximum at 1070 nm is characteristic of $C_{60}^{\bullet -}$ [17,18]. The absorption band at 420 nm may not be $^3C_{60}^*$, because the decay rate was slower than that at 740 nm. This is probably due to the cation radical of trisilane **1a**, which is unstable disappearing after 1 μs.

The observed time profiles of the absorption bands of $^3C_{60}^*$ and $C_{60}^{\bullet -}$ are shown in Fig. 2. In the absence of trisilane **1a**, appreciable decay of $^3C_{60}^*$ was not observed in 1 μs, because of its long lifetime (ca. 50 μs) [19]. In the presence of **1a** ($5.0 \times 10^{-3}$ mol dm$^{-3}$), the decay of $^3C_{60}^*$ at 740 nm was very much accelerated. With the decay of $^3C_{60}^*$, the absorption intensity of $C_{60}^{\bullet -}$ at 1070 nm increases up to about 0.5 μs. Since the rise of $C_{60}^{\bullet -}$ seems to be the mirror image of the decay of $^3C_{60}^*$, it is evident that $C_{60}^{\bullet -}$ is produced via $^3C_{60}^*$, which accepts one electron from trisilane **1a** as shown in Scheme 2. In Scheme 2, the interaction of $C_{60}$ with the cyclic silicon compounds in the ground state was not taken into consideration, because no appreciable change was observed in the absorption band of $C_{60}$ on mixing with compounds **1a** up to $10 \times 10^{-3}$ mol dm$^{-3}$.

First-order plots of the decay curve of $^3C_{60}^*$ are shown in Fig. 3. Each decay curve obeys first-order kinetics, giving a linear relationship between ln(Abs) and time. The slope yields the first-order rate constant ($k_{1st}$), which increases with the concentration of the cyclic trisilane **1a**. The pseudo-first-order plot gives the bimolecular quenching rate constant ($k_q$) for $^3C_{60}^*$ with **1a** to be $1.4 \times 10^9$ mol$^{-1}$ dm$^3$ s$^{-1}$ in benzonitrile.

Table 1
Oxidation potentials ($E_{ox}$) of *cyclo*-$(R_2Si)_{n-2}$ and *cyclo*-$(R_2Ge)_{n-2}$, free-energy changes for electron transfer from $^3C_{60}^*$ ($\Delta G°$), bimolecular quenching rate constants of $^3C_{60}^*$ ($k_q$), quantum yields of electron transfer via $^3C_{60}^*(\Phi_{et})$, and electron-transfer rate constants via $^3C_{60}^*$ ($k_{et}$) in benzonitrile

| | $E_{ox}$ [a] (V) | $\Delta G°$ [b] (kcal $mol^{-1}$) | $k_q$ [c] ($mol^{-1}$ $dm^3$ $s^{-1}$) | $\Phi_{et}$ [c] | $k_{et}$ [c] ($mol^{-1}$ $dm^3$ $s^{-1}$) |
|---|---|---|---|---|---|
| *cyclo*-$(Mes_2Si)_3$ [d] | 0.76 | −8.65 | $1.4\times10^9$ | 0.50 | $7.0\times10^8$ |
| *cyclo*-$(i\text{-}Pr_2Si)_4$ | 1.24 | 1.76 | $8.3\times10^6$ | 0.13 | $1.1\times10^6$ |
| *cyclo*-$(Ph_2Si)_5$ | 1.50 | 8.42 | $1.7\times10^7$ | 0.10 | $1.7\times10^6$ |
| *cyclo*-$(Mes_2Ge)_3$ [d] | 0.72 | −9.57 | $1.3\times10^9$ | 0.50 | $6.5\times10^8$ |
| *cyclo*-$(i\text{-}Pr_2Ge)_4$ | 1.09 | −1.04 | $3.4\times10^8$ | 0.23 | $7.8\times10^7$ |
| *cyclo*-$(Me_2Ge)_5$ [d] | | | $4.3\times10^7$ | 0.10 | $4.3\times10^6$ |

[a] $E_{ox}$ values in $CH_2Cl_2$ vs. SCE.
[b] $\Delta G°$ in benzonitrile.
[c] Each value contains estimation error of ± 5%.
[d] Mes = mesityl group and Me = methyl group.

On laser excitation of $C_{60}$ in the presence of cyclic tetrasilane **1b** or cyclic pentasilane **1c**, the transient absorption band due to $C_{60}^{\bullet-}$ appeared with the decay of $^3C_{60}^*$ in benzonitrile. The $k_q$ values evaluated from the decay rate of $^3C_{60}^*$ are summarized in Table 1. The $k_q$ value for **1a** is quite large ($1.4\times10^9$ $mol^{-1}$ $dm^3$ $s^{-1}$); on the other hand, the $k_q$ values for **1b** or **1c** are as small as about $10^7$ $mol^{-1}$ $dm^3$ $s^{-1}$. This trend can be interpreted on the basis of the oxidation potentials of **1a**, **1b** and **1c** [20–24] as listed in Table 1.

The efficiency of $C_{60}^{\bullet-}$ formation via $^3C_{60}^*$ was evaluated from the maximum concentration of $C_{60}^{\bullet-}$ and initial concentration of $^3C_{60}^*$ in each time profile. The observed absorption intensities can be converted into the concentrations by employing their reported molar extinction coefficients [25]. The efficiencies ($[C_{60}^{\bullet-}]_{max}/[^3C_{60}^*]_{max}$) are plotted against **1a**, **1b** and **1c** as shown in Fig. 4. Each plot shows the saturation curve; the limiting values yield the quantum yields ($\Phi_{et}$) for electron transfer via $^3C_{60}^*$ [26]. The $\Phi_{et}$ value decreases with the increase in the ring size (Table 1). The rate constant for electron transfer via $^3C_{60}^*$ ($k_{et}$) can be evaluated from the relation $k_{et} = \Phi_{et} \times k_q$ [26]. These $k_{et}$ values are also listed in Table 1; with increasing ring size, the $k_{et}$ values decrease more drastically than the $k_q$ values.

The time profile of $C_{60}^{\bullet-}$ over a longer time scale is shown in Fig. 5 for tetrasilane $\mathbf{1b}^{\bullet+}$. The back electron-transfer rate constant ($k_{bet}$) was evaluated from the decay of $C_{60}^{\bullet-}$ after reaching the maximum intensity. The second-order plot for the decay of $C_{60}^{\bullet-}$ shows a linear relation in the initial stage; the slope of the second-order plot is referred to as $k_{bet}/\varepsilon$. On substituting the reported $\varepsilon$ value at 1070 nm in a polar solvent (12 000 $mol^{-1}$ $dm^3$ $cm^{-1}$) [6,25], the $k_{bet}$ value was calculated as follows; for **1a**, $k_{bet} = 2.7\times10^9$ $mol^{-1}$ $dm^3$ $s^{-1}$ and for **1b**, $k_{bet} = 3.8\times10^9$ $mol^{-1}$ $dm^3$ $s^{-1}$. For **1c**, appreciable decay of $C_{60}^{\bullet-}$ was not observed, because of the low absorption intensity of $C_{60}^{\bullet-}$. The $k_{bet}$ values for **1a** and **1b** thus evaluated are slightly smaller than the diffusion-controlled limit ($k_{diff} = 5\times10^9$ $mol^{-1}$ $dm^3$ $s^{-1}$ in benzonitrile) [27].

In the later stage, the decay of $C_{60}^{\bullet-}$ slowed down. This behavior corresponds to the deviation from second-order decay kinetics as seen in the inset of Fig. 5. This implies that a part of the cation radical of **1b** was consumed independently by the reactions other than back electron transfer from $C_{60}^{\bullet-}$.

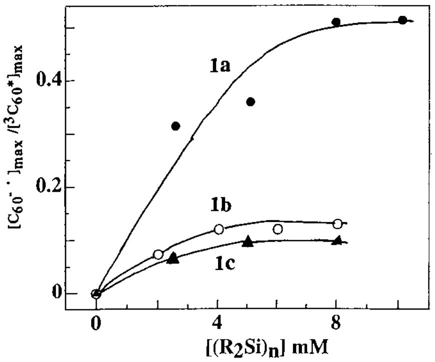


Fig. 4. Dependence of electron-transfer efficiency via $^3C_{60}^*$ ($[C_{60}^{\bullet-}]_{max}/[^3C_{60}^*]_{max}$) on the concentration of silicon compounds. **1a**; *cyclo*-$(Mes_2Si)_3$, **1b**; *cyclo*-$(i\text{-}Pr_2Si)_4$, and **1c**; *cyclo*-$(Ph_2Si)_5$.

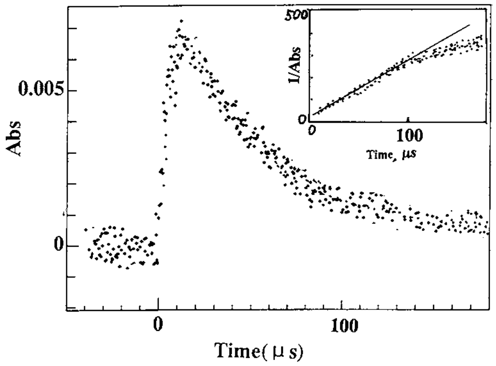


Fig. 5. Long time-scale decay of $C_{60}^{\bullet-}$ produced by electron transfer from *cyclo*-$(i\text{-}Pr_2Si)_4$ (**1b**) in deaerated benzonitrile. Inset: second-order plot.

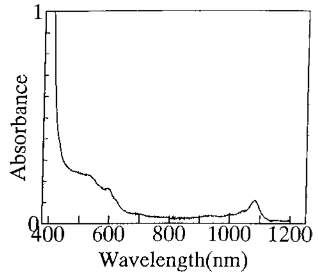
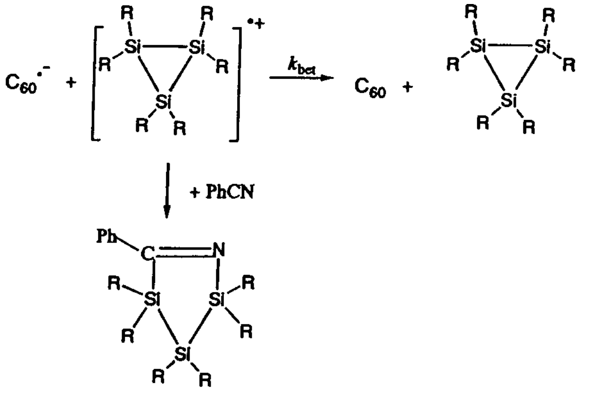


Fig. 6. Steady-state UV–vis spectral changes after repeated laser photolysis of $C_{60}$ ($0.15 \times 10^{-3}$ mol dm$^{-3}$) in the presence of *cyclo*-$(Mes_2Si)_3$ (**1a**; $5 \times 10^{-3}$ mol dm$^{-3}$) in deaerated benzonitrile.



Scheme 3.

The steady-state UV–vis spectrum after repeated 532 nm irradiation of $C_{60}$ in the presence of **1a** in deaerated benzonitrile is shown in Fig. 6. In the region 550–650 nm, the characteristic absorption shape of $C_{60}$ remains; however, the absorption band of $C_{60}{}^{\bullet -}$ appears at 1080 nm. The observation of the persistent $C_{60}{}^{\bullet -}$ absorption band implies that a part of the cation radical of **1a** was consumed by reactions other than back electron transfer. For this reaction, the ring-opening reaction and/or dimerization reaction of **1a**$^{\bullet +}$ can be considered. In the UV–vis spectrum, the characteristic band of the mono-adduct with $C_{60}$, which would be anticipated at 700 nm, was not observed.

The mass spectrum of the photo-irradiated solution did not give any appreciable peak in the region over $m/z = 720$, which coincides with the difficulty in forming the mono-adduct between $C_{60}{}^{\bullet -}$ and **1a**$^{\bullet +}$. On the other hand, the peak corresponding to $[(Mes_2Si)_3 + PhCN]$ was found, indicating that reaction between **1a**$^{\bullet +}$ and the benzonitrile solvent takes place. The decay behavior of $C_{60}{}^{\bullet -}$ suggests the reaction shown in Scheme 3, in which the high reactivity of benzonitrile with the cation radical of cyclic silicon compounds was proposed in our previous paper [28].

In our previous paper [14], we reported that photoinduced electron-transfer takes place from cyclic germanium compounds to $C_{60}$. In Table 1, both $\Phi_{et}$ and $k_{et}$ values of *cyclo*-$(Mes_2Si)_3$ are similar to those of *cyclo*-$(Mes_2Ge)_3$. The $\Phi_{et}$ and $k_{et}$ values of *cyclo*-$(Ph_2Si)_5$ are also similar to those of *cyclo*-$(Me_2Ge)_5$, although the $k_{et}$ value of the former is smaller by a factor of ca. 1/2. The $\Phi_{et}$ and $k_{et}$ values of *cyclo*-$(i\text{-}Pr_2Si)_4$ are quite smaller than those of *cyclo*-$(i\text{-}Pr_2Ge)_4$, which can be interpreted on the basis of the oxidation potentials. In the cyclic tetragermanium compounds, the $\Phi_{et}$ and $k_{et}$ values of *cyclo*-$(i\text{-}Pr_2Ge)_4$ were similar to those of *cyclo*-$(Ph_2Ge)_4$, which suggests that the difference between the aromatic and aliphatic substituent is small [14]. For silicon compounds, it is also presumed that the observed differences in the present study can be attributed to the effects of the ring size, but not to the substituent effect.

## 3. Experimental

$C_{60}$ of 99.9% purity was obtained from Texas Fullerenes. The cyclic silicon compounds shown in Scheme 1 were prepared in the manner described in the literature [20–24]. $C_{60}$ and the silicon compounds were dissolved in benzonitrile. The solution was deaerated with the silicon compounds bubbling before measurements were recorded.

The $C_{60}$ solution was excited by a Nd:YAG laser (6 ns fwhm) at 532 nm. For short-time-scale measurements (50 ns–5 μs), a pulsed xenon flash lamp was used as 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. For long-time-scale measurements (10–200 μs), an InGaAs detector (Hamamatsu) was used to monitor the continuous light. The steady-state UV–vis absorption spectra were recorded with a JASCO spectrophotometer. All experiments were carried out at 20°C.

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