Direct Observation of a Stannyl Radical in the Reactions of the Tributylstannyl Anion with Alkyl Halides by a Stopped-Flow Technique

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Summary: The reaction intermediate in reactions of the tributylstannyl anion with alkyl halides in THF was studied by a stopped-flow technique. The tributylstannyl radical was observed directly in the reactions of sec- and tert-butyl bromides and iodides. Generation of the stannyl radical suggests that electron transfer from the stannyl anion to alkyl halides is taking place.

Reactions of organostannyl anions with alkyl halides have been widely used in syntheses of organostannyl compounds for more than a half-century:[1,2]

$$R_3Sn^-M^+ + R'X \rightarrow R_3SnR' + MX \qquad (1)$$

$$M = Li, Na, K; X = Cl, Br, I$$

However, this reaction often shows unexpected behavior with respect to yields and stereochemistry. For example, Kuivila and co-workers reported that 2-bromooctane reacted with Me_3SnNa by an electron-transfer process.[3] On the other hand, San Filippo et al. reported that the reaction of Me_3SnNa with (−)-2-bromooctane proceeded with predominant inversion of configuration (S_N2 substitution).[4] Therefore, the reaction mechanism has been studied extensively.[5−8] The three basic mechanisms proposed are as follows: (a) classical S_N2 substitution, (b) substitution by an electron-transfer process, and (c) substitution by halogen−metal exchange. These proposals were based on stereochemical studies or quantitative analyses of product distributions. To this day the reaction mechanism still is unclear. The key problem that requires attention in order to clarify the reaction mechanism is the direct observation of a reaction intermediate. However, in the previous studies, no reaction intermediate was observed directly. The stopped-flow technique is a powerful method for direct observation of reaction intermediates generated in thermal reactions. If one-electron transfer from the stannyl anion to the alkyl halide occurs in the title reaction, stannyl radicals might be observed directly by this technique. Therefore, to clarify the question of the generation of the stannyl radical, we carried out stopped-flow measurements of the reaction of tributylstannyl anion with *sec*- and *tert*-butyl bromides and iodides. In the present study, we have succeeded in the direct observation of the stannyl radical for the first time.

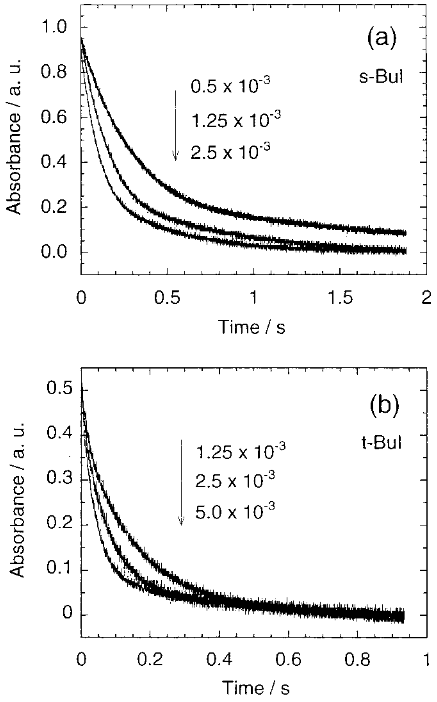

Figure 1. Time profiles observed at 320 nm for the reactions of tributylstannyl anion with (a) *s*-BuI (0.5×10^{-3}, 1.25×10^{-3}, and 2.5×10^{-3} mol dm^{-3}) and (b) *t*-BuI (1.25×10^{-3}, 2.5×10^{-3}, and 5.0×10^{-3} mol dm^{-3}).

(Tributylstannyl)potassium, the stannyl anion reagent used, was prepared by reaction of hexabutyldistannane ($Bu_3SnSnBu_3$, Aldrich Chemical Co.) with

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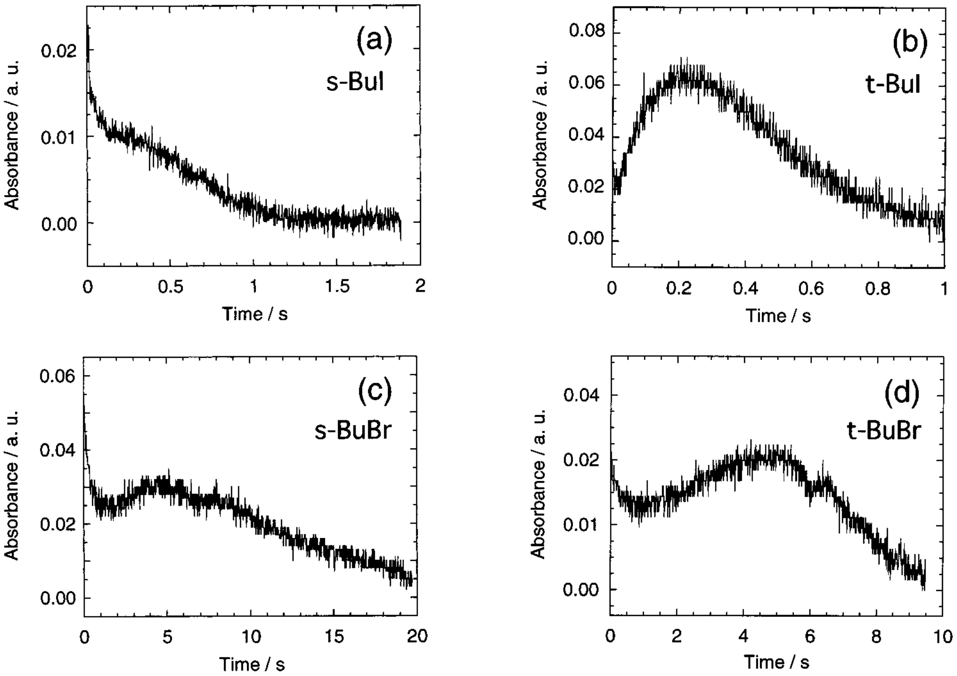

Figure 2. Time profiles observed at 400 nm for the reaction of tributylstannyl anion with (a) *s*-BuI (5.0×10^{-3} mol dm^{-3}), (b) *t*-BuI (1.25×10^{-3} mol dm^{-3}), (c) *s*-BuBr (2.5×10^{-3} mol dm^{-3}), and (d) *t*-BuBr (1.25×10^{-2} mol dm^{-3}).

potassium in dry THF under an argon atmosphere at 0 °C:[9]

$$Bu_3SnSnBu_3 + 2K \rightarrow 2Bu_3Sn^-K^+ \qquad (2)$$

As alkyl halides, *sec*- and *tert*-butyl bromides and iodides (BuX; X = Br, I) were used. For stopped-flow measurements, time profiles were observed by a Union Giken RA-401 stopped-flow spectrometer modified for anaerobic use.[10] Its time resolution was approximately 500 μs. All procedures were carried out in a glovebox under an argon atmosphere. The concentration of tributylstannyl anion in the employed THF solution was $(0.1-1.0) \times 10^{-3}$ mol dm^{-3}.

The THF solution of tributylstannyl anion was light yellow and λ_{max} was observed at 325 nm ($\epsilon \approx 10^4$). First, the disappearance of the stannyl anion was investigated at 320 nm by the stopped-flow technique. Typical time profiles observed for the reactions of the tributylstannyl anion with *s*-BuI and *t*-BuI are shown in Figure 1. This figure shows that the decay of the stannyl anion is accelerated with increasing concentration of *s*-BuI or *t*-BuI and that the absorption of the stannyl anion completely disappeared after reaction. Similar results were observed for *s*- and *t*-BuBr. The observed time profiles were analyzed by the least-squares method, and the reaction rate constants of tributylstannyl anion with *s*-BuBr, *s*-BuI, *t*-BuBr, and *t*-BuI were determined to be 1×10^3, 4×10^3, 8×10^1, and 4×10^3 s^{-1} mol^{-1} dm^3, respectively. These results indicate that the tributylstannyl anion reacts with all butyl halides used in the present study. Since it is unlikely that the stannyl anion reacts with sterically hindered *tert*-butyl halides by the classical S$_N$2 substitution, the disappearance of the stannyl anion may be due to the electron-transfer process from the stannyl anion to butyl halides.

Next, if one-electron transfer from the stannyl anion to the alkyl halide occurs in the present reaction, the stannyl radical is expected to be observed at 400 nm, because the tributylstannyl radical has a transient absorption peak at 400 nm ($\epsilon = 450$).[11–14] Therefore, we carried out stopped-flow measurements at 400 nm. The observed time profiles are shown in Figure 2. Although in the case of *s*-BuI, *s*-BuBr, and *t*-BuBr the time profiles are somewhat complicated and have a fast decay component, we can clearly see the rise of absorption at 400 nm in this figure. The fast decay component may be due to the stannyl anion. The molar extinction coefficient of the stannyl anion is relatively large so that the decay of stannyl anion may be observed at 400 nm. In addition, comparing the time profiles observed at 400 and 320 nm shown in Figures 1 and 2, we can see that the rise of absorption at 400 nm takes place in concert with the decay of stannyl anion at 320 nm. For example, in the case of *t*-BuI, the decay rate observed at 320 nm and the formation rate observed at 400 nm are calculated to be 8.7 and 8.4 s^{-1}, respectively. Since the decay rate and formation rate are in reasonable agreement with each other, we can conclude that the transient species observed at 400 nm was derived from the stannyl anion.

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(9) (Tributylstannyl)potassium was prepared similarly to the preparation of (trimethylstannyl)sodium, as described in ref 3.

(10) The stopped-flow apparatus, consisting of a four-jet mixer, a monitor cell, a control valve, two 30 mL reservoirs, and several valves, was placed in a glovebox under purified argon (H_2O and O_2 <10 ppb). A D_2 lamp was used as a monitor light source, and UV light was guided to the monitor cell by a quartz rod. One reservoir was charged with the Bu_3SnK solution in THF and the other with the butyl halide in THF, and a pressure of 7 kg/cm^2 of argon was applied. When the control valve was opened for a short time, two solutions were mixed in the four-jet mixer and the mixture flowed into the monitor cell. Then, the time profile of absorption was measured by a combination of photomultiplier and digital oscilloscope.

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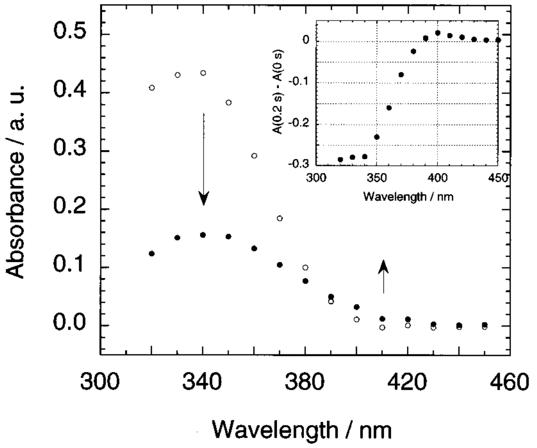
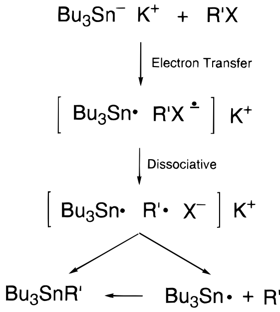


Figure 3. Time-resolved spectra observed for the reaction of tributylstannyl anion with t-BuI (1.25×10^{-3} mol dm^{-3}) at delay times of 0 s (○) and 0.2 s (●). Insert: Difference spectrum (A(0.2 s) − A(0 s)).

Furthermore, to characterize the transient species observed at 400 nm, we measured the time-resolved spectrum. A typical result observed for *t*-BuI is shown in Figure 3. We can see from this figure that the increase of absorption was observed only around 400 nm and that the transient absorption which grows concomitantly with the decay of the stannyl anion has a peak at 400 nm. The transient species observed at 400 nm can safely be assigned to the stannyl radical, from comparison of their spectral characteristics with those reported previously.[11−15]

To clarify the whole mechanism of the present reaction, one should carry out the qualitative and quantitative analysis of all products. However, such studies have been made extensively.[3−8] Additional study in this direction is beyond the scope of the present paper. In this study, we found the generation of the stannyl radical in concert with the decay of stannyl anion. This fact suggests that electron transfer from the stannyl anion to alkyl halides occurs. Therefore, the present reaction may be rationalized by Scheme 1. In the primary process of the present reactions, the stannyl radical and alkyl halide anion radical are generated by electron transfer. Since electron transfers to alkyl bromides and iodides are dissociative, the alkyl radical and the halogen anion are generated immediately.[8] In the cage, the stannyl and alkyl radicals are coupled with each other and the tetraalkylstannanes were formed. However, the stannyl and alkyl radicals can partially escape from the cage. Those which escaped also may be coupled to each other, resulting in the tetraalkylstannane. In the present study, the caged and escaped stannyl radicals were observed directly by the stopped-flow measurements.

Scheme 1



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(15) A reviewer suggested that the transient absorption observed at 400 nm might be assigned to the radical anion of Bu_3SnR, generated by an S$_{RN}$1 reaction (Yammal, C. C.; Podesta, J. C.; Rossi, R. A. *J. Org. Chem.* **1992**, *57*, 5720):

$$Bu_3Sn^- + RX \rightarrow\rightarrow Bu_3Sn^\bullet + R^\bullet + X^-$$

$$Bu_3Sn^- + R^\bullet \rightarrow Bu_3SnR^{\bullet -}$$

In the present study, the concentration of the stannyl anion employed is much smaller than that of the butyl halides. Therefore, the reaction of the alkyl radical with the stannyl anion by an S$_{RN}$1 process is considered to be very slow and negligible. In addition, if the transient absorption observed at 400 nm is assigned to the radical anion of Bu_3SnR, the decay rate of the stannyl anion and the formation rate of the radical anion may have a discrepancy, because the radical anion of Bu_3SnR is not directly derived from the reaction of the stannyl anion with the butyl halide. However, the decay rate and formation rate observed in the present reaction are in reasonable agreement with each other. Therefore, we believe that the S$_{RN}$1 reaction does not play a major role in the present reactions.