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Flash Photolysis Study for Halogen Abstraction of $Ph_3Sn\cdot$ and $Ph_3Si\cdot$ from Alkyl Halides

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The reaction rate constants for halogen abstraction of $Ph_3Sn\cdot$ and $Ph_3Si\cdot$ have been determined by xenon-flash photolysis method. The absolute rate constants for the reactivity of $Ph_3Sn\cdot$ with several alkyl halides have been compared with the relative ones; the agreement between the both methods was fairly good. For $Ph_3Sn\cdot$, the rate constant (in unit of $mol^{-1}\,dm^3\,s^{-1}$) of *n*-BuCl (5.2×10^2) was smaller than that of *n*-BuBr (3.1×10^6) by a factor of ca. $1/10^4$. With changing the alkyl halides, the rate constants for $Ph_3Si\cdot$ and $Ph_3Sn\cdot$ varied similarly, although the rate constants for $Ph_3Si\cdot$ were larger than those for $Ph_3Sn\cdot$ by factors of 50—100. The reactivity of alkyl halides increased with a decrease in the bond-dissociation energy of the R–X (X=Cl, Br).

The high reactivities of organostannyl and organosilyl radicals in halogen abstraction reactions have been well-known and utilized widely in synthetic chemistry.[1] The relative reactivities were evaluated by various methods such as product analysis[2] and ESR spectroscopy.[3] Some of them were converted into absolute rate constants by Carlsson and Ingold using the rotating sector/competitive method.[4] In order to obtain the absolute rate constants, the laser-flash photolysis has been applied to radical reactions including the organometallic radicals.[5—10] Although the usefulness of this method has been widely proved, it is hard to evaluate the rate constants smaller than ca. $10^5\,mol^{-1}\,dm^3\,s^{-1}$. For such relatively slow reactions, the xenon-flash photolysis would be expected to be useful.[11,12]

In this study, we report the absolute rate constants evaluated by following the direct decay of transient absorption bands due to $Ph_3Sn\cdot$ and $Ph_3Si\cdot$ in the presence of various alkyl halides. The absolute rate constants thus evaluated are compared with the relative rate constants obtained by a competitive method. Furthermore, we attempted to clarify the factors determining the reactivities.

Experimental

$Ph_3SnSnPh_3$ and $Ph_3SiSiPh_3$ used as the radical sources were prepared by refluxing Ph_3MCl (M=Sn, Si) with sodium metal in toluene under N_2.[13] Alkyl halides and solvents were purified by distillation before use.

Xenon-flash photolysis apparatus was of the standard design equipped with two xenon-flash lamps (Xenon Corp., N-851C); the half-duration of the lamp was ca. 8 μs. The solution containing the radical source was photodecomposed with the light longer than 270 nm which was selected by the cut-off light filter; thus, alkyl halides having absorption band shorter than 270 nm were chosen as substrates in this study. The solution was degassed up to ca. 10^{-2} Pa. All measurements were performed at 23 °C.

For competitive experiments to evaluate the relative reaction rate constants, the following chain reactions were used (Scheme 1).

$$(CH_3)_2(CN)CN{=}NC(CN)(CH_3)_2 \xrightarrow{h\nu} 2\ (CH_3)_2(CN)C\cdot + N_2 \qquad (1)$$

$$(CH_3)_2(CN)C\cdot + Ph_3SnH \longrightarrow Ph_3Sn\cdot + (CH_3)_2(CN)CH \qquad (2)$$

$$Ph_3Sn\cdot + RX \xrightarrow{k_x^r} Ph_3SnX + R\cdot \qquad (3)$$

$$R\cdot + Ph_3SnH \longrightarrow RH + Ph_3Sn\cdot \qquad (4)$$

Scheme 1.

By using azobisisobutyronitrile as a photo-initiator, which was decomposed with the light longer wavelength than 350 nm, one could obtain the relative rates for the alkyl halides with absorption band at longer wavelength than 270 nm. For such alkyl halides, it was difficult to obtain the absolute rate constants by the xenon-flash photolysis method. RH and RX were analyzed by gas chromatography; the relative rate constants were computed by the Ingold and Shaw method.[14]

Results and Discussion

Figure 1 shows the transient absorption spectra produced by the flash photolysis of $Ph_3SnSnPh_3$ and $Ph_3SiSiPh_3$ in degassed cyclohexane solution. The main peak appeared at 320—330 nm with the broad band near 450 nm. The main peaks at 320—330 nm are similar to the reported absorption bands for $Ph_3Sn\cdot$ and $Ph_3Si\cdot$ by Chatgilialoglu et al.[8]

$$Ph_3MMPh_3 \underset{k_b}{\overset{h\nu}{\rightleftharpoons}} 2\ Ph_3M\cdot \qquad (5)$$

$$(M = Si, Sn)$$

By the photolysis of some disilanes and digermanes, the biradical formation via the ipso addition was reported.[10,15] It is presumed that these species also show the absorption band at ca. 330 nm, although the decay rate was slower than that of the metal centered radicals.[10] However, in the case of photolysis of

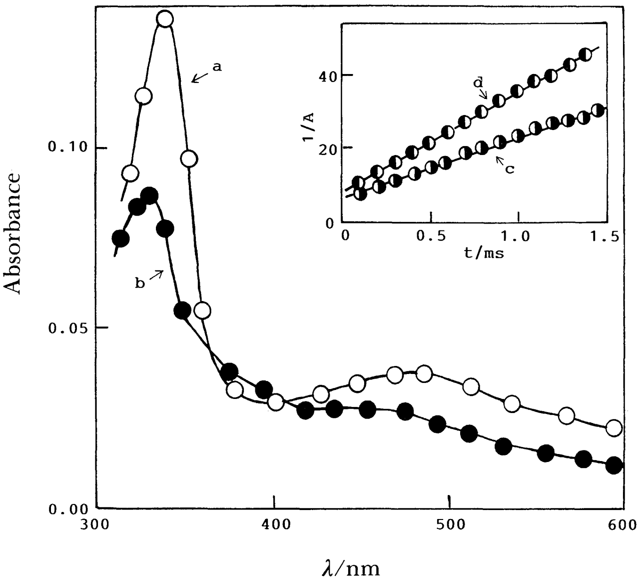


Fig. 1. Transient absorption spectra immediately after flash photolysis of 10^{-4} mol dm^{-3} of (a) $Ph_3SiSiPh_3$ and (b) $Ph_3SnSnPh_3$ in degassed cyclohexane in a cylindrical flash cell (10 cm optical path). Insert: Second-order plot at 330 nm of $Ph_3Sn\cdot$; (c) in cyclohexane and (d) in hexane.

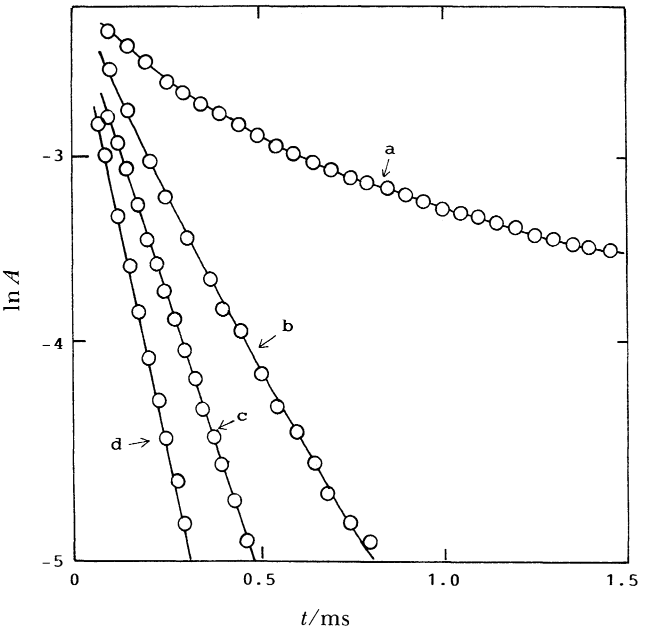


Fig. 2. First-order plots for decay of $Ph_3Sn\cdot$ (at 330 nm) in the presence of *t*-BuCl in degassed cyclohexane; (a) 0, (b) 0.21, (c) 0.47, and (d) 0.70 mol dm^{-3}.

$Ph_3SnSnPh_3$ and $Ph_3SiSiPh_3$, the formation of the biradicals may not be the main path because of the steric hindrance of many phenyl groups. The broad weak absorption band near 450 nm produced by the photolysis of the disilane was attributed to the free silanediyl (R_2Si:),[16] or to the rearrangement product.[17]

When *n*-donor solvent was used, the absorption of R_2Si: shifts to 320—330 nm by the complex formation.[18] Thus, we used cyclohexane as a solvent throughout this study. We followed predominately the decay of the main band at 320—330 nm to determine the reaction rates of $Ph_3Sn\cdot$ and $Ph_3Si\cdot$ with alkyl halides.

The insert of Fig. 1 shows the second-order plots (1/absorbance vs. time) for $Ph_3Sn\cdot$. The linear lines indicate that $Ph_3Sn\cdot$ predominately returns to $Ph_3SnSnPh_3$. The slope of the second-order plot, which refers to the ratio of $2k_b$ to the extinction coefficient (ε), varies with solvent viscosity, suggesting that k_b is near a diffusion controlled limit. The $2k_b/\varepsilon$ value in hexane is 3.5×10^5 cm^{-1} s^{-1}, which is close to the reported one by the laser flash photolysis.[8] On assuming k_b=ca. 2×10^9 mol^{-1} dm^3 s^{-1} which is about a half of $(C_2H_5)_3Si\cdot$, ε can be calculated to be ca. 10^4 cm^{-1} mol^{-1} dm^3; thus, the initial concentration of $Ph_3Sn\cdot$ produced by one flash exposure can be calculated from Fig. 1 to be ca. 10^{-6} mol dm^{-3}. In the case of $Ph_3Si\cdot$, the decay kinetics deviated from the second-order kinetics, suggesting that $Ph_3Si\cdot$ reacts with the phenyl group of the radical source.[8] On addition of small amount of oxygen, $Ph_3Sn\cdot$ and $Ph_3Si\cdot$ decayed rapidly; the rate constant for this reaction may be larger than 10^9 mol^{-1} dm^3 s^{-1}.

By the addition of appropriate concentration of alkyl halides to degassed solution, decay kinetics of $Ph_3Sn\cdot$ changed into first-order kinetics as shown in Fig. 2 for the reaction with *t*-butyl chloride. The decay rates were accelerated by the addition of the alkyl halides; thus, the following halogen abstraction reaction occurs.

$$Ph_3M\cdot + RX \xrightarrow{k_X} Ph_3MX + R\cdot \qquad (6)$$

When the concentration of RX was properly high, the first-order part became predominant as shown in Fig. 2, in which the slope refers to as $k_{\text{first-order}}$. When the concentration of RX was low, the contribution of the first-order term to the whole decay was small; for such case, the first-order term was separated from the mixed-order kinetics by a computer simulation method.[19,20] Figure 3 shows the pseudo-first-order plots for some reaction systems; the slope gave the k_X value. The k_X values for various alkyl halides are summarized in Table 1 for $Ph_3Sn\cdot$ and $Ph_3Si\cdot$.

The relative halogen abstraction reactivities (k^r_X) of alkyl halides by $Ph_3Sn\cdot$ were determined by the competitive experiment described in the experimental section. They are also summarized in Table 1, in which the k^r_Xvalue of CH_2Cl_2 was set to be 1.0. In Fig. 4, these k^r_Xvalues are plotted against the k_X values; a linear relation is seen, showing the reliability of the

Table 1. Absolute Rate Constants (k_x) and Relative Rate Constants (k_x^r) for Halogen Abstraction of $Ph_3Sn\cdot$ and $Ph_3Si\cdot$ from RX in Cyclohexane at 23 °C

RX	$Ph_3Sn\cdot$ k_x[a) mol^{-1} dm^3 s^{-1}	$Ph_3Sn\cdot$ k_x^r[b)	$Ph_3Si\cdot$ k_x[a) mol^{-1} dm^3 s^{-1}	IE[c) eV
n-BuCl	5.2×10^2	0.038	6.3×10^4	10.67
c-$C_6H_{11}Cl$		0.054		
$(CH_2Cl)_2$	4.5×10^3	0.15	5.7×10^5	11.12
t-BuCl	1.4×10^4	0.43	8.0×10^5	10.61
CH_2Cl_2	3.2×10^4	1.0	3.4×10^6	11.35
$PhCH_2Cl$		7.7		9.17
$CHCl_3$	2.0×10^6	55	1.1×10^8	11.42
n-BuBr	3.1×10^6	150		10.125
c-$C_6H_{11}Br$		250		

a) Each k_x value contains estimated error of ca. 10%. b) Estimation error of k_x^r is ca. 5%. c) Ionization energy from "Handbook of Chemistry and Physics," CRC Press, Bacon Raton, FL (1984), p. E-40.

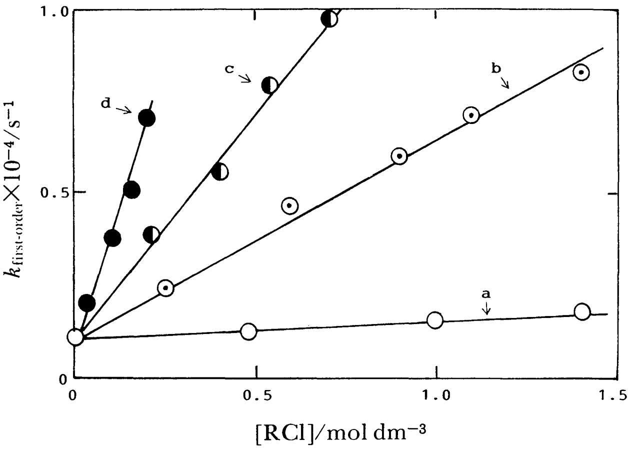


Fig. 3. Plots of pseudo-first-order rate constants ($k_{first\text{-}order}$) of $Ph_3Sn\cdot$ vs. concentration of alkyl halides; (a) *n*-BuCl, (b) $(CH_2Cl)_2$, (c) *t*-BuCl, and (d) CH_2Cl_2.

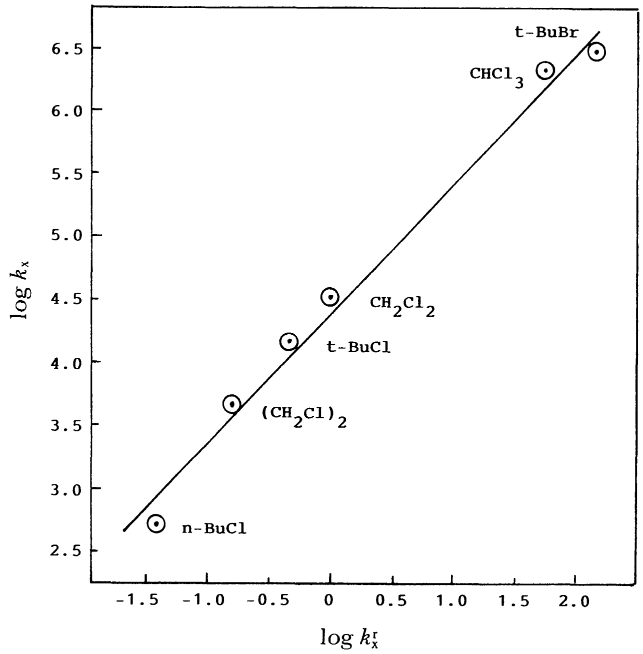
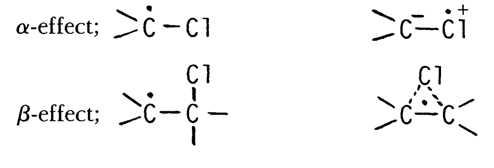


Fig. 4. Plot of log k_X (absolute rate constants) vs. log k_x^r (relative rate constant) for $Ph_3Sn\cdot$.

reaction rate constants obtained by the both methods. The k_X value for the reaction system of $Ph_3Sn\cdot$-*t*-BuCl obtained in this study (1.4×10^4 mol^{-1} dm^3 s^{-1}) was similar to the reported one (2.0×10^4 mol^{-1} dm^3 s^{-1}) which was determined with the rotating sector/ESR method reported by Carlsson and Ingold.[4)

For $Ph_3Sn\cdot$, the following orders in the reactivities were confirmed; RCl<RBr, $R_{primary}$–Cl<$R_{tertiary}$–Cl< cyclic halide. In order to investigate the factor controlling the reactivities, the k_X values are plotted against the bond-dissociation energy (BDE) of R–X.[21) In Fig. 5, linear correlations are found for the both radicals; the weaker the R–X bond is, the higher the reactivity is. A typical example is shown for the reactivity of RCl<RBr. Within the same halogen series, the low BDE value of R–X implies that the carbon radical (R·) is stable. Thus, the order of $R_{primary}$–Cl<$R_{tertiary}$–Cl is attributed to higher stability of tertiary carbon radical than the primary one. The α-halogen effect is more effective than the β-effect [$k_X(CH_2Cl_2)/k_X((CH_2Cl)_2)$=ca. 7]. The α-effect is intensified with additional halogen atom [$k_X(CHCl_3)/k_X(CH_2Cl_2)$=ca. 60].[22) Since the k_r values of these compounds are also on the line of Fig. 5, these effects can be interpreted by the stability of the carbon centered radicals; some of the resonance structures can be written as follows;



As for the polar contribution to the transition states of these reactions, charge transfer from the radical

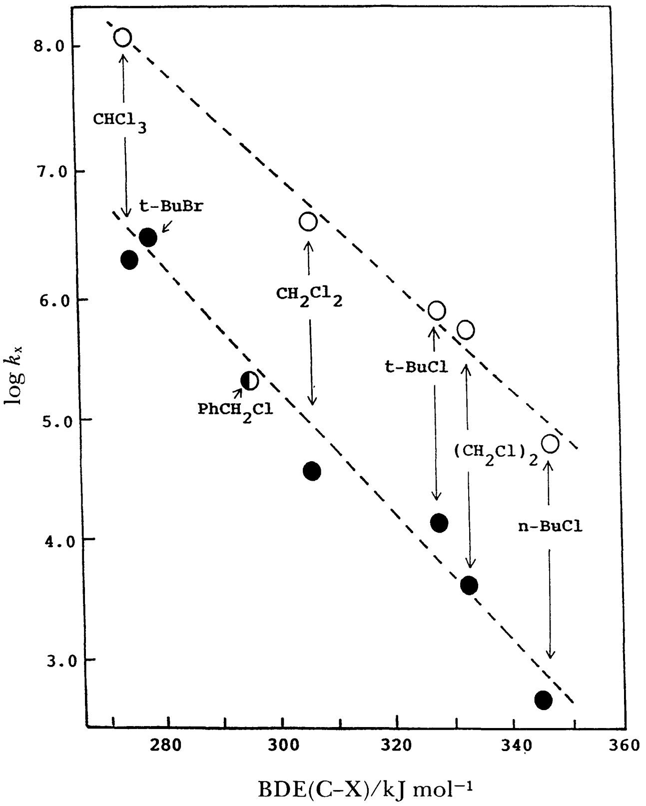


Fig. 5. Plots of log k_X vs. bond-dissociation energy of R–X [BDE(C–X)]. (●) $Ph_3Sn\cdot$ and (○) $Ph_3Si\cdot$; (◐) k_x for $PhCH_2Cl$ was evaluated from Fig. 4.

center to RX has been presumed from the Hammett plot by Chatgilialoglu et al.[23] In Table 1, however, no clear tendency that k_X values increase with the ionization energy can be found. This suggests that the polar effect is not the main factor in determining the reactivity, when a wide range of RX is compared.

From Table 1 and Fig. 5, it is confirmed that the reactivity of $Ph_3Si\cdot$ is higher than that of $Ph_3Sn\cdot$; this tendency is in agreement with the order of reactivities in the halogen abstraction of n-$Bu_3Sn\cdot$ and $Et_3Si\cdot$.[8] The order of the reactivity of $R_3Sn\cdot$ and $R_3Si\cdot$ can be well interpreted by the thermodynamic data; i.e., in the case of $(CH_3)_3MCl$, BDE of Sn–Cl (422 kJ mol^{-1}) is smaller than that of Si–Cl (485 kJ mol^{-1}),[24] which indicates that Cl-abstraction of $(CH_3)_3Sn\cdot$ is more endothermic than that by $(CH_3)_3Si\cdot$. Although the thermodynamic data for Ph_3MX are not available, this tendency is in good agreement with our observed tendency in the reactivities of $Ph_3Sn\cdot$ and $Ph_3Si\cdot$ for halogen abstraction.

The k_X value for $Ph_3Sn\cdot$–n-BuBr is ca. 1/10 of n-$Bu_3Sn\cdot$, in which the latter rate constant was determined by the laser-flash probe method.[6] The k_X value for $Ph_3Si\cdot$–t-BuCl is also ca. 1/10 of $Et_3Si\cdot$–t-BuCl.[7] The slightly lower reactivity of $Ph_3M\cdot$ compared with the corresponding $R_3M\cdot$ can be confirmed in this study. In the case of the $Ph_3C\cdot$ and $R_3C\cdot$, the former is extremely less reactive than the latter, because of the delocalization of the unpaired electron into the phenyl groups even though the π-orbitals are not in the same plane. On the other hand, the delocalization of the unpaired electron would not be expected for $Ph_3Sn\cdot$ and $Ph_3Si\cdot$, because of the small overlap between the orbitals of unpaired electron of the central atom [Si(3p) or Sn(5p)] and phenyl 2p-orbital. Thus, the difference in the reactivity between $Ph_3M\cdot$ and $R_3M\cdot$ is quite small.

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