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Direct Observation of Stannyl Radicals by Laser-Photolysis of Carbon-Tin and Tin-Tin Bonds

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Photochemical primary processes of carbon-tin and tin-tin bonds were studied at room temperature. The stannyl radicals generated were observed directly by laser-photolysis.

Organostannyl radicals $R_3Sn\cdot$ are important intermediates in both photochemistry and synthetic chemistry.1) The stannyl radicals can be generated by a variety of methods, including hydrogen abstraction from the tin hydride,2) attack of alkoxyl radicals on ditin compounds,3-5) and direct photolysis of the organotin compounds.6-9) Despite the studies mentioned above, there are only limited studies on the direct observation of stannyl radicals.5,10-13) Particularly, the stannyl radicals which are expected to be produced by direct photolysis of the organotin compounds with carbon-tin bonds have not yet been detected directly. The stannyl radicals which are produced by direct photolysis of tin-tin bonds have only been studied with ESR and CIDNP (chemically induced dynamic nuclear polarization) techniques.12,13)

Recently, we have carried out the laser-photolysis studies of group 4B compounds.14-18) In the present investigation, we have undertaken the laser-photolysis studies of tetraorganotin and ditin compounds (R_4Sn, **1** for R=Ph and **2** for R=Bu, and $R_3Sn\text{-}SnR_3$, **3** for R=Ph and **4** for R=Bu, respectively). In this communication, we describe results of the direct observation of the transient absorption spectra of the generated stannyl radicals and their decay behavior.

The syntheses and identification of **1**-**4** were carried out as described in literature.19) A tetrahydrofuran (THF) solution containing **1** or **2** in a quartz tube was degassed and then irradiated at room temperature by a high-pressure Hg lamp for 2 h. The reaction products were analyzed with a gas chromatograph and liquid chromatograph.

Laser-photolysis measurements were performed on the degassed solutions at room temperature by using the fourth harmonic pulse (266 nm and 5 ns width) of a Quanta-Ray DCR-1 Nd:YAG laser as the exciting light source. The laser-photolysis apparatus and measuring system were similar to those published elsewhere.[20)]

The time dependence of absorbance of the transient absorption, A(t), was measured with each of the THF solutions of 1-4. The transient absorption spectra of 1 and 2 observed at 100 and 500 ns, respectively, after excitation are shown in Fig. 1. As shown in Fig. 1 (A), the transient spectrum observed with the THF solution of 1 has a peak at 325 nm. As shown in Fig. 1 (B), the spectrum observed with the solution of 2 has a weak peak at 390 nm and may have a bigger peak at < 300 nm. From the plots of 1/A(t) against t for 1 and 2, the early stages of the A(t) curves observed with these compounds were proved to be fitted with second-order kinetics. As a typical example, the plots of 1/A(t) against t for 1 were shown in Fig. 2. The $k/\varepsilon\ell$ values were obtained to be 2.8 (at 325 nm) for 1, and 16 (at 320 nm) and 29 (at 420 nm) x 10^6 s^{-1} for 2, respectively. Transient spectra of 3 and 4 observed at 200 ns after excitation agreed well with obtained those for 1 and 2, respectively. Each signals obtained for the THF solutions of 3 and 4 decayed with second-order kinetics ($k/\varepsilon\ell$ =2.5 x 10^6 s^{-1} at 330 nm for 3 and $k/\varepsilon\ell$ =29 x 10^6 s^{-1} at 420 nm for 4). Here k is the rate constant for the second order decay; ε, the molar extinction coefficient; ℓ, the optical length of the apparatus employed (about 5 mm).

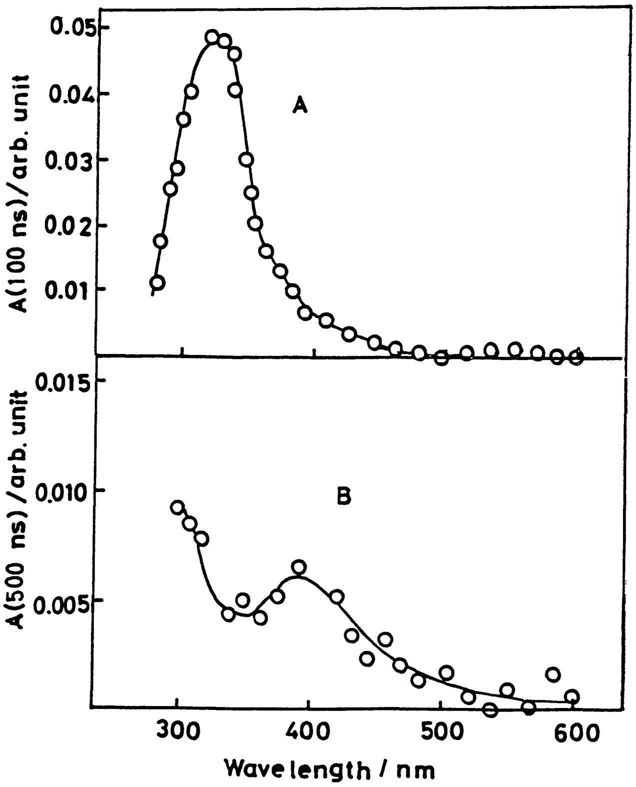
Spectrum A (B) of Fig. 1 can safely be assigned to the triphenylstannyl radical, $Ph_3Sn\cdot$, (the tributylstannyl radical, $Bu_3Sn\cdot$) generated by laser-photolysis of 1 and 3 (2 and 4) in comparison with the reported spectrum of $Ph_3Sn\cdot$[11)] ($Bu_3Sn\cdot$[11)]). These radicals observed in the present study are considered to be proposed by direct photolysis of R_4Sn and $R_3Sn\text{-}SnR_3$ as follows:

$$R_4Sn \xrightarrow{h\nu} R_3Sn\cdot + R\cdot \tag{1}$$

$$R_3Sn\text{-}SnR_3 \xrightarrow{h\nu} 2\ R_3Sn\cdot \tag{2}$$

R=Ph and Bu

The radicals, $Ph_3Sn\cdot$ and $Bu_3Sn\cdot$, generated in reactions 1 and 2 were found to decay



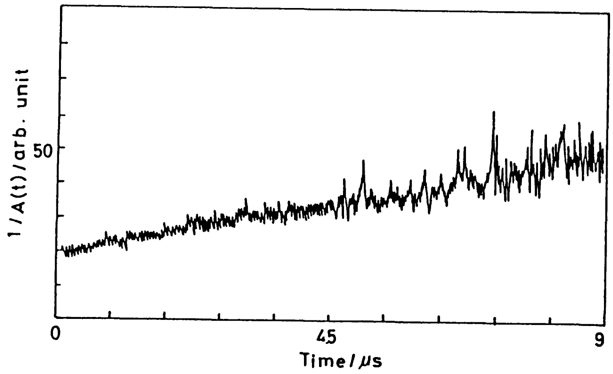


Fig. 2. Plots of 1/A(t) against t observed with the THF solution of 1 (at 325 nm).

Fig. 1. Transient absorption spectra observed 100 ns and 500 ns after excitation of the THF solutions containing (A) 1 (2.5 x 10^{-3} mol dm^{-3}) and (B) 2 (1.1 mol dm^{-3}), respectively.

with second-order kinetics, suggesting that the stannyl radicals disappeared by recombination according to reaction 3.

$$2\ R_3Sn\cdot \longrightarrow R_3Sn\text{-}SnR_3 \qquad (3)$$

In fact, upon irradiation of the THF solution of 1 or 2 with a high-pressure Hg lamp for 2 h at room temperature, the corresponding ditin compound was obtained.

To the best our knowledge, this is the first observation of the transient absorption spectra of stannyl radicals generated by direct photolysis of only tetraorganotin and ditin compounds. The present study will give useful information on photochemistry and synthetic chemistry of organotin compounds.

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