

# Spectroscopic Studies of Tributylstannyl Radical. Rates of Formation, Termination, and Abstraction Determined by Transient Absorption Spectroscopy

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Received January 26, 2004

Transient absorption spectroscopy (TAS) was used to measure the rate of formation and the rate of self-termination of the main group metal hydride, tri-*n*-butyltin hydride (Bu<sub>3</sub>SnH). Irradiation of di-*tert*-butyl peroxide in the presence of Bu<sub>3</sub>SnH generates the tri-*n*-butylstannyl radical (Bu<sub>3</sub>Sn•) by hydrogen atom abstraction. Analysis of the growth of the Bu<sub>3</sub>Sn• at 400 nm, corrected for radical termination, yields  $k_{\text{H-abs}} = (3.5 \pm 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . The extinction coefficient of the Bu<sub>3</sub>Sn• ( $\epsilon = 1620 \pm 40 \text{ cm}^{-1} \text{ M}^{-1}$  at 400 nm), measured for the first time in this work, is 3.5 times greater than the literature estimate. The experimental value for  $\epsilon(\text{Bu}_3\text{Sn}\cdot)$  permits the quantitative measurement of the rate of Bu<sub>3</sub>Sn• self-termination ( $2k_t = (3.6 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) in benzene at 296 K. This experimental value is greater than previous literature estimates but less than predicted by the Smoluchowski equation ( $2k_t^s = (4.4 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) using our measured diffusion coefficient for tin hydride ( $D = (1.34 \pm 0.08) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  at 296 K in benzene). This work shows that the rates of hydrogen abstraction from Bu<sub>3</sub>SnH by *tert*-butoxyl radical and self-termination of Bu<sub>3</sub>Sn• are both more rapid than previously reported. A mechanistic kinetic model was developed with this new kinetic information to fit the time-dependent TAS signal of Bu<sub>3</sub>Sn•. This approach provides the optimum reaction conditions, both low hydride and halide concentrations, to measure the rate of bromine atom abstraction from 2-phenethyl bromide ( $k_{\text{Br-abs}} = (3.7 \pm 0.3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ).

## Introduction

Main group metal hydrides are important hydrogen atom donors utilized in synthetic free radical strategies and as hydrogen atom donors in fundamental studies of organic free radicals.<sup>1</sup> Tin hydride and the corresponding stannyl radical in particular have been used as kinetic and thermodynamic standards for developing basis rate reactions.<sup>2</sup> However, discrepancies in the literature regarding the self-termination rate due to ambiguities reported for the optical properties of the stannyl radical,<sup>3</sup> kinetic measurements performed under

experimental conditions favoring competing pathways,<sup>4,5</sup> and empirical corrections used to correct bond enthalpies<sup>6</sup> prompted us to undertake a closer examination of the spectroscopic properties of the tri-*n*-butylstannyl radical (Bu<sub>3</sub>Sn•). An improved understanding of the spectroscopic, kinetic, and thermodynamic properties of the tin hydride and stannyl radical is necessary to improve the accuracy of basis rate determinations for competitive rate studies. In particular, an Arrhenius rate expression for halide abstraction by the stannyl radical from 2-phenethyl bromide would provide an important basis reaction in our competitive rate studies.<sup>7</sup>

Scheme 1 shows the detailed mechanistic pathway for the radical chain reduction of alkyl halides (RX → RH). Irradiation of a photoinitiator, di-*tert*-butyl peroxide, with a pulsed laser leads to the prompt (within the 20 ns laser pulse) formation of *tert*-butoxyl radicals (t-BuO•), eq 1. In the presence of tin hydride (Bu<sub>3</sub>SnH) the t-BuO• abstracts a H atom to yield t-BuOH and Bu<sub>3</sub>Sn•, eq 2. In the absence of halide, the Bu<sub>3</sub>Sn• will be consumed by radical self-termination at diffusion-

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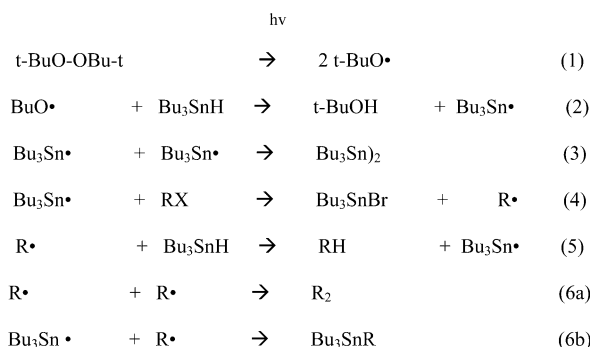
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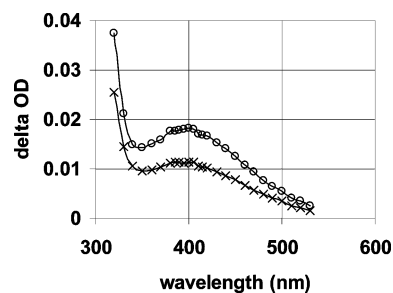
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## Scheme 1



controlled rates, eq 3. However, in the presence of an alkyl halide (RX), halide abstraction competes with radical termination to yield alkyl radical, eq 4. At low radical concentrations, chain propagation, eq 5, competes with alkyl radical termination, eq 6.

Although Scheme 1 details a multistep free radical chain reaction, the rate of each step can be measured by time-resolved spectroscopic methods under appropriate experimental conditions. Fischer and co-workers have measured the rates of self-termination of several organic free radicals by EPR methods;<sup>8</sup> however, the tri-*n*-butylstannyl radical is not easily observable by EPR in solution.<sup>9</sup> Fortunately,  $\text{Bu}_3\text{Sn}\cdot$  is reported to have a characteristic absorption feature at 400 nm that is sufficiently strongly absorbing<sup>10</sup> to be monitored by transient absorption spectroscopy (TAS), and the rate of halide abstraction can be obtained by monitoring the disappearance of  $\text{Bu}_3\text{Sn}\cdot$  as a function of halide concentration. However, the accuracy and precision of the observed rate will be suspect if the experimental conditions are not carefully controlled. Specifically, to obtain an unambiguous bromide abstraction rate constant from a measure of the radical decay as a function of halide concentration, three experimental conditions must be met. First, the  $\text{Bu}_3\text{Sn}\cdot$  is not still being formed; that is, all the *tert*-butoxyl radical has completely reacted, eq 1. Second, self-termination of  $\text{Bu}_3\text{Sn}\cdot$ , i.e., disappearance by a competing second-order reaction, does not dominate the transient decay, eq 3.<sup>11</sup> Third, the subsequent reaction of the alkyl radical with tin hydride must not regenerate significant concentrations of stannyl radical on the time scale of our measurement, i.e., eq 5. Alternatively, knowledge of an accurate extinction coefficient for  $n\text{-Bu}_3\text{Sn}\cdot$  also allows quantitative kinetic modeling of the suite of eqs 1–6. The goal of this work is to improve the accuracy of time-resolved spectroscopic measurements, by discovery of the optimum experimental reaction conditions, to obtain a quantitative description of the chemical and physical properties of the  $\text{Bu}_3\text{Sn}\cdot$  species. The work below describes a more accurate measurement of the rate of  $\text{Bu}_3\text{Sn}\cdot$  formation, eq 2, the rate of  $\text{Bu}_3\text{Sn}\cdot$  self-termination, eq 3, and the rate of halide abstraction, eq 4, by using time-resolved transient absorption spectroscopy. The rate data determined in this work are combined with rate data from



**Figure 1.** Transient absorption spectra of tri-*n*-butylstannyl radical obtained from 308 nm pulsed irradiation of di-*tert*-butyl peroxide in 0.02 M tri-*n*-butyltin hydride at 90 ns (○) and 150  $\mu\text{s}$  (×) after photolysis.

the literature to develop a mechanistic kinetic model that accurately describes the time-dependent absorption properties of  $\text{Bu}_3\text{Sn}\cdot$ .

## Results and Discussion

Irradiation of di-*tert*-butyl peroxide in an argon-purged benzene solution containing tin hydride yields a transient intermediate with a strong absorbance feature at 400 nm, as shown in Figure 1. The rate of formation of the transient is dependent on the tin hydride concentration and decays to baseline over a period of several microseconds by second-order pathways. In the presence of a primary halide, phenethyl bromide ( $\text{PhCH}_2\text{CH}_2\text{Br}$ ), the lifetime of the 400 nm transient is reduced and the observed decay is first-order in bromide concentration at lower tin hydride concentrations. These observations are consistent with the previous assignment of the 400 nm transient as  $\text{Bu}_3\text{Sn}\cdot$ .<sup>4</sup> One notable anomaly is the decay behavior of the transient at higher hydride concentrations; the absorption signal at 400 nm does not appear to come back to baseline over several microseconds. The “persistent absorption” is due to the chain reaction that regenerates the tri-*n*-butylstannyl radical, not from the hydrogen atom abstraction by *tert*-butoxyl radical, but from hydrogen atom abstraction by the alkyl radical, eq 5. At higher halide concentrations the chain reaction leads to a persistent absorption on the microsecond time scale that leads to an error in the measured abstraction rate.

Beckwith and co-workers<sup>12</sup> have recently suggested that the tri-*n*-butylstannyl radical may add to benzene at 70 °C, as inferred from rate retardation in the reduction of benzoate esters relative to cyclohexane. We did not observe any absorbance in the room-temperature TAS in the wavelength region where cyclohexadienyl radical derivatives have been observed as formed by other pathways.<sup>13</sup>

**Rate of  $\text{Bu}_3\text{Sn}\cdot$  Self-Termination ( $2k_t$ ).** Assuming radical–radical reactions are diffusion controlled, the rate of self-termination can be estimated from the Smoluchowski equation, eq 7, where  $\sigma$  is a spin statisti-

$$2k_t^s = (8\pi/1000)\sigma\rho_A D_{AB}N \quad (7)$$

cal factor,  $\rho$  is the reaction diameter of the radical

(8) Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200.  
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 (10) Wakasa, M.; Kugita, T. *Organometallics* **1998**, *17*, 1913.  
 (11) Cross-termination reactions of stannyl radical with alkyl radical, reaction 6b, can also decrease the observed absorbance. See: Rügge, D.; Fischer, H. *Int. J. Chem. Kinet.* **1986**, *18*, 145.

(12) Beckwith, A. L. J.; Bowry, V. W.; Bowman, W. R.; Mann, E.; Parr, J.; Storey, J. M. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 95. We thank a reviewer for bringing this reference to our attention.

(13) Effio, A.; Griller, D.; Ingold, K. U.; Scaiano, J. C.; Sheng, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 6063.

species,  $D_{AB}$  is the diffusion coefficient of the radical solute  $A$  in the solvent  $B$ , and  $N$  is Avogadro's number. For several organic radical species this empirical approach has been demonstrated to be accurate to within 20% of the corresponding experimental values.<sup>8</sup>

Assuming that only solvent-caged singlet radical pairs react (i.e.,  $\sigma = 1/4$ ), all that is needed to calculate the Smoluchowski termination rate,  $2k_t^s$ , are the radical reaction diameter and diffusion coefficient. It is generally assumed that both  $\rho$  and  $D$  of the radical ( $R^\bullet$ ) are well modeled by the corresponding hydrocarbon (RH).<sup>14</sup> These two assumptions have been shown to be valid for several organic radicals in nonassociating organic solvents, and we believe it is a valid approximation for tri-*n*-butylstannyl radical in benzene. Specifically, it is unlikely that addition of hydrogen atom to the tri-*n*-butylstannyl radical will significantly change the reaction diameter.<sup>15</sup> Since the reaction diameter is twice the radius of the reacting species, we calculate the radius of  $\text{Bu}_3\text{SnH}$  from the known molar density to obtain an estimate of the reaction diameter of the radical assuming close packing spheres.<sup>16</sup> To be confident that the assumption is valid for  $D_{AB}$  (i.e.,  $D_{\text{Bu}_3\text{SnH}} = D_{\text{Bu}_3\text{Sn}^\bullet}$ ), there must be no significant interactions between the radical and the solvent. This assumption appears reasonable given the recent demonstration that  $D$  values for aryl alcohols are comparable to  $D$  of the corresponding ketyl radicals in hydroxylic solvents.<sup>17</sup> With our confidence in the above pair of assumptions two paths were used to determine  $D$  of  $\text{Bu}_3\text{SnH}$  to be used as a representation for  $D$  of  $\text{Bu}_3\text{Sn}^\bullet$  in benzene.

Our first approach uses the Stokes–Einstein (SE) equation, eq 8, which predicts that the diffusion coefficient of the solute is proportional to the ratio of the temperature ( $T$ ) to viscosity ( $\eta$ ) multiplied by a numerical constant ( $k_B/6\pi r_a$ ), where  $k_B$  is the Boltzmann constant and  $r_a$  is the radius of the solute. The Sperrnol–Wirtz (SW) modification of the SE equation, eq 9, uses a microfriction factor ( $f$ )<sup>18,19</sup> to correct the diffusion coefficient for differences in solute–solvent molecular size and shape.

$$D_{\text{SE}} = (T\eta)(k_B/6\pi r_a) \quad (8)$$

$$D_{\text{SW}} = D_{\text{SE}}/f \quad (9)$$

Our second approach, the Taylor's dispersion (TD),<sup>20</sup> method was used to measure the diffusion coefficient

(14) Shuh, H.-H.; Fischer, H. *Int. J. Chem. Kinet.* **1976**, *8*, 341.

(15) MW  $n\text{-Bu}_3\text{SnH} = 290.7$ , MW  $n\text{-Bu}_3\text{Sn}^\bullet$  radical = 289.7. On the other hand for a lighter molecule the molecular volume of HO radical (14.4 mL/mol, MW 17 versus 18 mL/mol for  $\text{H}_2\text{O}$ , MW = 18). This amounts to a 93% smaller  $\rho(\text{HO})$  compared to  $\rho(\text{H}_2\text{O})$ . Autrey, T.; Brown, A. K.; Camaioni, D. M.; Dupuis, M.; Foster, N. S.; Getty, A. *J. Am. Chem. Soc.* **2004**, *126*, 3680.

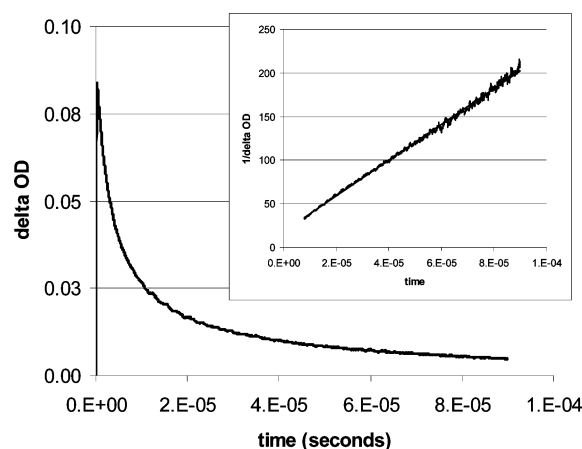
(16)  $\rho$ , the reaction diameter,  $8.73 \times 10^{-8}$  cm, is twice the radius  $r$  ( $r = (3 \times V_x N/4\pi)^{1/3}$ ).  $V_x$  is the molecular volume  $4.47 \times 10^{-22}$  cm<sup>3</sup>/molecule calculated from molar density,  $x = 0.74$ , the volume fraction for cubic closest-packing spheres, and  $N$  is Avogadro's number.

(17) Autrey, T.; Kandamarachchi, P.; Franz, J. A. *J. Phys. Chem. A* **2001**, *105*, 5948.

(18) Shuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *91*, 2130.

(19) Sperrnol–Wirtz microfriction factor  $f = (0.16 + 0.4r_A/r_B)(0.9 + 0.4T_A r - 0.25T_B r)$ . Reduced temperatures,  $T_r$ , are given by,  $T_r = (T - T_{\text{db}})/(T_{\text{db}} - T_{\text{df}})$ , where  $T_{\text{df}}$  and  $T_{\text{db}}$  are freezing and boiling points of species  $x = n\text{-Bu}_3\text{SnH}$  (A) and benzene (B). The radii in the microfriction factor term are given by  $r_A = (3V_A(c)/4\pi N)^{1/3}$ , where  $c = 0.74$ , the volume fraction for cubic closest-packed spheres. Andrade viscosity of benzene is given by the expression  $\ln(\eta, \text{cP}) = -4.117 + 2093.7/RT$ .

(20) Taylor, S. G. *Proc. R. Soc. London A* **1953**, *219*, 186.



**Figure 2.** Decay of 400 nm transient generated from 308 nm pulsed irradiation of di-*tert*-butyl peroxide in 0.02 M tri-*n*-butyltin hydride. Inset is observed second-order decay at 400 nm,  $2k_t/\epsilon = 2.16 \times 10^6 \text{ s}^{-1}$ .

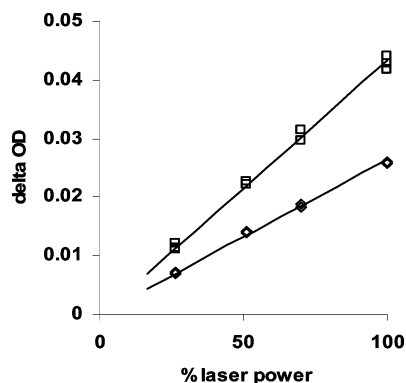
of  $\text{Bu}_3\text{SnH}$  in benzene. Comparison of our experimentally measured  $D_{\text{TD}} (= (1.34 \pm 0.08) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  at 296 K) coefficient obtained from the dispersion method with  $D_{\text{SW}} (= 1.30 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  at 296 K) shows excellent agreement between the experimental method and the empirical calculation for tri-*n*-butyltin hydride in benzene. Setting  $\sigma = 1/4$  and using the average of  $D_{\text{TD}}$  and  $D_{\text{SW}} ((1.32 \pm 0.08) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$  combined with  $\rho (= 8.73 \times 10^{-8} \text{ cm})$ <sup>16</sup> obtained from the molar volume of tin hydride we calculate the rate of self-termination of  $\text{Bu}_3\text{Sn}^\bullet$  in benzene at 296 K ( $2k_t^s = (4.4 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).

Alternatively, the rate of a radical self-termination reaction,  $2k_t$ , can be determined experimentally from the observed second-order decay of the transient absorbance,  $A(t)$ , shown in Figure 2. Least-squares analysis of  $1/A(t)$  versus time yields the absorbance termination rate constant,  $2k_t/\epsilon = (2.2 \pm 0.2) \times 10^6 \text{ s}^{-1}$  at 400 nm for our experimental apparatus.<sup>21</sup> Given an accurate value for the extinction coefficient of  $\epsilon(\text{Bu}_3\text{Sn}^\bullet)$  at 400 nm, the rate constant for tri-*n*-butylstannyl radical self-termination can be obtained. The cited literature value ( $\epsilon_{\text{lit}} = 450 \text{ M}^{-1} \text{ cm}^{-1}$ ) at 400 nm<sup>3</sup> yields  $2k_t = (9.9 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  in benzene at 296 K, which is significantly slower than expected for a diffusion-controlled reaction pathway.

Our experimental termination rate constant determined from the published extinction coefficient and our decay data is well outside the typical uncertainty of the Smoluchowski equation. This is a surprising result given that Fischer has demonstrated that the Smoluchowski equation is generally very close to experiment (within  $\pm 20\%$ ) for conventional organic radicals in nonassociating organic solvents, such as benzene. Therefore, either the Smoluchowski method fails badly for tri-*n*-butylstannyl radical in benzene or the literature report of  $\epsilon_{400 \text{ nm}}$  is in error by as much as 400%. Resolution of this discrepancy is important. If the Smoluchowski equation fails to predict  $\text{Bu}_3\text{Sn}^\bullet$  self-termination in benzene, this may indicate unique radical termination dynamics occurring with  $\text{Bu}_3\text{Sn}^\bullet$  in

(21) The decay is proportional to  $2k_t/\epsilon l$ , where  $\epsilon$  is the extinction coefficient of the transient and  $l$  is the path length, in our experiment = 1 cm.





**Figure 3.** Extinction coefficient measurement of tri-*n*-butylstannyl radical measured at 400 nm ( $\epsilon = 1620 \pm 40 \text{ M}^{-1} \text{ cm}^{-1}$ ) using Aberchrome 540. The absorbances of fulgide and tin radical were measured as a function of laser power (308 nm) just after the laser was fired. The extinction coefficient of the stannyl radical is proportional to the slope of the actinometer ( $m_{\text{act}}$ ) ( $\diamond$ ) and to the slope of tin radical ( $m_{\text{Sn}}$ ) ( $\square$ ).

benzene, e.g.,  $\sigma \neq 1/4$  and/or  $D_{\text{Bu}_3\text{Sn}^*} \neq D_{\text{Bu}_3\text{SnH}}$ . The likelihood that the quoted literature value for the extinction coefficient was in serious error convinced us to revisit the determination of  $\epsilon$  of the  $\text{Bu}_3\text{Sn}^*$  radical.

**Extinction Coefficient of  $\text{Bu}_3\text{Sn}^*$ .** Pulsed irradiation of Aberchrome 540 at 308 nm generates a deep red ( $\lambda_{\text{max}} = 540 \text{ nm}$ ) cyclized isomer within nanoseconds with a quantum efficiency of 0.20.<sup>22</sup> In the same sample cell a solution of di-*tert*-butyl peroxide solution with matching absorbance, containing 20 mM  $\text{Bu}_3\text{SnH}$ , was irradiated under identical conditions. Since t-BuO $^*$  is rapidly and quantitatively converted to  $\text{Bu}_3\text{Sn}^*$ <sup>23</sup> under the reaction conditions, the quantum yield for tri-*n*-butylstannyl radical can be determined from the literature quantum yield of t-BuO $^*$ ,  $\Phi_{\text{Sn}^*} = \Phi_{\text{tBuO}^*}$ .<sup>24</sup> A plot of  $\Delta\text{OD}$  at time = 0 for both the  $\text{Bu}_3\text{Sn}^*$  ( $\lambda = 400 \text{ nm}$ )<sup>25</sup> and the actinometer ( $\lambda_{\text{max}} = 540 \text{ nm}$ ,  $\epsilon_{\text{act}} = 8200 \text{ cm}^{-1} \text{ M}^{-1}$ ) as a function of incident laser power is shown in Figure 3. Least-squares fit of the data provides the ratio of  $\epsilon_{\text{Sn}^*}/\epsilon_{\text{act}}$  by direct comparison of the slopes ( $m_{\text{Sn}^*} = 4.32 \times 10^{-4}$ ,  $\rho = 0.996$ ;  $m_{\text{act}} = 2.62 \times 10^{-4}$ ,  $\rho = 0.996$ ). Using eq 10 the extinction coefficient for  $\text{Bu}_3\text{Sn}^*$  was determined ( $\epsilon_{\text{Sn}^*} = 1620 \pm 40 \text{ M}^{-1} \text{ cm}^{-1}$  at 400 nm).

$$\epsilon_{\text{Sn}^*} = \epsilon_{\text{act}}(\Phi_{\text{act}}/\Phi_{\text{Sn}^*}) \times (m_{\text{Sn}^*}/m_{\text{act}}) \quad (10)$$

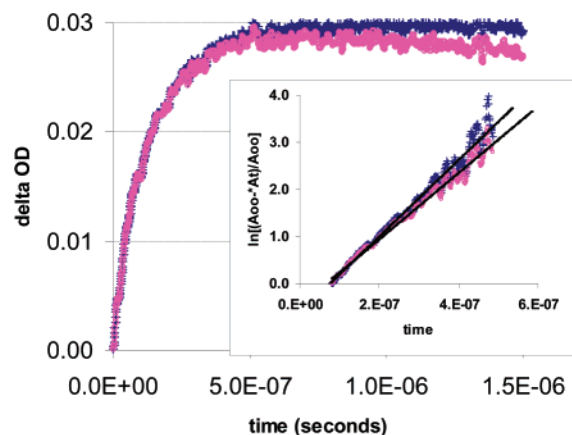
The discrepancy between our experimental extinction coefficient,  $\epsilon_{\text{exp}} = 1620 \pm 40 \text{ M}^{-1} \text{ cm}^{-1}$  at 400 nm, and the literature extinction coefficient,  $\epsilon_{\text{lit}} = 450 \text{ M}^{-1} \text{ cm}^{-1}$  at 400 nm, appears due to a previous misunderstanding. Close examination of the original citation shows that there was no direct experimental measure of the extinction coefficient. It appears that the  $\epsilon_{\text{lit}}$  at 400 nm was estimated<sup>4</sup> from an estimate of  $2k_t$  in cyclohexane<sup>1e</sup> and

(22) Wintgens, V. J.; L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 511.

(23) Millimolar concentrations of tin hydride are sufficient to trap all the *tert*-butoxyl radical. The rate of  $\beta$ -scission of *tert*-butoxyl radical is  $1.4 \times 10^4 \text{ s}^{-1}$  in benzene. Tsentalovich, Y. P.; Kulik, L. V.; Gristan, N.; Yurkovskaya, A. V. *J. Phys. Chem. A* **1998**, *102*, 7975.

(24) The quantum yield for t-BuO radical formation from irradiation of di-*tert*-butyl peroxide in benzene at ambient temperature was 1.66. Wayner, D. D. M.; Luszytk, E.; Page, D.; Ingold, K. U.; Mulder, P.; Laarhoven, L. J. J.; Aldrich, H. S. *J. Am. Chem. Soc.* **1995**, *117*, 8737.

(25) The absorbance at time = 0 is calculate by fitting the second-order decay and extrapolating back to time = zero.



**Figure 4.** Irradiation of a benzene solution of di-*tert*-butyl peroxide containing 0.02 M  $\text{Bu}_3\text{SnH}$ . Comparison of 400 nm transient ( $n\text{-Bu}_3\text{Sn}^*$ ) before (red  $\circ$ ) and after (black  $+$ ) termination correction. Inset shows first-order analysis of rise time with correction,  $k_{\text{abs}} = 3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , and without correction,  $k_{\text{abs}} = 4.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , for radical termination.

subsequently taken as a direct experimental measure.<sup>3</sup> Thus, our value provides the first experimental measure of the  $\epsilon(\text{Bu}_3\text{Sn}^*)$ . Using our experimentally determined extinction coefficient of  $\text{Bu}_3\text{Sn}^*$  we obtain the rate of self-termination from our experimental decay data at 400 nm ( $2k_t^{\text{exp}} = (3.6 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). The difference between the empirical Smoluchowski estimate of  $2k_t^s$  ( $(4.4 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and our experimental value is almost within the 20% error bars typically observed in this type of comparison as noted by Fischer.<sup>8</sup> If the difference between  $2k_t^s$  and  $2k_t^{\text{exp}}$  is real, the difference may be explained by solvent cage dynamics dictating competition between cage-escape versus cage-recombination. Lui and Scott<sup>26</sup> observed the opposite effect for phenylthiyl radical termination: the observed radical termination was faster than expected on the basis of Smoluchowski. This is most likely due to  $\sigma > 1/4$  due to the fast intersystem crossing of triplet radical pairs in the solvent cage.<sup>27</sup> In the present case one would have to argue that  $\sigma < 1/4$  for tri-*n*-butylstannyl radical termination in benzene. Further work over an extended temperature range is planned with a goal to elucidate the origin of this difference.

**Rate of Formation of  $\text{Bu}_3\text{Sn}^*$ .** At the radical concentrations generated by a pulsed laser,  $10^{-6} \text{ M} < [\text{R}^*] < 5 \times 10^{-5} \text{ M}$ , radical termination will occur during the rise time of the experiment, leading to reduction in the transient absorbance on the time scale of the experiment. Therefore,  $A_t$  and consequently  $A_\infty$  are reduced in amplitude by radical self-termination. This leads to errors in the measurement of  $k_{\text{abs}}$  (ca. 5–90%).<sup>28</sup> To obtain an accurate measure of  $k_{\text{abs}}$ , the quantity of  $\text{Bu}_3\text{Sn}^*$  consumed by self-termination pathways occurring during the growth of  $\text{Bu}_3\text{Sn}^*$  can be accounted for with a termination correction value ( $=2k_t/\epsilon$ )( $A(\theta^2\Delta t)$ ), as shown in eq 11. Substitution of  $A_t$  for  $A_\infty$  in the conventional first-order analysis yields eq 12. The results of this approach are illustrated in Figure 4,

(26) Lui, S. N.; Scott, T. W. *J. Phys. Chem.* **1989**, *93*, 1393.

(27) Autrey, T.; Devadoss, C.; Sauerweun, B.; Franz, J. A.; Schuster, G. B. *J. Phys. Chem.* **1995**, *99*, 869.

(28) Franz, J. A.; Bushaw, B. A.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 268.

**Table 1.** Kinetic and Optical Property Data for Tri-*n*-butyltin Hydride and the Corresponding Stannyl Radical, Comparison of Experimental and Literature Data<sup>a</sup>

pathway	this work	literature	citation
Rate (M <sup>-1</sup> s <sup>-1</sup> )			
t-BuO• + n-Bu <sub>3</sub> SnH	$(3.5 \pm 0.3) \times 10^8$	$1.9 \times 10^8$	<i>b</i>
n-Bu <sub>3</sub> Sn• + n-Bu <sub>3</sub> Sn•	$(3.6 \pm 0.3) \times 10^9$	$2.1 \times 10^9$	<i>c</i>
n-Bu <sub>3</sub> Sn• + PhCH <sub>2</sub> CH <sub>2</sub> Br	$(3.7 \pm 0.3) \times 10^7$	$2.6 \pm 0.4 \times 10^7$	<i>d</i>
PhCH <sub>2</sub> CH <sub>2</sub> • + n-Bu <sub>3</sub> SnH	ND	$2.3 \times 10^9$	
Extinction Coefficient (cm <sup>-1</sup> M <sup>-1</sup> at 400 nm)			
n-Bu <sub>3</sub> Sn•	1620 ± 40	450	<i>f</i>
Diffusion Coefficient (cm <sup>2</sup> s <sup>-1</sup> )			
n-Bu <sub>3</sub> SnH	$(1.34 \pm 0.08) \times 10^{-5}$	$1.30 \times 10^{-5}$	<i>g</i>

<sup>a</sup> Reported errors are 1 standard deviation. <sup>b</sup>Ref 4. <sup>c</sup>Ref 1f in cyclohexane,  $1.4 \times 10^9$  s<sup>-1</sup>, corrected for differences in viscosity  $\eta(\text{cyclohexane})/\eta(\text{benzene}) = 0.898/0.603$ . <sup>d</sup>Ref 5, *n*-propyl bromide. <sup>e</sup>ND, not determined in this work; ref 26, ethyl radical + tin hydride was used for kinetic model. <sup>f</sup>Refs 3 and 4. <sup>g</sup>Calculated at 296 K by the Spornol–Wertz method as discussed in ref 18.

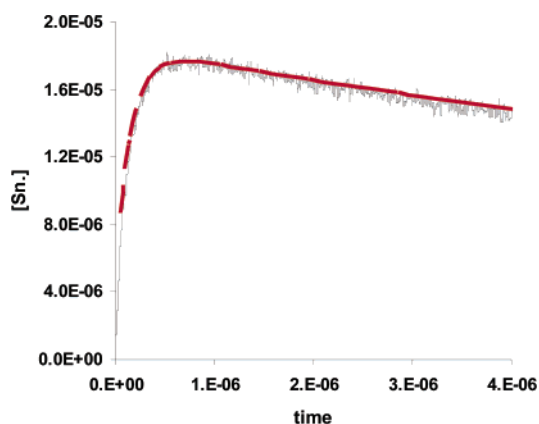
which compares the observed absorption of tri-*n*-butylstannyl radical to the absorption corrected for radical termination occurring during the rise time of the observed signal.

$$*A(t) = A(t) + \sum (2k_t/\epsilon)(A(t)^2 \Delta t) \quad (11)$$

$$k_{\text{abs}} [\text{Bu}_3\text{SnH}] = \ln[A_\infty/(A_\infty - *A_t)] \quad (12)$$

The rate of formation of Bu<sub>3</sub>Sn• generated by H atom abstraction from Bu<sub>3</sub>SnH by t-BuO• can be obtained from the rise time of the termination-corrected absorption data shown in Figure 4. By correcting the observed experimental *A<sub>t</sub>* measured at 400 nm using this approach the rate constant for *k<sub>abs</sub>* is  $(3.5 \pm 0.3) \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>. Without correction, the apparent rate of hydrogen atom abstraction (*k<sub>abs</sub>* =  $(4.0 \pm 0.3) \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>) is overestimated, even though the radical concentration is kept relatively low, about  $1.9 \times 10^{-5}$  M total radical concentration, by attenuation of the excitation pulse (<2 mJ). Although this termination-correction approach does not lead to an increase in precision of the measurement, it does result in an improvement of the experimental accuracy. In the present example, at low laser power, the experimental accuracy is enhanced by ~10%; however, at higher laser power (increased radical concentrations) obviously the error in rate accuracy can become quite significant. Our measured value for *k<sub>abs</sub>* is well outside the error of the previous literature determination (see Table 1). The source of this discrepancy reflects the challenge inherent in accurate measurements of fast pseudo-first-order kinetics using nanosecond TAS. In a subsequent paper we will describe our measurements of this abstraction reaction by time-resolved photoacoustic calorimetry, which is better suited to measure kinetics on this time scale.<sup>29</sup>

**Primary Halide Abstraction by Bu<sub>3</sub>Sn•.** The experimental data obtained in this work,  $\epsilon_{\text{Bu}_3\text{Sn}^\bullet}$ , *k<sub>abs</sub>* (eq 2), and  $2k_t$  (eq 3), combined with the literature value<sup>30</sup>



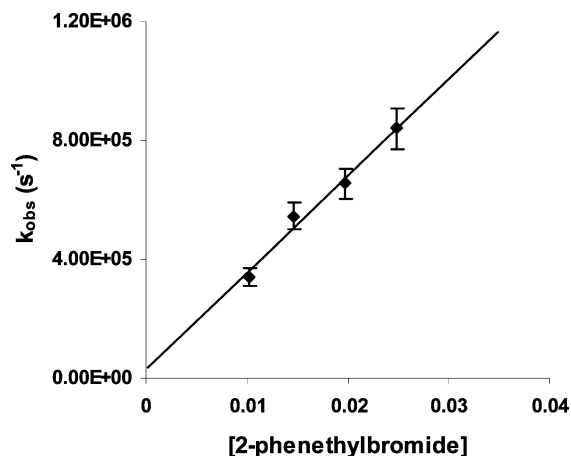
**Figure 5.** Comparison of experimental 400 nm transient (n-Bu<sub>3</sub>Sn•) growth and decay with the mechanistic kinetic model prediction using data determined in this study,  $\epsilon = 1620$  M<sup>-1</sup> cm<sup>-1</sup>,  $k_{\text{H-abs}} = 3.5 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>, and  $2k_t = 3.6 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. The solid red line through the absorbance is model prediction.

for primary alkyl radical abstraction from tin hydride (eq 5), allow us to develop a mechanistic kinetic model (MKM) that predicts the concentration of [Bu<sub>3</sub>Sn•] as a function of both halide and hydride concentration that we can directly compare with our experimental TAS data. One of the goals in the present work was to discover a TAS “time window” to measure the rate of bromide abstraction by Bu<sub>3</sub>Sn• from 2-phenethyl bromide, eq 4. A comparison of the MKM developed from Scheme 1 using rate data from Table 1 with the experimental absorbance of Bu<sub>3</sub>Sn• as a function of time is shown in Figure 5. It is apparent from examination of Figure 5 that there exists a finite window in time where Bu<sub>3</sub>Sn• has completely formed and has not begun to undergo self-termination to a significant extent. Furthermore, this time window is dependent on the concentration of Bu<sub>3</sub>SnH. For the reaction conditions shown in Figure 5 ([Bu<sub>3</sub>SnH] = 0.02 M) Bu<sub>3</sub>Sn• has reached a maximum after ca. 500 ns. After about 2.5 μs Bu<sub>3</sub>Sn• has decayed to ca. 85% of the initial concentration. These results suggest that a time window between 0.5 μs < *t* < 2.5 μs should provide the best opportunity to measure the bromide abstraction rate by transient absorption spectroscopy. One might be tempted to use higher tin hydride concentrations to reduce the lifetime of t-BuO• to enable the measurement of the kinetic experiment earlier; however this leads to greater interference from subsequent chain reaction. At higher halide and/or tin hydride concentrations the alkyl radical formed by abstraction (eq 4) subsequently attacks the tin hydride to yield a “second” Bu<sub>3</sub>Sn• (eq 5). This series of chain reactions will occur at high tin hydride concentrations and result in a persistent absorbance on the TAS time scale.

The persistent absorbance or “offset” created by the chain reaction may explain the apparent low rate of abstraction reported previously for *n*-propyl bromide ( $(2.6 \pm 0.4) \times 10^7$  M<sup>-1</sup> s<sup>-1</sup> at 295 K).<sup>5</sup> At higher halide concentrations, the chain reactions occur on the observed time scale of the TAS experiment to regenerate the tri-*n*-butylstannyl radical and consequently lead to

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**Figure 6.** Observed rate of transient decay at 400 nm ( $n\text{-Bu}_3\text{Sn}^\bullet$ ) as a function of 2-phenethyl bromide concentration at 299 K. Least-squares analysis of the slope provides the rate of bromine atom abstraction by ( $n\text{-Bu}_3\text{Sn}^\bullet$ ) from a primary alkyl bromide,  $(3.7 \pm 0.3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .

underestimating the halide abstraction rate; thus while the initial tri-*n*-butylstannyl radical is consumed by halide abstraction, the tri-*n*-butylstannyl radical is regenerated by the subsequent chain reactions! However, at lower halide and hydride concentrations the offset can be minimized. Kinetic modeling shows that at a tin concentration of 20 mM the halide concentration should be kept  $< 25 \text{ mM}$  to reduce the formation of an offset arising from the subsequent chain reactions. The rate of bromide atom abstraction by  $\text{Bu}_3\text{Sn}^\bullet$  measured under optimum conditions, low halide (10–25 mM) and hydride concentrations (20 mM), fit between 1.5 and  $2.5 \mu\text{s}$ , yields the rate for primary bromide abstraction  $((3.7 \pm 0.3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1})$  at 299 K, as derived from Figure 6.

A narrow window of reagent concentrations is thus dictated for these determinations; however, at higher bromide concentrations, the generated alkyl radical reacts with tin hydride to regenerate the tri-*n*-butylstannyl radical, and at lower halide concentrations, tri-*n*-butylstannyl radical termination begins to contribute to the decay at 400 nm.

### Summary and Conclusions

In this work we have used transient absorption spectroscopy (TAS) to show that the rates of hydrogen abstraction from  $\text{Bu}_3\text{SnH}$  by *tert*-butoxyl radical, bromine atom abstraction by  $\text{Bu}_3\text{Sn}^\bullet$ , and self-termination of  $\text{Bu}_3\text{Sn}^\bullet$  are all more rapid than previously reported. The extinction coefficient of  $\text{Bu}_3\text{Sn}^\bullet$  is shown to be 3.5 times larger than the literature estimate. This new datum was used to develop a kinetic model to predict optimal experimental conditions to measure the rate of bromine atom abstraction by  $\text{Bu}_3\text{Sn}^\bullet$  from a primary alkyl bromide. These experimental results and the kinetic modeling will permit a more accurate evaluation of absolute rate of bromine atom abstraction to be used in competitive rate studies.

### Experimental Section

**General Procedures.** All reagents were purchased from commercial vendors. Aberchrome 540 (Aberchromics Ltd.), di-

*tert*-butyl peroxide, tri-*n*-butyltin hydride, and phenethyl bromide (Aldrich) were used as received. Benzene was distilled and recrystallized from the melt to minimize interference from fluorescent impurities. AcuChem,<sup>31</sup> used in the kinetic modeling, uses a variable step integrator to solve stiff integration problems.

**Transient Absorption Spectroscopy.** The laser flash photolysis system has been described previously.<sup>10</sup> The attenuated output ( $< 2 \text{ mJ}$ ) of an excimer laser (Lambda Physik Compex-100, XeCl, 308 nm) was directed onto a fluorescent sample cell perpendicular to the direction of probe beam (150 W Xe lamp, model XMN-150, Optical Radiation Corp., enclosed within a Spectral Energy lamp housing, LH 150, Universal arc lamp power supply, LPS 251). The filtered output of the probe lamp was focused (L1, 250 mm cylindrical lens) at the center of the fluorescence cell. Luminescence from the solvent was minimized, but not completely eliminated, by placing an iris (2 mm) in the path of the probe beam placed between the flow cell and the monochromator (MC, Oriel model 77250). A second lens (L2, 50 mm) was placed before the entrance slit to the MC. In the kinetic experiments the MC was set to 400 nm to detect the absorbance maximum of the visible  $\text{Bu}_3\text{Sn}^\bullet$  absorption. A PMT tube (RCA 6199 wired in a 4-dynode chain, powered by a negative high-voltage power supply, Pacific Photometric Instruments, model 226) was fixed in a housing attached to the exit slit of the MC. The output of the PMT tube was digitized on a Lecroy 534 transient digitizer, and the data were transferred to a PC for analysis.

### Extinction Coefficient of Tri-*n*-butylstannyl Radical.

The methods demonstrated by Wintgens et al.<sup>15</sup> were used to measure the extinction coefficient of the stannyl radical. A solution of the Fulgide actinometer, Aberchrome 540, was prepared in toluene with an absorbance of  $0.24 \text{ cm}^{-1}$ . Irradiation of the pale yellow fulgide actinometer with a pulsed UV light source (308 nm) generates the deep red cyclized isomer with a quantum yield of 0.2. The extinction coefficient of the red cyclized isomer has an absorbance maximum at 540 nm ( $\epsilon = 8200 \text{ cm}^{-1} \text{ M}^{-1}$ ). The solution was pumped through the fluorescence cell (20 mL/min), and the  $\Delta\text{OD}(t)$  of the sample was measured at 540 nm as a function of excitation pulse energy. A second solution containing tin hydride (0.02 M) and di-*tert*-butyl peroxide (ca. 2 vol %) providing an absorbance of  $0.24 \text{ cm}^{-1}$  at 308 nm was prepared in benzene. The solution containing the tin hydride was pumped through the quartz fluorescence cell (2 mL/min), and the  $\Delta\text{OD}(t)$  was measured at 400 nm. Analysis of the time-dependent decay at 400 nm followed expected second-order behavior. Care must be exercised in using TAS to measure second-order kinetics due to radical concentration gradients that can affect the precision of the measurement. For 1 cm TAS cells the perpendicular pump/probe geometry is preferred for measuring second-order kinetics to minimize concentration gradients across the diameter of the probe beam. In our experiments,  $\text{OD} = 0.24 \text{ cm}^{-1}$ , the concentration gradient across the probe beam, front side to back side, is ca. 5%. Alternative, short path cells, e.g., 1 mm, have been used to minimize the concentration gradient.<sup>32</sup>

**Bromine Atom Abstraction.** Stock solutions of the tri-*n*-butyltin hydride (0.02 M) and di-*tert*-butyl peroxide (0.2 M) were prepared in benzene containing phenethyl bromide (10.2, 14, 19.8, and 24.9 mM). The solutions were purged with solvent-saturated argon and charged into a gastight syringe. The samples were pumped (Sage syringe pump, model 355) through a low-volume quartz fluorescent flow cell (NGS T59FL) to avoid the formation of photoproducts and to ensure the bromide concentration did not change significantly under the reaction conditions. Control experiments showed that a

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long pass filter (LP-365) was necessary to attenuate the ultraviolet output from the probe beam (150 W Xe lamp) to prevent decomposition of the primary bromide.

**Diffusion Coefficient of  $\text{Bu}_3\text{SnH}$  in Benzene, Experimental Dispersion, and Calculated (Spernol–Wirtz) Methods.** The diffusion coefficients of tri-*n*-butyltin hydride in benzene were measured with Taylor's dispersion method using a coil of PEEK tubing (length 22.8 m; internal radius  $0.0247 \pm 0.0004$  cm; coil diameter 21 cm) held at constant temperature in a Neslab RTE-211 temperature bath. A detailed description of our apparatus used to measure diffusion coefficients is described elsewhere.<sup>33</sup> Briefly, 10  $\mu\text{L}$  of dilute  $\text{Bu}_3\text{SnH}$  solutions (0.06–0.15 M) were injected and loaded (Rheodyne on the PEEK tubing coil containing helium-purged solvent pumped through the coil at a flow rate of 0.2 mL/min using Waters associate HPLC pump with Waters 410 differential refractometer or Waters 2410 refractive index detector). The variance ( $\sigma^2$ ) of the tri-*n*-butyltin hydride peak was determined by the least-squares analysis of a Gaussian curve of the refractive index data. The experimental diffusion coefficient,  $D$ , is related to the internal radius of the coiled

tube ( $r$ ), the retention time ( $t$ ), and the variance ( $\sigma^2$ ) by the equation  $D = r^2 t / 24 \sigma^2$ . The  $D$  was calculated using the Spernol–Wirtz treatment;  $D_{\text{AB}}/T = k/(6\pi\eta r_A f)$  where  $f$  is the microfriction factor.

**Acknowledgment.** Support for this work from the Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division, is gratefully acknowledged. The work was conducted at Pacific Northwest Laboratory, which is operated for the U.S. Department of Energy by Battelle under Contract DE-ACO6-76RL01830.

**Supporting Information Available:** Input file for MKM of chain reaction shown in Scheme 1 to predict time-dependent behavior of tri-*n*-butylstannyl radical. Output of MKM for high halide (0.1 M RBr and tin hydride (0.06 M). The MKM input file can be used to predict time-dependent behavior of tri-*n*-butylstannyl radical as a function of initial tin hydride and alkylbromide concentrations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM049933K

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