Radical Cation of Dodecamethylcyclohexagermane Generated by Pulse Radiolysis

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The radical cation of dodecamethylcyclohexagermane, $(Me_2Ge)_6$, generated by pulse radiolysis technique showed two transient absorption bands at 310 and 410 nm. These transient peaks were quenched with triphenylamine as a radical cation scavenger.

The group 14 element (silicon, germanium, and tin) cyclic oligomers are excellent electron donors.[1-3] As an electron-rich species, they are readily oxidized by outer-sphere electron transfer to various oxidants in solution.[4-7] Although the existence of radical cations of group 14 element cyclic oligomers as direct products has been postulated, there have been few reports regarding radical cations of group 14 element cyclic oligomers owing to their extremely short lifetimes.[8] It is very important to establish unambiguously the existence of radical cations of group 14 element cyclic oligomers by direct observation and to study their properties. In this paper, we give the first report of the generation of the radical cation of a cyclic oligogermane, dodecamethylcyclohexagermane $(Me_2Ge)_6$ (**1**) (Ip=7.68 eV),[9] by pulse radiolysis technique.

Cyclohexagermane **1** used for the pulse radiolysis study was synthesized by the Wurtz coupling reaction of dimethyldichlorogermane (Me_2GeCl_2) with lithium metal in THF and was purified by repeated recrystallization from ethanol.[10] The purity of **1** was confirmed by NMR and GC-MS analysis. The radical cation of **1** in CH_2Cl_2 was generated by using the linear accelerator system (LINAC) (28 MeV single pulse electron beam, 2 ns pulse width).

The transient absorption spectra of **1** (ca. 0.1 M) in CH_2Cl_2 at 293 K immediately and at 100 ns after an electron pulse are shown in Figure 1. These differences in spectra before and after pulse irradiation, therefore, represent the newly produced cyclic oligogermane radical cation species.

Radical cations of cyclic oligogermanes are produced by the reaction with the radical cation of CH_2Cl_2 generated by electron pulse radiation.[11] Pulse radiolysis of the CH_2Cl_2 solution of **1** gave a sharp transient peak at 310 nm with a subband at 410 nm, as shown in Figure 1. In Figure 2, the time profiles of the absorption bands observed under the conditions described in Figure 1 are shown. Absorption intensities of the radical cation of **1** at 310 and 410 nm decay single-exponentially with a lifetime of ca. 0.23 μs. Thus, both bands are due to the radical cation of **1**.

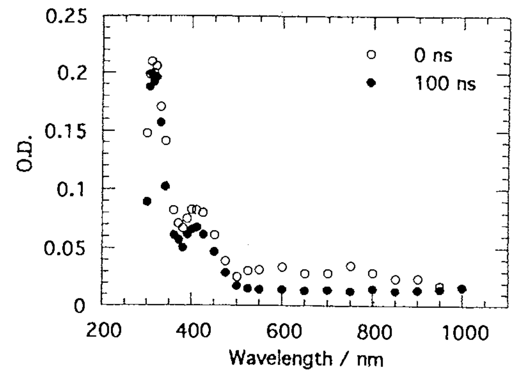

Figure 1. Transient absorption spectra of radical cation of $(Me_2Ge)_6$ immediately and at 100 ns after pulse.

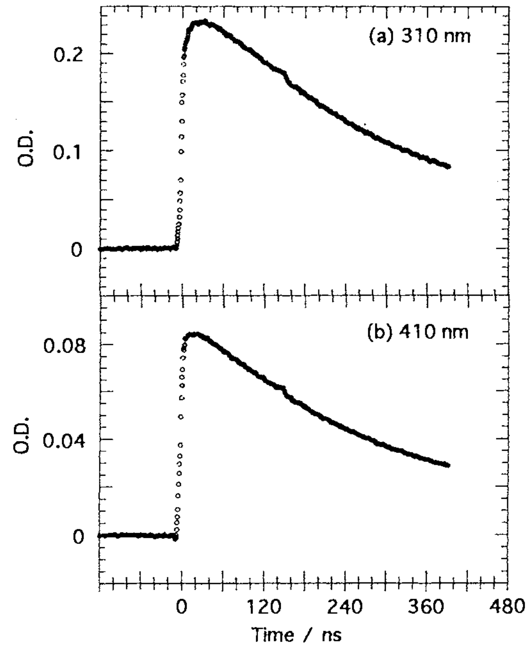

Figure 2. The absorption profile recorded at (a) 310 and (b) 410 nm representing the decay of the transients for $(Me_2Ge)_6$ in CH_2Cl_2.

$$\underset{\mathbf{1}}{(Me_2Ge)_6} \xrightarrow[CH_2Cl_2]{\text{pulse radiolysis}} \mathbf{1}^{+\bullet} \qquad (1)$$

$$\mathbf{1}^{+\bullet} + Ph_3N \xrightarrow{k_{et}} \mathbf{1} + Ph_3N^{+\bullet} \qquad (2)$$

On addition of a radical cation scavenger, triphenylamine (Ph_3N) (Ip=6.86 eV),[12] the transient peak at 410 nm disappeared, resulting in the build-up of a transient peak around 360 nm. An isosbestic point was observed at 420 nm as shown in Figure 3. The absorption band at 360 nm is a characteristic band of the radical cation of triphenylamine.[13] This result confirms that the transient peak at 410 nm is due to the radical cation of **1**. The

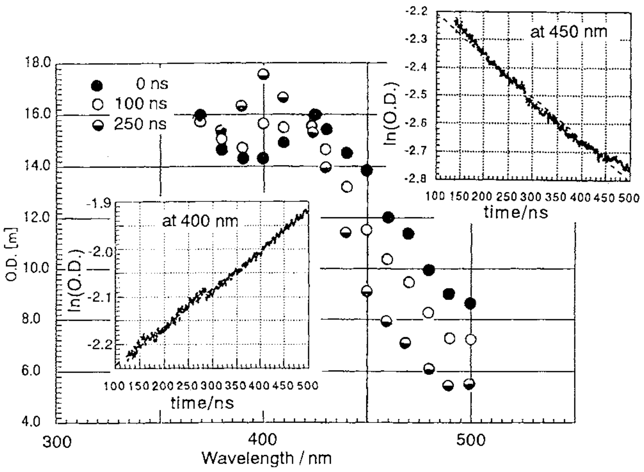

Figure 3. Transient absorption spectra of radical cation of $(Me_2Ge)_6$ in the presence of Ph_3N (10 mM). Insert: First-order plot of (a) decay of radical cation of $(Me_2Ge)_6$ at 450 nm; (b) appearance of radical cation of Ph_3N at 400 nm.

transient peak at 310 nm was overlapped with that of the radical cation of Ph_3N. Both absorption bands ascribed to the radical cation of **1** have longer wavelengths compared with those of neutral **1** (235.0 and 250 nm).

The reaction rate constant of the electron transfer step (k_{et}) was determined by the decay rate of radical cation of **1** at 450 nm under various concentrations of Ph_3N. The decay of the radical cation of **1** obeys the first-order kinetics as shown in the insert in Figure 3. From the slope of the line of pseudo-first-order rate constant against the concentration of Ph_3N, the second-order rate constant for the quenching reaction of the radical cation of **1** with Ph_3N was evaluated to be 8.1×10^7 $M^{-1}s^{-1}$. The back-electron-transfer reaction from radical cation of Ph_3N to **1** seems to be slow.

So far as we are aware, this work represents the first observation of the radical cation of $(Me_2Ge)_6$. The present finding should reveal the excited state and σ electron delocalization of the group 14 element cyclic oligomers.

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