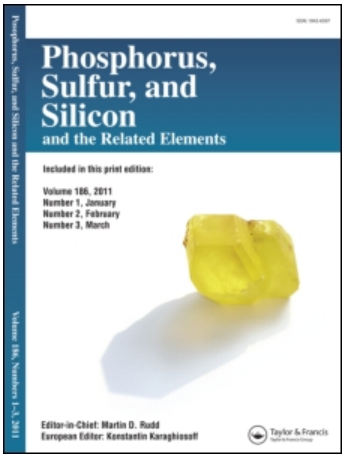

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An Investigation of the Photodegradation of Tetraphenyltin(IV) in THF

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The decomposition process of triphenyltin radical produced by the irradiation of tetraphenyltin (IV) using 266 nm laser pulse (10 ns) was studied in tetrahydrofuran with and without the existence of water. NMR measurements were carried out to examine the decomposition products. The effect of water and propane-2-ol on the decay process of Ph_3Sn • was also examined, which revealed that the primary process for the disappearance of the Ph_3Sn• radical was the recombination reaction with Ph• when no appreciable amount of water and propane-2-ol exists in the reaction system. The second-order rate constant for the reaction of Ph_3Sn• with water was estimated as 4.4×10^6 $dm^3mol^{-1}s^{-1}$ from the results obtained under the condition of $[H_2O]_0$, $[propane\text{-}2\text{-}ol]_0 >> [Ph_3Sn•]_0$.

Keywords: organotin; photodecomposition; kinetic study

INTRODUCTION

Various organotin(IV) compounds are widely used in the environment as antifoulants, agrochemicals, etc. [1-3]. From the environmental point of view, the investigation of the photo-induced decomposition of organotin (IV) in solution is important for the better understanding of their reactivities in the natural environment.

It has been suggested that the primary products of the photodecomposition of tetraphenyltin(IV) in tetrahydrofuran (THF) are the triphenyltin radical ($Ph_3Sn·$) and the phenyl radical (Ph·) [4]. The disappearance of the absorption at 325 nm region, which was assigned

to the absorption of transient $Ph_3Sn\cdot$ species, was explained by the dimerization process expressed by the following equation in dry THF.

$$Ph_4Sn \xrightarrow{h\nu} Ph_3Sn\cdot + Ph\cdot$$
$$2\,Ph_3Sn\cdot \longrightarrow Ph_3SnSnPh_3$$

However, neither the quantum yield nor the molar extinction coefficient for $Ph_3Sn\cdot$ has been reported to date.

EXPERIMENTAL

Tetraphenyltin(IV) and triphenyltin(IV) hydroxide from Wako Pure Chemicals Inc. were washed with water and acetone, and then dried at 100 °C. Deuterated water and tetrahydrofuran-d_8 were obtained from Aldrich. Tetrahydrofuran (THF) was obtained from Wako (AR grade), which was redistilled under nitrogen atmosphere prior to each experiment. No peroxo species was detected in freshly distilled THF by the examination using the potassium iodide solution.

A Surelite I YAG Laser (Contimuum Co. Ltd., U. S. A.) was used at 266 nm for the excitation of tetraphenyltin(IV) in a quartz cell. All the sample solutions were deacrated by Ar before each run. The amount of water in THF was adjusted by addition of redistilled water using a micro pipette. Exact concentrations of water in sample solutions were then determined by a Karl-Fisher Moisturemeter. The temperature of the cell compartment was adjusted to 25.0 ± 0.1 °C. The laser power was monitored by a PHIR Power Meter.

RESULTS

Measurement of the transient absorption spectrum

The transient absorption spectrum of the triphenyltin radical was observed 250 ns after the excitation of the 2.5 mmol dm^{-3} solution of tetraphenyltin(IV) in THF (10 mW). As shown in Fig. 1, a single absorption band was observed with a band maximum at 325~330 nm, which was in good agreement with the previous observation by Mochida *et al* [4].

^{1}H NMR measurements

To examine the reaction products, ^{1}H NMR measurements of the irradiated samples were carried out for the solutions containing tetraphenyltin(IV) in sealed quartz sample tubes. After irradiation of the

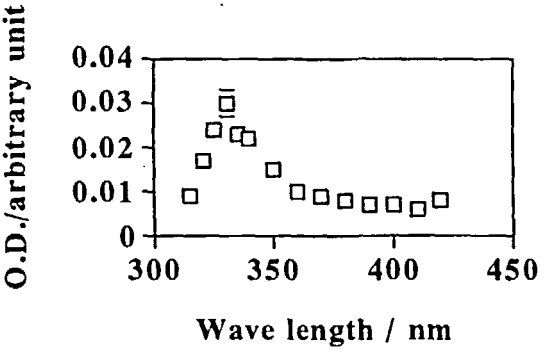

Figure 1. Transient absorption spectrum of triphenyltin(IV) radical observed 250 ns after excitation of the THF solution of tetraphenyltin(IV). $[tetraphenyltin(IV)]_0 = 2.5 \times 10^{-3}$ M.

sample solution at 266 nm, a new signal at 7.4 ppm (corresponding to benzene) appeared while the water signal at 2.6 ppm decreased significantly. This observation indicates that the existence of water in THF induces the formation of benzene during the photo-decomposition process of Ph_4Sn(IV). A broad signal observed in the 6.8 to 8.0 ppm region corresponds to the decomposed Ph_ntin(IV) species (n=1~3), probably Ph_3SnOH.

The irradiation of Ph_3SnOH in THF-d_8 for 1 hour (at 266 nm) yielded benzene signal and other small signals in the 7.5 ppm region, and the formation of white precipitate was observed, which confirms that the irradiation of 266 nm light causes consecutive release of phenyl radicals form $Ph_nSn(OH)_{4-n}$ (n = 1~3) and that the final products are benzene and inorganic SnO_2 [5].

Kinetic measurements

The dependence of the initial rate constant on the concentration of water at 25 °C is shown in Fig. 2A. It is clear that the addition of water suppress the apparent first-order rate constant corresponding to the decay of the $Ph_3Sn\cdot$ radical. In the previous report, a second-order kinetic behavior was observed for the sample solutions at sufficiently low water concentrations [4]. In this study, a similar result was obtained at water concentrations less than 1 mM (lower than the detection limit by the Karl-Fisher instrument). Further retardation of the decay of $Ph_3Sn\cdot$ was observed by the addition of propane-2-ol (isopropanol) (Fig. 2B).

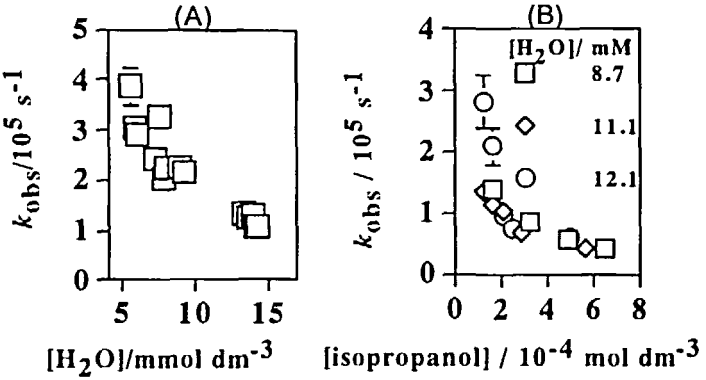

Figure 2. The dependence of the first-order rate constant for the disappearance of $Ph_3Sn\cdot$ on the concentration of added water (A) and isopropanol (B) at 25 °C.

DISCUSSION

In this study, the authors successfully observed the similar transient absorption spectra to that reported in the previous report [4]. Therefore, the primary process involved in the formation and decay of triphenyltin(IV) radical is expressed by the following equations.

$$Ph_4Sn(IV) \xrightarrow{h\nu} Ph_3Sn\cdot + Ph\cdot \quad (1)$$

$$Ph_3Sn\cdot + Ph\cdot \xrightarrow{k_r} Ph_4Sn(IV) \quad (2)$$

$$2\,Ph_3Sn\cdot \xrightarrow{k_d} Ph_3Sn\text{-}SnPh_3 \quad (3)$$

Both the recombination (k_r) and the dimerization (k_d) processes are second-order with respect to the concentration of the triphenyltin radical in case no radical scavenger exists in the reaction medium. At very low concentrations of water, Mochida *et al* reported that the k_d process in THF is expressed by $k_d = 2.8 \times 10^6\, \varepsilon l$ dm^3 mol^{-1} s^{-1} (ε is the unknown molar extinction coefficient of $Ph_3Sn\cdot$ and l is the path length of the observation cell) [4]. Although they attributed the second-order rate constant for the disappearance of $Ph_3Sn\cdot$ only to the k_d process, involvement of the k_r process may not be excluded from their results.

When an appreciable amount of water exists in the sample solutions, the following reactions may also be considered as the decay process of $Ph_3Sn\cdot$.

$$Ph_3Sn\cdot + H_2O \xrightarrow{k_{w1}} Ph_3SnOH + H\cdot \quad (4)$$

$$Ph_3Sn\cdot + H_2O \xrightarrow{k_{w2}} Ph_3SnH + OH\cdot \quad (5)$$

The k_{w2} process is not thermodynamically favored, as the thermodynamic stability of Ph_3SnH is very low when an appreciable amount of water exists in the reaction medium [1]. The combination of reactions (2) ~ (5), however, cannot explain the retardation effect by water shown in Fig. 2A, as all of these processes accelerate the decay of $Ph_3Sn\cdot$.

The formation of benzene detected by the NMR measurements suggests the following additional reaction.

$$Ph\cdot + H_2O/THF \xrightarrow{k_{w3}} \text{benzene} \quad (6)$$

Although the reactivity of water with phenyl radicals is reported to be rather low[6], some kind of concerted effect with THF may have enhanced the reactivity of water / THF mixture. The apparent hydrogen abstraction by Ph· from water may be attributed to the concerted action of THF and water in the reaction mixture: the product of reaction 6 may lead to the formation of OH·. As seen in Fig. 2B, a significant retardation of the decay of $Ph_3Sn\cdot$ was observed by the addition of propane-2-ol, and the first-order rate constant for the decay of the $Ph_3Sn\cdot$ signal became independent of the concentration of added propane-2-ol at higher concentrations than *ca* 4 x 10^{-4} mol/kg, indicating that reaction 7 is not a significant process.

$$Ph_3Sn\cdot + \text{propane-2-ol} \longrightarrow \text{products} \quad (7)$$

The existence of isopropanol retards the recombination reaction 2 also through the direct reaction with Ph·[7].

$$Ph\cdot + \text{propane-2-ol} \xrightarrow{fast} \text{benzene} + \text{isopropanol-H}\cdot$$

Therefore, by the addition of sufficient amounts of propane-2-ol (>4 x 10^{-4} mol/kg) with the existence of water, only the reaction corresponding to eq 4 may be observed.

The overall reaction corresponding to the decay of $Ph_3Sn\cdot$ is, therefore, expressed by the following rate laws:

Without the existence of water:

$$-\frac{d[Ph_3Sn\cdot]}{dt} = k_r[Ph_3Sn\cdot]^2 \quad (\text{or } k_r[Ph_3Sn\cdot][Ph\cdot]) \tag{8}$$

With the existence of water / isopropanol:

$$-\frac{d[Ph_3Sn\cdot]}{dt} = (k_{w1}[H_2O]_0 + k_r[Ph\cdot] + k_{OH}[OH^-])[Ph_3Sn\cdot] \tag{9}$$

$$-\frac{d[Ph\cdot]}{dt} = (k_{w3}([H_2O/THF] + [\text{isopropanol}]) + k_r[Ph_3Sn\cdot])[Ph\cdot] \tag{10}$$

The simultaneous differential equations 9 and 10 caused the complex behavior of $[Ph_3Sn\cdot]$ against time. The retardation effect by the addition of excess amounts of water and isopropanol is clearly explained by the k_{w3} process. Kinetic traces are, therefore, linear for more than 3 half-lives when sufficient amounts of propane-2-ol and water exist in THF. The value of k_{w1} was calculated as $(4.4\pm0.7) \times 10^6$ $dm^3mol^{-1}s^{-1}$ from the limiting rate constant in Fig. 2B.

As no chain reaction is expected with the existence of excess H_2O and propane-2-ol in the reaction system, the lower limit of the molar extinction coefficient of $Ph_3Sn\cdot$ as $(6.0 \pm 0.1) \times 10^4$ dm^3 mol^{-1} cm^{-1} by assuming the quantum yield of reaction 1 is unity. On the other hand, the upper limit of the molar extinction coefficient, ε, of $Ph_3Sn\cdot$ may be estimated by assuming that the k_r process is diffusion controlled in THF ($k_{diff} = 4.5 \times 10^{11}$ dm^3 $mol^{-1}s^{-1}$). By comparing thus estimated upper and lower limits of the molar extinction coefficients (1.6×10^5 and 6.0×10^4 dm^3 mol^{-1} cm^{-1}), it is concluded that the quantum yield of reaction 1 must be close to unity.

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