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Electronic spectra of radical ions of cyclic polysilanes

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Abstract

The absorption spectra of the radical ions of cyclic polysilanes, $(Me_2Si)_n$, where $n = 5$, 6, and 7, formed by γ-irradiation have been recorded for rigid matrices at 77 K. The absorption maxima of radical anions of the cyclic polysilanes showed a red shift from 670 to 900 nm with increasing ring size. $(Me_2Si)_5^{\cdot+}$ shows a broad single band at 720 nm, whereas $(Me_2Si)_6^{\cdot+}$ shows two bands in the wavelength region from 500 to 1000 nm. A single peak is observed for $(Me_2Si)_7^{\cdot+}$ at 900 nm. Ring-size reduction of the cyclic polysilanes with production of dimethylsilylene was not observed for the radical ions below 173 K, in sharp contrast to the behavior shown by the photoexcited states.

Introduction

Cyclic polysilanes have attracted much attention because of unique properties which distinguish them from saturated catenates of carbon [1]. Cyclic polysilanes resemble in the aromatic hydrocarbons, in that they show long-wavelength ultraviolet absorption [2], undergo one-electron reduction to radical anions [3], form charge-transfer complexes with π-acceptors [4], and have a low first ionization potential [5].

In a previous paper, we reported the absorption spectra of radical anions and cations of polysilastyrene, which were produced by γ-irradiation or by pulse electrons [6]. We have now extended the study to include cyclic polysilanes, $(Me_2Si)_n$, where $n = 5$, 6, and 7. West et al. have shown from the absorption spectroscopy measurement that the radical anions of $(Me_2Si)_5$ and $(Me_2Si)_6$ are produced in tetrahydrofuran by electrolytic reduction at low temperature [3]. The

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seven-membered ring $(\mathrm{Me_2Si})_7$, however, does not undergo electrolytic reduction to the anion radical. On the other hand, chemical reduction of $(\mathrm{Me_2Si})_6$ and $(\mathrm{Me_2Si})_7$ with NaK gives only the anion radical of the five-membered ring, $(\mathrm{Me_2Si})_5^{\overset{\cdot}{-}}$ [1,3]. Moreover, electrolytic reduction of $(\mathrm{Me_2Si})_6$ at temperature above 173 K gave a mixture of $(\mathrm{Me_2Si})_6^{\overset{\cdot}{-}}$ and $(\mathrm{Me_2Si})_5^{\overset{\cdot}{-}}$. These results indicate that six- and seven-membered ring polysilanes on reduction are readily transformed into five-membered ring anion radicals whose absorption spectra have not yet been reported.

ESR measurement provides useful information on the nature of the radical ions. Several ESR studies have been reported for the radical anions and cations of the cyclic polysilanes [1,3,7–10]. The compounds $(\mathrm{Me_2Si})_5$ and $(\mathrm{Me_2Si})_6$ were reduced by an electrolytic method or with NaK and the ESR spectra were recorded. The ESR studies have shown that unpaired electrons of these cyclic anions are delocalized over the ring skeleton. ESR studies have also been reported for radical cations of cyclic polysilanes, which were produced by one-electron oxidation with $\mathrm{AlCl_3}$ [10]. For the radical cation system, only the radical cation of $(\mathrm{Me_2Si})_6$ gave an ESR spectrum at 193 K. The ESR spectra of the radical cations of $(\mathrm{Me_2Si})_5$ and $(\mathrm{Me_2Si})_7$ have not yet been observed.

In this study, we carried out the absorption spectroscopy in rigid matrices at low temperature in order to detect the radical anions and cations of $(\mathrm{Me_2Si})_n$, $n = 5$, 6, and 7, which were produced by γ-irradiation.

Experimental

The cyclic polysilanes, $(\mathrm{Me_2Si})_n$, where $n = 5$, 6, and 7 were synthesized by the method of Carberry and West [3]. The cyclic polysilanes were purified by preparative gas chromatography. The air-sensitive $(\mathrm{Me_2Si})_5$ was freshly collected immediately before use. The purity of the compounds was confirmed by GC-MS analysis. 2-Methyltetrahydrofuran (MTHF), n-butyl chloride (n-BuCl), and 3-methylpentane were purified by repeated distillation.

All sample solutions were prepared under vacuum. The solvents MTHF and n-BuCl were dehydrated with sodium metal and calcium hydride, respectively, and were distilled into Suprasil cells (optical path length, 2 mm) in vacuo. The samples were degassed several times under 1×10^{-5} Torr and the frozen solution was γ-irradiated with a dose of 1.2×10^{19} eV/g.h at 77 K. The changes in optical absorption induced by the irradiation and by subsequent warming were measured with a Hitachi 323 spectrophotometer. Photobleaching was carried out with a 500-W tungsten lamp.

The products were identified by GLC with a Hitachi G-3000 instrument with a 0.53 mm × 25 m capillary column containing methyl phenyl silicone.

Results and discussion

Radical anions and cations are selectively produced in specific solvents by radiolysis [11]. To produce the radical anion of an aromatic hydrocarbon, the hydrocarbon is dissolved in 2-methyltetrahydrofuran (MTHF, $\mathrm{C_5H_{10}O}$), frozen to a glassy solid at 77 K, and irradiated with γ-rays to induce the reactions as follows:

$$\mathrm{C_5H_{10}O} + \gamma \rightarrow \mathrm{C_5H_{10}O}^{\overset{\cdot}{+}} + \mathrm{e}^- \tag{1}$$

$$\mathrm{C_5H_{10}O}^{\overset{\cdot}{+}} + \mathrm{C_5H_{10}O} \rightarrow \mathrm{C_5H_{10}O \cdot H^+} + \cdot \mathrm{C_5H_9O} \tag{2}$$

$$\mathrm{e}^- + \mathrm{s} \rightarrow \mathrm{s}^{\overset{\cdot}{-}} \tag{3}$$

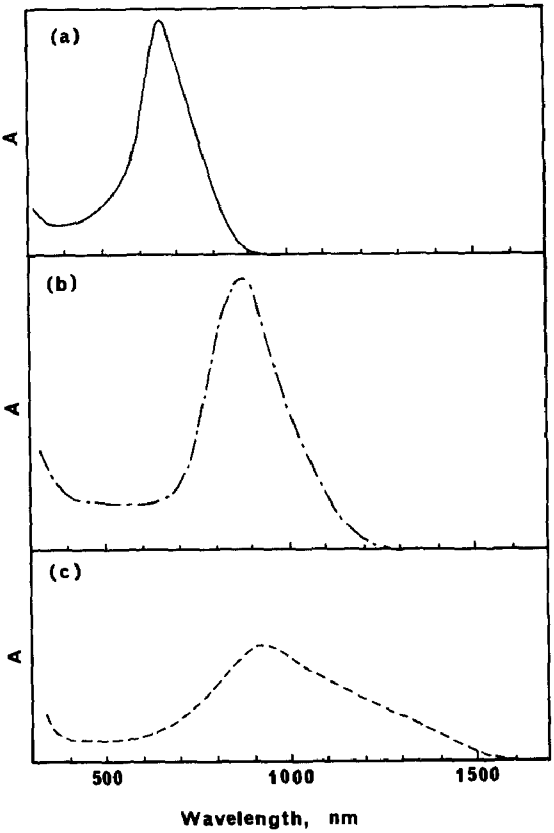

Fig. 1. Absorption spectra of cyclic polysilanes irradiated with a dose of 3×10^{19} eV/g at 77 K, in MTHF solutions (1×10^{-2} *M*); (a) $(Me_2Si)_5$, (b) $(Me_2Si)_6$, and (c) $(Me_2Si)_7$.

where e^- and s denote an electron and a solute molecule, respectively. Electrons released by reaction 1 travel through the bulk of the rigid solution until they find a solute molecule of sufficiently high electron affinity to yield the corresponding radical anion. Thus, solute anions are selectively produced in MTHF matrices.

On the other hand, the type of matrix molecules used for the generation of radical cations comprises alkyl halides (RX) such as n-butyl chloride (n-BuCl). The major processes that occur under irradiation are summarized as follows:

$$RX + \gamma \rightarrow RX^{+} + e^{-} \qquad (4)$$

$$e^{-} + RX \rightarrow R^{\cdot} + X^{-} \qquad (5)$$

$$RX^{+} + s \rightarrow s^{+} + RX \qquad (6)$$

where e denotes electrons and s, solute molecules. Solute anions are not formed because reaction 5, i.e., electron removal, predominates, and accordingly solute cations are selectively produced in n-BuCl matrices.

Figure 1 shows the absorption spectra of MTHF solutions containing 1×10^{-2} *M* cyclic polysilanes ((a) $(Me_2Si)_5$, (b) $(Me_2Si)_6$, and (c) $(Me_2Si)_7$) at 77 K irradiated with a dose of 3×10^{19} eV/g. From the above discussion, the spectra (a), (b), and (c) are assigned to the radical anions of $(Me_2Si)_5$, $(Me_2Si)_6$, and $(Me_2Si)_7$, respectively. The disappearance of these bands on addition of an electron scavenger such as n-BuCl, is consistent with the assignment. The absorption spectrum of $(Me_2Si)_5^{\cdot -}$ obtained by γ-irradiation is identical with the spectrum reported for $(Me_2Si)_5^{\cdot -}$, which was produced by electrolytic reduction [3]. Chemical reduction of $(Me_2Si)_5$ also gave the identical spectrum [3]. As seen in Figure 1, the absorption maxima of $(Me_2Si)_6^{\cdot -}$, and $(Me_2Si)_7^{\cdot -}$ show a very large red shift compared with the maximum of $(Me_2Si)_5^{\cdot -}$. Although the electrolytically reduced $(Me_2Si)_6^{\cdot -}$ is reported to have an absorption band at 425 nm [3], the band was not observed for the radical anion of $(Me_2Si)_6$ formed by γ-irradiation. Tagawa et al. similarly could not detect any distinct transient absorption bands in the 300–600 nm region for $(Me_2Si)_6^{\cdot -}$ produced by pulse radiolysis [12].

Irradiation with visible light ($\lambda > 600$ nm) decreases the absorption intensity of these radical anions. The decrease is due to photochemical detachment of electrons from the molecules. The photostimulated bleaching rate depends on the ring size; $(Me_2Si)_7^{\cdot -}$ was bleached readily within 1 min, the bleaching rate of $(Me_2Si)_5^{\cdot -}$ is very slow, the radical anion of $(Me_2Si)_5^{\cdot -}$, seemed stable even after photoirradiation for 30 min. $(Me_2Si)_6^{\cdot -}$ was bleached after 1–30 min. The periods required for complete bleaching is consistent their electron affinities [3]. As noted in the introductory part, $(Me_2Si)_6^{\cdot -}$ and $(Me_2Si)_7^{\cdot -}$ are very unstable in solution and convert to $(Me_2Si)_5^{\cdot -}$. At 77 K, both $(Me_2Si)_6^{\cdot -}$ and $(Me_2Si)_7^{\cdot -}$ were observed stable.

In order to follow the conversion process of $(Me_2Si)_7^{\cdot -}$ and $(Me_2Si)_6^{\cdot -}$ to $(Me_2Si)_5^{\cdot -}$, the samples were annealed at 100 K. At 100 K the blue radical anion of $(Me_2Si)_5^{\cdot -}$ remained stable, whereas $(Me_2Si)_6^{\cdot -}$ and $(Me_2Si)_7^{\cdot -}$ were found to disappear quickly. The associated absorption which grows at 670 nm was not observed. The conversion from $(Me_2Si)_6^{\cdot -}$ and $(Me_2Si)_7^{\cdot -}$ to $(Me_2Si)_5^{\cdot -}$ was not detected in our system, and suggests that the conversion from the six- or seven-membered ring radical anions to five-membered ones observed in electrolytic reduction and chemical reduction is not an exothermic unimolecular reaction but involves multistep processes.

The photochemical and thermal stabilities of the radical anions fall in the order: $(Me_2Si)_5^{\cdot -} > (Me_2Si)_6^{\cdot -} > (Me_2Si)_7^{\cdot -}$. It is inferred from this sequence that planarity of the molecules controls the stability of the radical anions. $(Me_2Si)_5^{\cdot -}$ is almost planar so that good overlap of orbitals on adjacent silicon atoms can take place to give an essentially π molecular orbital [1]. The π structure gives a stable radical anion molecule. The deviation from planarity increases in the six- and seven-membered rings, and decreases the electron affinity which destabilizes the radical anion state.

Radical cations of solute molecules are produced in irradiated n-BuCl by the reaction of a positive hole with a solute molecule [11]. Figure 2 shows the absorption spectra of n-BuCl solution containing 5×10^{-2} *M* of cyclic polysilanes ((a) $(Me_2Si)_5$, (b) $(Me_2Si)_6$, and (c) $(Me_2Si)_7$) at 77 K irradiated with a dose of 3×10^{19} eV/g. The absorptions disappear on addition of hole scavengers such as MTHF to the n-BuCl matrix. Therefore, the spectra a, b, and c are assigned to the radical cations of $(Me_2Si)_5$, $(Me_2Si)_6$, and $(Me_2Si)_7$, respecively. $(Me_2Si)_5^{\cdot +}$ shows a broad single band at 720 nm, whereas $(Me_2Si)_6^{\cdot +}$ shows two bands in the region from 500 to 1000 nm. A single peak is observed for $(Me_2Si)_7^{\cdot +}$ in the near infrared region. All of these spectra remained stable even after prolonged photoirradiation at 77 K. Upon thermal annealing, the absorptions of the greenish blue radical cation $(Me_2Si)_5^{\cdot +}$, of the blue radical cation $(Me_2Si)_6^{\cdot +}$ and of the colorless radical cation $(Me_2Si)_7^{\cdot +}$

disappeared at a similar rates. It seems that the thermal stabilities of these radical cations do not depend on the molecular structures of the cyclic polysilanes.

It is known that photolysis of $(Me_2Si)_6$ gives dimethylsilylene and $(Me_2Si)_5$, which in turn gives two more silylenes successively [13,14]. Ultraviolet irradiation of $(Me_2Si)_6$ in 3-methylpentane glass at 77 K produces dimethylsilylene which shows an absorption peak at 460 nm, and a lower cyclic polysilane $(Me_2Si)_5$ which was detected by gas chromatography. The generation of dimethylsilylene by irradiation with ultraviolet light was observed not only for $(Me_2Si)_6$, but also for $(Me_2Si)_7$. The photolysis of $(Me_2Si)_7$ in 3-methylpentane at 77 K, readily eliminates dimethylsilylene from the ring to give the lower homologues, $(Me_2Si)_5$ and $(Me_2Si)_6$ as determined from the product analysis. In the case of $(Me_2Si)_5$, however, the generation of dimethylsilylene by irradiation with ultraviolet light was less evident in the 3-methylpentane glass matrix at 77 K. The ease of photo-generation of dimethylsilylene depends on the size of cyclic polysilanes.

The γ-irradiated cyclic polysilanes ($(Me_2Si)_5$, $(Me_2Si)_6$, and $(Me_2Si)_7$) in MTHF, n-BuCl and 3-methylpentane at 77 K, respectively, on the other hand, showed no absorption at 460 nm expected for dimethylsilylene. The formation of a lower homologue, $(Me_2Si)_5$ or $(Me_2Si)_6$, was not detected by product analysis of a 3-methylpentane solution containing $(Me_2Si)_6$ or $(Me_2Si)_7$, respectively, that had been irradiated with 3×10^{19} eV/g at 77 K. These results indicate that dimethylsily-

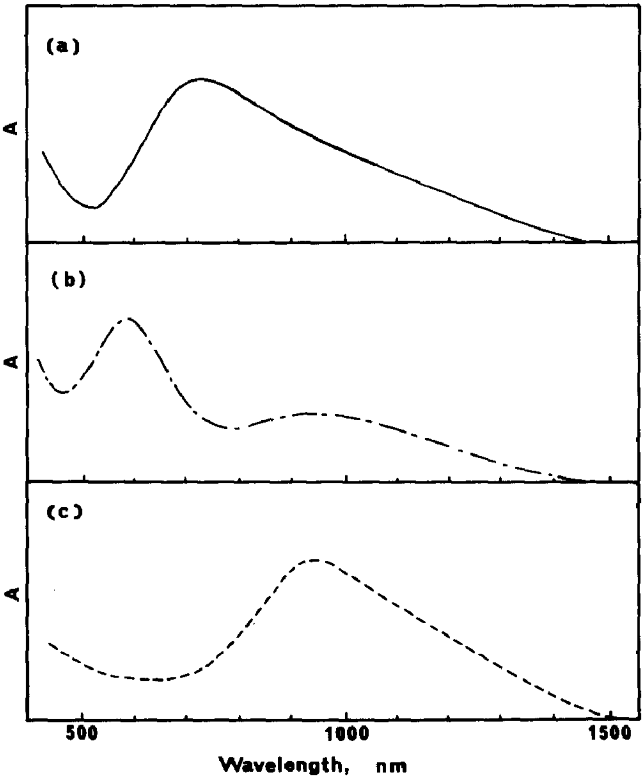

Fig. 2. Absorption spectra of cyclic polysilanes, irradiated with 3×10^{19} eV/g at 77 K, in n-BuCl solutions (5×10^{-2} *M*): (a) $(Me_2Si)_5$, (b) $(Me_2Si)_6$, and (c) $(Me_2Si)_7$.

lene is not produced from radical ions by unimolecular reaction, and the radiolysis process is different from that of photolysis. These results are also consistent with the fact that γ-irradiation of $(Me_2Si)_6$ did not generate dimethylsilylene in n-hexane solution at room temperature [15].

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