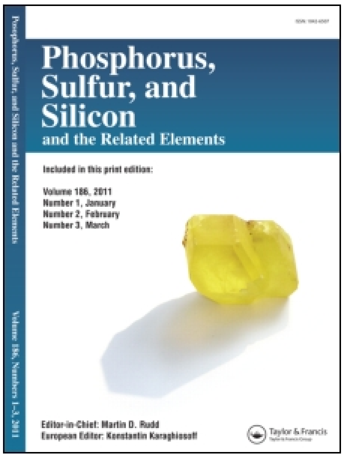

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Temperature Effect on the Kinetics for the Reaction of Stannyl Anion with Primary Butyl Bromide

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The decay of the tributylstannyl anion in the presence of primary butyl bromide were measured with a modified stopped-flow apparatus at low temperatures. The investigation for the differences between that decay at 10°C and −60°C revealed the formation of the stannyl radical as the intermediate of this reaction.

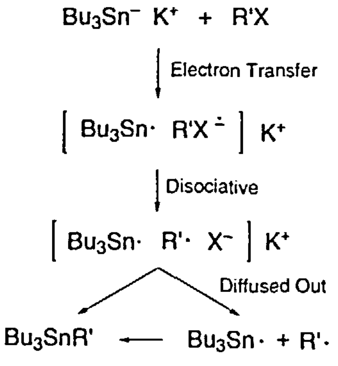
Keywords: stannyl anion; kinetics; reaction mechanism; stopped-flow; low temperature

The formation mechanism of tetraalkyltin compounds by the reaction of trialkylstannyl anions with alkyl halides has been investigated actively, and three basic mechanistic pathways, (a) classic SN2 substitution, (b) substitution by an electron-transfer (ET) process and (c) substitution by halogen-metal exchange (HME), have been proposed.[1-5] The entire reaction mechanism, however, is not completely clear, because these proposals were based on the stereochemical studies or quantitative analysis of product distributions.

$$R_3Sn^- + R'X \longrightarrow R_3SnR' + X^- \qquad (1)$$

The kinetic study is important to clarify a reaction mechanism, nevertheless, that for these reactions have never been carried out. It is difficult to perform kinetic studies on the group 14 element centered anions such as the stannyl anion because of their high oxygen and moisture sensitivities. Although the stopped-flow experiment is a powerful method for the measurement of the rate constants for several reactions in solution, the kinetic studies which have been previously performed by this technique are limited to the reactions of compounds which are stable in air or when exposed to moisture.

In the previous work[6], we have succeeded to measure the decay of the tributylstannyl anion in the reactions with several butyl halides by a modified stopped-flow apparatus and obtained the rate constants of these reactions for the first time. Furthermore, we also have found that the stannyl radical produced as the intermediate in the reactions with secondary and tertiary butyl halides. These results were strongly indicated that one electron transfer from the stannyl anion to the secondary or the tertiary butyl halides occurred to produce the stannyl and



Scheme 1

alkyl radicals, and then, these radicals were coupled each other in the solvent cage to form the tetraalkyl tin compound as shown in scheme 1. The stannyl radical that we found is probably that diffused out of the solvent cage.

In the similar experiments for the reactions with primary butyl bromide and iodide, however, the stannyl radical have never been detected. The conceivable reasons for this result are as follows: (a) the reactions of stannyl anion with primary butyl halides are proceeded via an ionic pathway rather than an ET pathway, or (b) since the rate of coupling reaction of stannyl and primary alkyl radicals is so fast, the detectable free stannyl radical is too small in quantity, and then, the weak absorbance of the radical is overlapped with the strong that of the stannyl anion.

In this time, to analysis the decay of stannyl anion in the presence of primary butyl bromide in detail, we performed the temperature controlled kinetic investigation by a stooped-flow technique. If the stannyl radical is generated during the reaction, we expected to be able to isolate to detect its absorbance from the slope of that for the stannyl anion at low temperature.

An UNION GIKEN RA-401 stopped-flow apparatus was modified for anaerobic use by isolating the flow circuit from the atmosphere, as previously described.[6] Two cooling jackets were attached to each pressure glass column used as reservoirs and let cold ethanol run through them to cool both of stannyl anion and alkyl halide solutions. A thermocouple was inserted into one reservoir to monitor the temperature of the solution during the reaction.

Tributylstannyl potassium was used as the stannyl anion prepared by the treatment of hexabutylditin with potassium in THF at 0°C.[7] The stannyl anion was prepared in order to obtain required concentration (approximate 1×10^{-3} mol dm^{-3}) by dry oxygen-free THF in the glove box. One reservoir was then filled with this anion solution, and the other was filled with 5×10^{-2} mol dm^{-3} THF solution of primary butyl bromide.

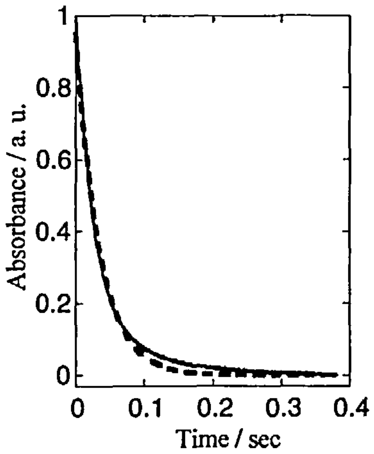


FIGURE 1 The absorbance change at 320 nm in the reaction of tributylstannyl anion with n-BuBr in THF at 10°C, solid line, and its theoretical curve, broken line.

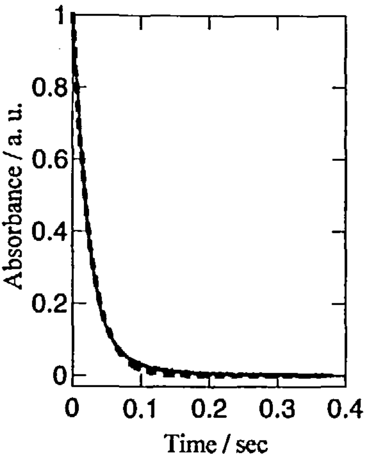


FIGURE 2 The absorbance change at 320 nm in the reaction of tributylstannyl anion with n-BuBr in THF at -60°C, solid line, and its theoretical curve, broken line.

This anion solution has a yellow color and has the λmax at 325 nm, so the absorbance changes were monitored at 320 nm.

The absorbance change at 320 nm in the reaction of tributylstannyl anion with primary butyl bromide at 10°C was shown in Figure 1. The broken line in this figure is the theoretical curve obtained by direct exponential fit as $y = Ae^{-kx}$ to the experimental data, where k is a pseudofirst order rate constant for the stannyl anion, and its value was obtained as -28.7 s^{-1} here. This theoretical curve, however, could not fit to the experimental curve so favorable. A slight difference between the experimental and the theoretical curves means the former curve contains a second component but for the stannyl anion decay. Since tributylstannyl radical also has an absorption peak around 320 nm[8, 9], the second component is considered to be the rise and decay of the absorbance for the stannyl radical as reaction intermediate. Then, to obtain a more accurate *k* value, we recalculated it by the same exponential fit to the decay data for the only first 20 ms which can be considered to be not affected with the second component very much, and got it as 35.6 s^{-1}.

On the other hand, the absorbance change at 320 nm in the same reaction at -60°C agree well with the theoretical curve obtained by direct exponential fit as $y = Ae^{-kt}$ as shown in Figure 2. Therefor, we can consider this absorbance change as the decay of the stannyl anion in the reaction with primary butyl bromide, and the *k* value was obtained as -39.8 s^{-1}, here.

Contrary to our expectation, we could not detect the isolated stannyl radical as the reaction intermediate at the low temperature, but we could observe the individual decay curve for the stannyl anion without any obstruction of the stannyl radical. Furthermore, we found that the *k* value obtained at -60°C was close to that for the initial rate constant at 10°C.

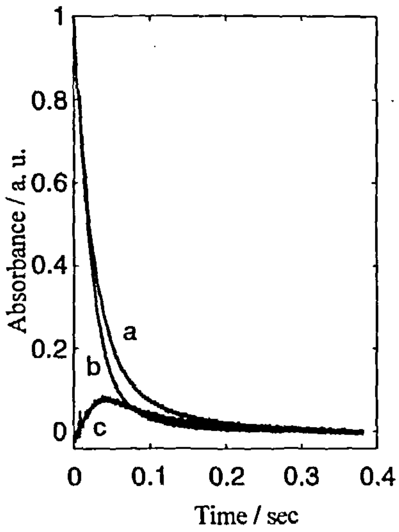


FIGURE 3 The absorbance change at 320 nm in the reaction of tributylstannyl anion with primary butyl bromide in THF at 10°C, (a), at -60°C, (b), and the difference curve between (a) and (b), (c).

These results can be explained as follows. The electron-transfer from the stannyl anion to primary butyl bromide occurred not only at 10°C, but also at -60°C, to produce the stannyl and the butyl radicals in the solvent cage. The rate of the electron-transfer was independent on the temperatures in the range we used here. It is known that radicals diffuse out of the solvent cage during reaction to a high extent as the viscosity of solvent decreases. As the temperature increases, the viscosity of THF solvent decreases, therefore the stannyl radical diffused out of the solvent cage was much in quantity at 10°C than at -60°C. The resulting absorbance change at 320 nm at 10°C consists of both the decay of the stannyl anion and the rise and decay of the stannyl radical. While, in the relative high viscous THF solution at -60°C, almost all produced stannyl radical predominately and quickly reacted with alkyl radical in the solvent cage. Then, we could observe only the decay of the stannyl anion.

We also showed the difference curve between the absorbance changes at 10 and -60°C together with each parent curve in Figure 3. Because the decay rates of stannyl anion at both temperatures can be considered to be same, this difference curve can be approximated by the rise and decay of the absorbance of stannyl radical at 10°C From this figure, it is seen that the absorbance of the stannyl radical rises in response to the decay for that of the stannyl anion. It suggests that an the electron-transfer from the stannyl radical to primary butyl halide occurs at the initial step of the title reaction.

References

[1] M. Newcomb and A. R. Courtney. J. Org. Chem., **45,** 1707 (1980).
[2] K.-W. Lee and J. S. Filippo, Jr., Organometallics, **2,** 906 (1983).
[3] M. S. Alnajjar, G. F. Smith, and H. G. Kuivila, J. Org. Chem., **49,** 1271 (1984).
[4] M. S. Alnajjar and H. G. Kuivila. J. Am. Chem. Soc.. **107,** 416 (1985).
[5] E. C. Ashby, W.-Y. Su, and T. N. Pham, Organometallies, **4,** 1493 (1985).
[6] M. Wakasa and T. Kugita, Organometallics, **17,** 1913 (1998).
[7] The concentration of tributylstannyl potassium was determined as follows. An aliquot was treated with excess water. The yield of tributylstannane was then obtained by GLC using a 20% SE-30 on Chromosorb W column (2.1 m x 3.2 mm).
[8] J. C. Scaiano, J. Am. Chem. Soc., **102,** 5399 (1980).
[9] K. Mochida, M. Wakasa, Y. Sakaguchi, and H. Hayashi, Chem. Lett. 1793 (1986).