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Transient absorption spectroscopy of radical ions of rigid *anti*- and *syn*-tetrasilane

Shu Seki ^a, Kazumasa Okamoto ^a, Yoshinori Matsui ^a, Seiichi Tagawa ^{a,*},
Hayato Tsuji ^b, Akio Toshimitsu ^b, Kohei Tamao ^{b,*}

^a The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka, Ibaraki, Osaka 567-0047, Japan

^b Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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Abstract

Transient absorption spectra of ion radicals were observed for tetrasilanes with rigid *syn* or *anti* Si units by electron beam pulse radiolysis. Two transient absorption bands at 4.1 and 2.8 eV were clearly resolved for the anion radical of *syn*-tetrasilane, while for *anti*-tetrasilane, the anion radical produced a broad absorption band at 4.4 eV. Cation radicals of the tetrasilanes gave similar optical transitions at 3.6 and 2.1 eV for the *syn* form, and 3.8 eV for the *anti* form. The spectra for the ion radicals of *anti*-tetrasilane are identical to those of ion radicals of permethylated pentasilanes or hexasilanes, suggesting that the ion radicals of oligosilane without configurational constraint take an *anti* conformation. The unique spectra of ion radicals of *syn*-tetrasilane reflect the large gap between the second and third HOMO (LUMO) of neutral molecules, which is also induced by the configurational constraint.

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1. Introduction

Polysilanes and oligosilanes have elicited great interest as materials with interesting optical and electronic properties [1]. The attractive properties of polysilanes originate from the delocalization of σ -electrons along the Si skeleton [2–4]. The energy states of the σ -conjugated system, however, are strongly dependent on the conformations of the Si

skeletons because polysilanes have a saturated Si backbone without multiple bonds. Considerable research effort has been directed toward the polymerization of polysilanes with rigid rod-like Si backbones through modification of substitution patterns, as well as quantitative analysis of the correlation between the physical properties of the product and the backbone conformations in order to realize polysilanes with the ideal one-dimensional Si skeleton [5–10]. The *syn*-(S-Si₄) and *anti*-(A-Si₄) tetrasilanes investigated in the present study are conformational isomers that represent the shortest analogs of a polysilane backbone [11,12].

* Corresponding authors. Fax: +81-6-6876-3287 (S. Tagawa); Fax: +81-774-38-3186 (K. Tamao).

E-mail addresses: tagawa@sanken.osaka-u.ac.jp (S. Tagawa), tamao@scl.kyoto-u.ac.jp (K. Tamao).

The electronic structure of tetrasilanes has been investigated theoretically and experimentally based on changes in spectroscopic properties [13,14]. Photoelectron spectroscopy of conformationally constrained tetrasilanes has revealed a clear dependence on the dihedral angle of the Si chain, in agreement with the computed lowest ionization potentials.

Transient spectroscopy of radical ions by pulse radiolysis is a powerful technique for obtaining direct information on molecular orbitals higher than the LUMO (and lower than the HOMO). The method is employed in the present study to aid in the interpretation of the role of *anti* and *syn* Si units in intra-molecular charge transport along a linear Si skeleton in real polysilane systems.

2. Experimental

The synthesis of S-Si₄ and A-Si₄ has been described elsewhere [12]. The ultraviolet (UV) absorption spectra of S-Si₄ and A-Si₄ exhibit maxima at >210 and 238 nm, with ϵ values of $>1.3 \times 10^4$ and $3.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively [12]. Pulse radiolysis measurements were performed at room temperature using an L-band electron linear accelerator at the Institute of Scientific and Industrial Research, Osaka University. The compounds were dissolved in THF and CH₂Cl₂ at 0.011 and $6.8 \times 10^{-3} \text{ mol dm}^{-3}$ concentration, respectively. The solution was deaerated in a suprasil quartz cell having a 2-cm optical path and subsequently irradiated with an 8-ns single electron pulse. The details of the apparatus have been described elsewhere [15].

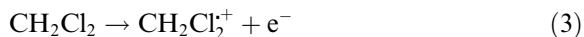
3. Results and discussion

The incident electron pulses in the solutions produce anion and cation radicals of the tetrasilanes in THF and CH₂Cl₂ as follows:

(in THF)



(in CH₂Cl₂)



where Si₄ is the solute tetrasilane molecule, e_{sol}[−] is the solvated electrons, and k_1 and k_2 are the reaction rate constants. The typically reported values of k_1 and k_2 are $>10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at 293 K [16], suggesting that the formation of anion radicals occurs within the instrumental function of the present system. The extinction coefficient of Si₄[−] (ϵ^-) is determined by the electron transfer reactions between Si₄[−] and pyrene (Py), and can be written as follows:



where the value of $\epsilon(\text{Py}^{\cdot-})$ is known to be $5.0 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ [17]. The values of k_3 are obtained as $5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for A-Si₄ and $5.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for S-Si₄. The value of ϵ^+ is determined relative to that of the other molecules estimated using the present system [18].

Fig. 1 shows transient absorption spectra recorded for the anion radicals of S-Si₄ and A-Si₄. An absorption band is observed in the UV region for A-Si₄[−], with a broad tail extending into the visible region. The maximum is no longer detectable, although a reasonably sharp absorption band is observed at 300 nm associated with a clear peak at 450 nm for S-Si₄[−]. The kinetic traces at 300 and 450 nm show the considerable faster decay by adding CCl₄ which is the typical quenching agent for anion radicals.

Cation radicals give similar changes in the spectra of both A-Si₄⁺ and S-Si₄⁺, as shown in Fig. 2. The absorption band in the visible region disappears in the spectra for A-Si₄⁺, whereas the peak is clearly observable at 600 nm for S-Si₄⁺.

The formation of ion radicals by reactions (2) and (4) induces a SOMO between the HOMO and LUMO. The SOMOs of anion and cation radicals originate from the LUMO (for anions) and HOMO (for cations) of neutral molecules. Two observed peaks: A[−] (300 nm) and B[−] (450 nm) for S-Si₄[−] are ascribed to SOMO → LUMO + 1 (4.1 eV) and SOMO → LUMO (2.8 eV) transi-

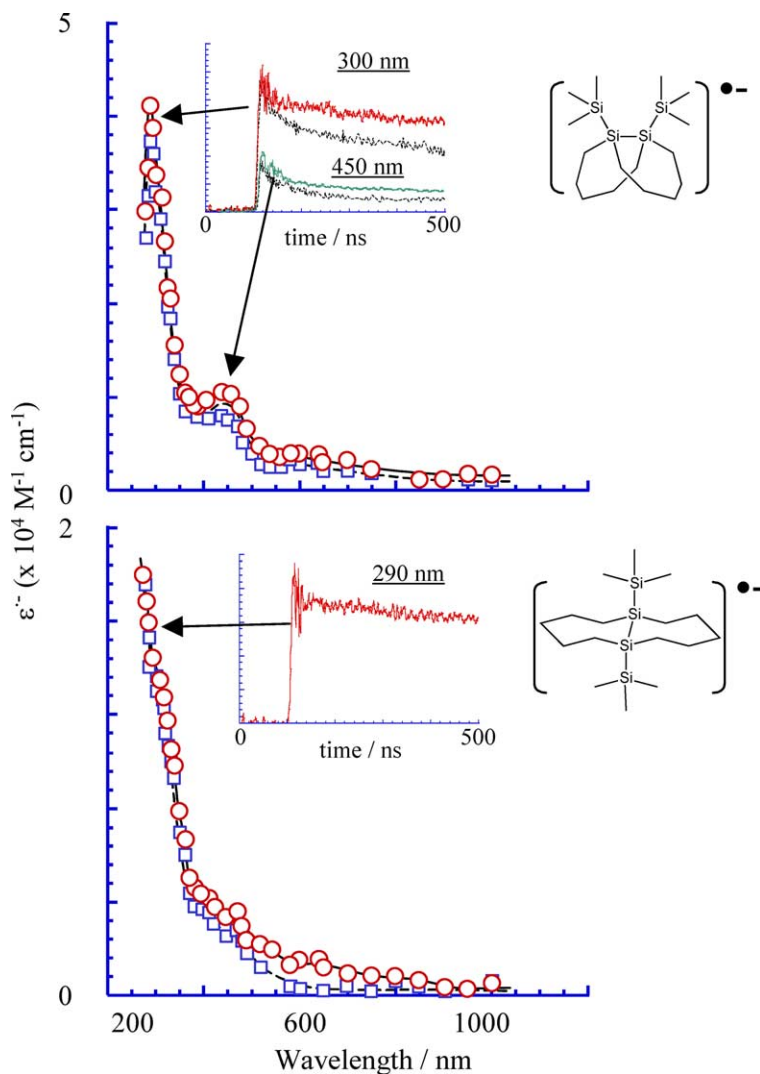


Fig. 1. Transient absorption spectra for anion radicals of *syn*- and *anti*-tetrasilanes in tetrahydrofuran at 1.1×10^{-2} M dm³ conc. Circles (solid line) and squares (dashed line) indicate the transient spectra 100 and 250 ns after electron pulse irradiation, respectively. The inset shows the kinetic traces at the indicated wavelength. Dashed lines in the inset are the kinetic traces observed for the solutions with CCl₄ at 2.0×10^{-2} M dm³ conc. The molar extinction coefficient is calibrated with respect to the concentration of anion radicals 100 ns after pulse irradiation.

tions, respectively. The absorptions of S-Si_4^+ are interpreted as $\text{HOMO} - 1 \rightarrow \text{SOMO}$ (3.6 eV; \mathbf{A}^+) and $\text{HOMO} \rightarrow \text{SOMO}$ (2.1 eV; \mathbf{B}^+) transitions.

Photoelectron spectroscopy of tetrasilanes, including S-Si_4 and A-Si_4 , has indicated a clear dependence of the ionization potentials on the Si–Si–Si–Si dihedral angles (ω) [13]. As ω varies from 0° to 180° , the energy difference between the second and third ionization potentials decreases

from 0.8 eV to <0.1 eV. The energy gap was observed to be 0.7 eV for S-Si_4 and <0.1 eV for A-Si_4 . This small gap (<0.1 eV) suggests a small difference in energy between HOMO and $\text{HOMO} - 1$ in A-Si_4^+ , giving optical transitions in the same wavelength range as the monitored broad near-UV band in the present study. The relatively large gap in S-Si_4 is observed as two distinct optical transitions (\mathbf{A} and \mathbf{B} bands) in S-Si_4^+ . The

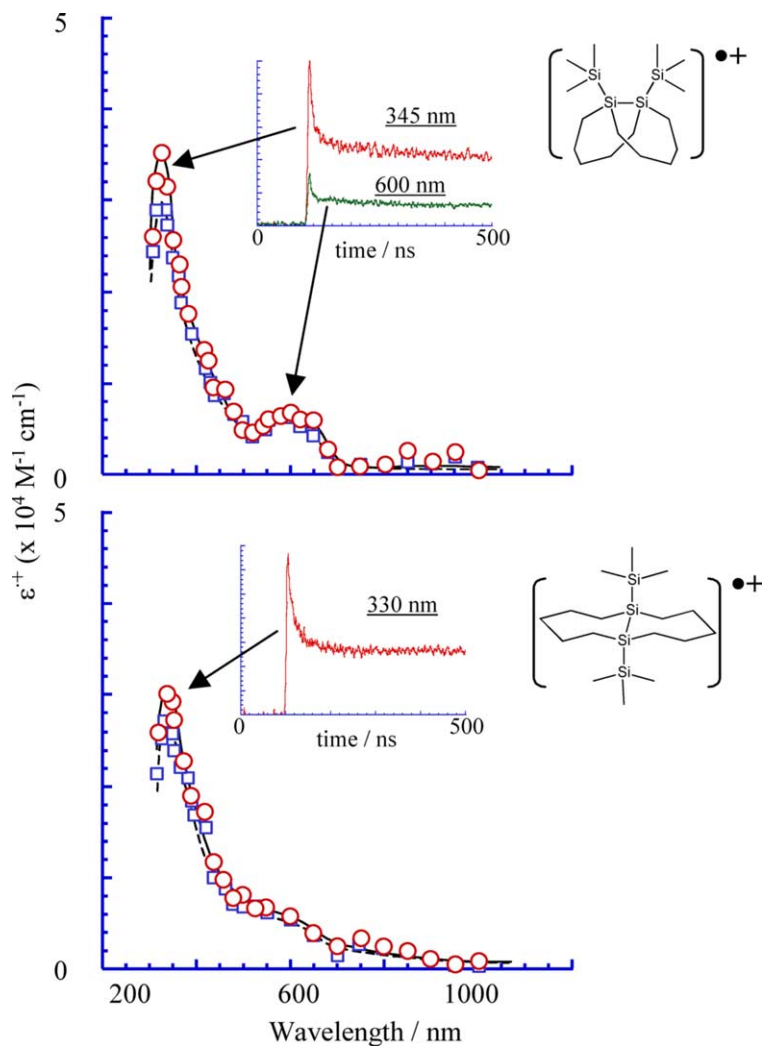


Fig. 2. Transient absorption spectra for cation radicals of *syn*- and *anti*-tetrasilanes in CH_2Cl_2 at $6.8 \times 10^{-3} \text{ M/dm}^3$ conc. Circles (solid line) and squares (dashed line) represent the transient spectra 100 and 250 ns after electron pulse irradiation, respectively. Inset shows the kinetic traces at the indicated wavelength. The molar extinction coefficient is calibrated with respect to the concentration of anion radicals 100 ns after pulse irradiation.

numerical integration of the transient absorption spectra gives the apparent oscillator strength (f) of the transient optical transition as follows:

$$f = 4.32 \times 10^{-9} \int \epsilon \, d\nu. \quad (6)$$

Based on the values of ϵ^+ summarized in Table 1, the calculated values of f are 0.116 and 0.112 for S-Si_4^+ and A-Si_4^+ , respectively, by the integration in the range from 300 nm ($3.33 \times 10^4 \text{ cm}^{-1}$) to

1000 nm ($1.00 \times 10^4 \text{ cm}^{-1}$). The consistent values of f also suggest the overlap of A and B transitions in the near-UV range for A-Si_4^+ .

The HF/TZ MO calculations of S-Si_4 and A-Si_4 were suggested that the first, second, and third HOMOs of both neutral S-Si_4 and A-Si_4 were intrinsically σ_{SiSi} orbitals with the different symmetries [13]. Assuming that the effect of positive charge on the third ionization potentials is relatively small in comparison with the other tetrasil-

Table 1
Transition energies of anion and cation radicals of tetrasilanes

Entry	E^{a} (eV)	$E^{-\text{b}}$ (eV)	$E^{+\text{b}}$ (eV)
S-Si ₄	5.21 (3.0) ~5.90 ^c	4.1 (4.0) 2.8	3.6 (3.5) 2.1
A-Si ₄	~5.90 ^c (1.3)	>4.4 (>1.9)	3.8 (2.9)

^a E^{a} denotes the transition energy of the steady-state molecules, quoted from [12].

^b E^{-} and E^{+} are the transition energies of the A and B bands observed in the transient absorption spectra of anion and cation radicals. Values in parentheses are the molar extinction coefficients at the maximum absorption ($10^4 \text{ cm}^{-1} \text{ M}^{-1}$).

^c Shoulder.

anes without any configurational constraint, the SOMO levels occur at 5.1 eV below the vacuum level for both A-Si₄⁺ and S-Si₄⁺. The two clear peaks of S-Si₄⁻ can also be interpreted in terms of the large computed gap between the second and third LUMO of neutral S-Si₄ [14]; reduction of the gap with increasing ω will result in the observed single optical transition for A-Si₄⁻.

Several groups have reported a dependence of the transition energy of A⁻ and A⁺ bands on the conjugation length in Si and Ge chains, and the present results for A⁻ and A⁺ in A-Si₄ are consistent with those for permethylated Si₆, *c*-Si₆, and Ge₅ [15,19–22]. Thus, *anti*-tetrasilane appears to exhibit a similar degree of charge delocalization to that of pentamer and hexamers of Si and Ge. It can therefore be concluded from these results that linear oligosilanes without conformational constraint assume *anti* or similar conformations, even in solvents under conditions of ion radical formation.

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