# The Kinetics and Rate Constants for the Reduction of Alkyl Halides by Organotin Hydrides[1,2]

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**Abstract:** The kinetics of the photochemically initiated reactions between some alkyl halides (chlorides, bromides, and iodides) and some triorganotin hydrides have been examined in cyclohexane at 25°. Chains are generally terminated by bimolecular radical-radical reactions. In general, with alkyl chlorides, the rate-controlling step for chain propagation involves chlorine abstraction by a triorganotin radical, while with bromides and methyl iodide, the rate-controlling step involves hydrogen abstraction from the hydride by the alkyl radicals. The deuterium kinetic isotope effect for this step, $k_H/k_D$, is about 3. Absolute rate constants have been determined by the rotating-sector technique. Chain termination rate constants are near the diffusion-controlled limit for the self-reactions of both alkyl radicals and triorganotin radicals. Rate constants for halogen abstraction by tri-*n*-butyltin radicals vary from $8 \times 10^2\ M^{-1}\ \text{sec}^{-1}$ for 1-chloropentane to $2.5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ for methyl iodide. The rate constants for hydrogen abstraction from tri-*n*-butyltin hydride by a number of alkyl radicals are $\sim 10^6\ M^{-1}\ \text{sec}^{-1}$. The evaluation of the rate constants for both propagation reactions and for two out of the three possible termination reactions means that these processes are now among the best understood two-step chain reactions.

Kuivila and coworkers[4] and others[5] have shown that the reduction of an alkyl halide, RX, with an organotin hydride, $R'_3SnH$, proceeds by a free-radical chain reaction.

$$RX + R'_3SnH \longrightarrow RH + R'_3SnX$$

These workers have measured the relative reactivities of a number of halides with some tin hydrides. The reactivities of alkyl halides toward a given tin hydride increase in the order RF < RCl < RBr < RI and for any particular halogen the reactivities increase in the order primary < secondary < tertiary halide. However, the kinetics of the reaction have so far received little or no attention. These reactions have been found suitable for the application of the rotating sector method for the determination of absolute rate constants.

## Experimental Section

**Reagents.** Commercial organic halides were carefully purified by distillation and/or crystallization. This was particularly important with those halides which readily dehydrohalogenate since unsaturated compounds inhibit the reaction (see below). The organotin hydrides were generally prepared by reduction of the appropriate chlorides with lithium aluminum hydride[6,7] (or deuteride). Di-*n*-butylchlorotin hydride was prepared by mixing equimolar quantities of dibutyltin dichloride and dihydride.[8] The tin hydrides were stored under nitrogen at −30°. Fisher Certified cyclohexane was generally used as the solvent. The other hydrocarbon solvents were Phillips Research grade materials. The halides and hydrocarbons were passed through alumina before use.

$\alpha,\alpha'$-Azobiscyclohexylnitrile (ACHN) was used as the photoinitiator (maximum absorption at 348 mμ). The reaction was also initiated thermally with 2,2,3,3-tetraphenylbutane and *t*-butyl hyponitrite.[9]

**Apparatus and Procedure.** The general features of the apparatus and the experimental procedure have been described earlier.[10] The reaction was followed by measuring the heat evolved in the exothermic chain process with a Pt *vs.* Pt-10% Rh thermocouple placed at the center of a cylindrical Pyrex cell about 1.5 cm long and 3 cm in diameter. The reaction was generally initiated photochemically with the light from a 200–250 V, 250 W ME/D B.T.H. ultraviolet lamp. The light beam was passed through 1 cm of Plexiglas (polymethyl methacrylate) and a Corning C.S. No. 7-51 filter (maximum transmittance at 365 mμ). While conditions at the center of the cell remain adiabatic (~10–20 sec after the start of photolysis) the rate of temperature increase is proportional to the reaction rate. A dark interval of about 10 min between pairs of measurements was necessary to allow for thermal reequilibration.

Carefully degassed reagents were added to the cell which was then sealed off under vacuum.[10] A short induction period was occasionally observed with some of the less reactive chlorides but never with the bromides. In contrast, methyl iodide and the more reactive bromides sometimes exhibited an irreproducible self-initiated reaction upon being added to the organotin hydrides. This reaction was generally of short duration and relatively small quantities of the reactants were consumed before it ceased. Small traces of olefins in the reactants retarded the reaction. Similarly, the addition of an olefin to a reaction already underway greatly reduced the rate. For example, 0.1 *M* cyclohexene reduced the rate of a *t*-butyl bromide (2.8 *M*)–tributyltin hydride (0.12 *M*) reaction by 97%. It seems probable that inhibition by olefins is due to a lowering of the steady-state concentration of tin radicals resulting from their fast, though reversible, attack on double bonds.[11,12]

The ACHN concentration was generally about $3\text{-}4 \times 10^{-3}\ M$. The rate of chain initiation was directly proportional to the ACHN concentration in the range $5 \times 10^{-4}$ to $5 \times 10^{-3}\ M$. At ACHN concentrations of $1 \times 10^{-2}\ M$ and greater, self-absorption by the ACHN caused the rate of initiation to fall below the value expected on the basis of extrapolation from lower concentrations. Biacetyl, benzil, benzophenone, and 9-fluorenone were also tested as photoinitiators using light of the appropriate wavelength. Benzophenone and 9-fluorenone gave very low rates of reaction. Biacetyl and

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[2] For a preliminary report on a portion of this work see D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 1055 (1968).

[3] NRC Postdoctorate Fellow, 1965–1967.

[4] (a) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, **84**, 3584 (1962); (b) H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963); (c) L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964); (d) C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966).

[5] See, for example, (a) E. J. Kupchik and R. J. Kiesel, *ibid.*, **29**, 764 (1964); (b) L. Kaplan, *J. Am. Chem. Soc.*, **88**, 4531 (1966); (c) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *ibid.*, **88**, 5361 (1966); (d) F. D. Greene and N. M. Lowry, *J. Org. Chem.*, **32**, 882 (1967).

[6] H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.*, **83**, 1246 (1961).

[7] H. G. Kuivila, W. Rahman, and R. H. Fish, *ibid.*, **87**, 2835 (1965).

[8] A. K. Sawyer and H. G. Kuivila, *Chem. Ind.* (London), 260 (1961).

[9] H. Kiefer and T. G. Traylor, *Tetrahedron Letters*, 6163 (1966).

[10] D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **89**, 4885 (1967).

[11] H. G. Kuivila and R. Sommer, *ibid.*, **89**, 5616 (1967); R. Sommer and H. G. Kuivila, *J. Org. Chem.*, **33**, 802 (1968).

[12] W. P. Neumann, H. J. Albert, and W. Kaiser, *Tetrahedron Letters*, 2041 (1967).

benzil were reasonably efficient initiators at 430 mμ but the over-all rate declined rapidly. These two compounds are consumed in the reaction.

Several halides were unsuitable for study in the present experimental system. Fluorides were too unreactive and carbon tetrachloride underwent a spontaneously initiated reaction which continued until the hydride was consumed. Benzyl chloride underwent rapid photolysis in the absence of ACHN. There was a high percentage of first-order radical termination with bromobenzene. Both allyl chloride and bromide gave extremely low reaction rates and there was extensive first-order termination. All the work described in this paper was done at 25°.

**Calibration of the Rate.** The heat ($\Delta H$) of the over-all process

$$RX + R'_3SnH \longrightarrow RH + R'_3SnX$$

was measured in the reaction vessel for several pairs of reactants (Table I). The reactions were generally run to completion. The experimental values of $\Delta H$ for the $n$-$Bu_3SnH$ + $t$-BuCl reaction are in excellent agreement with a value calculated from Stack, Nash, and Skinner's accurate determination of the heat of the $n$-$Bu_3SnH$ + HCl reaction[13] and Benson's compilation of bond dissociation energies.[14] That is

**Table I.** Heats of Reaction in Cyclohexane

| Initiation | $R'_3SnH$ [$M$] | RX [$M$] | $\Delta H$, kcal/mol |
|---|---|---|---|
| Photo | $n$-$Bu_3SnH$ [0.42] | $t$-BuCl [2.7] | 41 |
| Photo | $n$-$Bu_2SnHCl$ [0.36] | $t$-BuCl [1.4] | 42 |
| Photo[a] | $Ph_3SnH$ [0.35] | $t$-BuCl [1.6] | 47 |
| Photo[a] | $n$-$Bu_3SnH$ [0.34] | $t$-BuCl [1.6] | 39 |
| Thermal[b] | $Ph_3SnH$ [0.22] | $t$-BuCl [2.9] | 41 |
| Thermal[b] | $Ph_3SnH$ [0.25] | $t$-BuCl [2.9] | 36 |
| Photo | $Ph_3SnH$ [0.25] | $t$-BuBr [2.0] | 37 |
| Photo | $n$-$Bu_3SnH$ [0.58] | $t$-BuBr [2.7] | 32 |
| Thermal[c] | $n$-$Bu_3SnH$ [0.24] | $c$-$C_6H_{11}Br$ [1.5] | 41 |
| Thermal[b] | $n$-$Bu_3SnH$ [0.07] | $CH_3I$ [3.6] | 34 |

[a] Not run to completion. Extent of reaction determined by glpc analysis. [b] Tetraphenylbutane. [c] $t$-Butyl hyponitrite.

$$\begin{array}{rr}
n\text{-}Bu_3SnH + HCl \longrightarrow n\text{-}Bu_3SnCl + H_2 & -27.85\ \text{kcal/mol} \\
H\cdot + Cl\cdot \longrightarrow HCl & -103.0\ \text{kcal/mol} \\
H_2 \longrightarrow 2H\cdot & 104.2\ \text{kcal/mol} \\
t\text{-}BuCl \longrightarrow t\text{-}Bu\cdot + Cl\cdot & 78.6\ \text{kcal/mol} \\
t\text{-}Bu\cdot + H\cdot \longrightarrow t\text{-}BuH & -90.9\ \text{kcal/mol} \\
\hline
n\text{-}Bu_3SnH + t\text{-}BuCl \longrightarrow n\text{-}Bu_3SnCl + t\text{-}BuH & -38.95\ \text{kcal/mol}
\end{array}$$

The results in Table I indicate that there is no significant variation in $\Delta H$ from one tin hydride to another. The strengths of alkyl–H and alkyl–Cl bonds[14] suggest that the reduction of primary alkyl chlorides should be about 5 kcal/mol, and secondary alkyl chlorides about 3 kcal/mol, more exothermic than the reduction of tertiary chlorides. Differences in the heats of formation of triorganotin chlorides and bromides ($(\Delta H_f^\circ)_{R'_3SnCl} - (\Delta H_f^\circ)_{R'_3SnBr} = -13.0$ kcal/mol for the tri-$n$-butyl[13] and $-8.1$ kcal/mol for the trimethyl compounds[15]) are comparable to the differences in the heats of formation of alkyl chlorides and bromides (*e.g.*, $(\Delta H_f^\circ)_{EtCl} - (\Delta H_f^\circ)_{EtBr} = -10.4$ kcal/mol for the ethyl halides[14]). The over-all heat of reaction should therefore be similar for the reduction of both chlorides and bromides.[16] Similarly, the difference in the heats of formation of trimethyltin bromide and iodide[15,17] is comparable to the difference in the heats of formation of alkyl bromides and iodides,[14] *i.e.*, $(\Delta H_f^\circ)_{Me_3SnBr} - (\Delta H_f^\circ)_{Me_3SnI} = -14.2$ kcal/mol[15,17] and $(\Delta H_f^\circ)_{EtBr} - (\Delta H_f^\circ)_{EtI} = -13.1$ kcal/mol.[14] The experimental variations in $\Delta H$ do not justify the application of the individually measured values to each reaction and, for this reason, a mean value of 40 kcal/mol was used in all the calculations. The true values of $\Delta H$ will, hopefully, all lie within 10% of this mean. Since the measured rates are only reproducible to about ±10% the errors introduced by assuming that $\Delta H$ is constant should be relatively unimportant.

**Determination of the Rate of Photoinitiation.** The experimental details of the methods used to determine the rates of photoinitiation have been described previously.[10] The photoinitiation rates were measured directly by the induction period method and indirectly by a comparison of the photorate with the rates of reaction in the presence of thermal initiators. Galvinoxyl, which was assumed to terminate one chain per molecule,[18] gave well-defined induction periods in the reactions of triphenyltin hydride with $t$-butyl chloride and of tributyltin hydride with $t$-butyl and cyclohexyl chloride. Although galvinoxyl absorbs fairly strongly at 360 mμ the very low concentrations used for the induction period measurements ($\sim 8 \times 10^{-6}$ $M$) did not appear to interfere with photoinitiation. That is, the directly calculated rates of photoinitiation are in reasonably good agreement with the values determined by comparison with thermally initiated reactions. Photoinitiation rates in alkyl bromide containing reaction mixtures were about 20% lower than the values obtained with the chlorides. This is probably due to the absorption of some of the initiating radiation by the bromides which absorb weakly up to 400 mμ. However, this self-absorption did not result in significant self-initiation. In contrast, photoinitiation rates in methyl iodide containing reaction mixtures were about twice as great as the values found for chlorides, presumably because of a direct photolysis of the iodide to free radicals.

Some other potential inhibitors were also examined. Hydroquinone[5a] did not inhibit the reaction.[19] 2,2,6,6-Tetramethyl-4-pyridone nitroxide[10] underwent a violently exothermic reaction with the tin hydrides. Cyclohexene acted as a retarder rather than as an inhibitor and did not give well-defined induction periods.

The rate of radical formation from tetraphenylbutane (TPB) at 25° ($2ek_d$[TPB]) was determined by esr spectroscopy by measuring the rate of consumption of the stable radical tetramethylpyridone nitroxide. Values of $2ek_d$ in three degassed hydrocarbon mixtures are given in Table II. The differences between these values presumably reflect an effect of the solvent on the fraction of geminate recombination. The change in cage effects with change in solvent is clearly no simple function of the bulk viscosity (*cf.* ref 20).

**Table II.** Rates of Chain Initiation by 2,2,3,3-Tetraphenylbutane[a]

| Solvent (vol ratio) | Viscosity, cP | $2ek_d \times 10^6$, $sec^{-1}$ |
|---|---|---|
| $n$-Pentane-benzene (3.5:1) | 0.28 | 2.1 |
| Cyclohexane-benzene (3.5:1) | 0.77 | 1.5 |
| $n$-Tridecane-benzene (3.5:1) | 1.19 | 1.8 |

[a] [TPB] = $3 \times 10^{-2}$ $M$; [nitroxide] = $1.4 \times 10^{-4}$ $M$.

The rate constant for the decomposition of $t$-butyl hyponitrite was taken to be $1.3 \times 10^{-8}$ $sec^{-1}$ at 25° in cyclohexane[9] and the efficiency of initiation, $e$, was assumed to be 0.9.[9,20]

**Competitive Experiments.** Pairs of halides, together with a saturated hydrocarbon as an internal standard, were allowed to react with a deficiency of $n$-$Bu_3SnH$ in evacuated Pyrex glass bombs under conditions (concentration, light intensity, temperature) generally similar to those employed in the kinetic experiments. The bombs were opened after complete consumption of the hydride and were analyzed by gas chromatography for loss of reactants and/or formation of the hydrocarbon products. Benzyl chloride was used in competition with cyclohexyl chloride and cyclohexyl bromide in order to interrelate the alkyl chlorides and bromides. The large differences in the reactivities of these pairs of reactants necessitated the use of cyclohexyl chloride as the solvent in the first

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(13) W. F. Stack, G. A. Nash, and H. A. Skinner, *Trans. Faraday Soc.*, **61**, 2122 (1965).

(14) S. W. Benson, *J. Chem. Educ.* **42**, 502 (1965); S. W. Benson and R. Shaw, Preprints of the International Oxidation Symposium, Vol. 1, San Francisco, Calif., 1967, p 565.

(15) G. A. Nash, H. A. Skinner, and W. F. Stack, *Trans. Faraday Soc.*, **61**, 640 (1965).

(16) The slightly lower value of $\Delta H$ for $t$-BuBr relative to $t$-BuCl (Table I) might be due to some loss of heat in the initial stages of the bromide reaction (see above). An initial heat loss may also have occurred in the methyl iodide reaction.

(17) J. B. Pedley, H. A. Skinner, and C. I. Chernick, *Trans. Faraday Soc.*, **53**, 1612 (1957).

(18) P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962).

(19) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964), see especially pp 63–65.

(20) H. Kiefer and T. G. Traylor, *J. Am. Chem. Soc.*, **89**, 6667 (1967).

Table III. The Kinetics and Rate Constants for the Reaction of *t*-Butyl Bromide with Some Tin Hydrides[a]

| [RX], $M$ | [R$'_3$SnH], $M$ | [R$'_3$SnH]/[RX] | $R_s \times 10^5$ | $R_s/(R_i)^{1/2} \times$ [R$'_3$SnH] | $2k_t \times 10^{-9}$ | $k_p \times 10^{-5}$ |
|---|---|---|---|---|---|---|
| *t*-BuBr | $Ph_3SnH$ | | | | | |
| 8.7 | 0.11 | 0.013 | 130 | 66 | | |
| 2.4 | 0.035 | 0.015 | 42 | 67 | | |
| 2.4 | 0.11 | 0.046 | 120 | 61 | | |
| 2.4 | 0.11 | 0.046 | 140 | 71 | ~3 | ~39 |
| 2.4 | 0.25 | 0.10 | 290 | 65 | | |
| *t*-BuBr | *n*-$Bu_3SnH$ | | | | | |
| 2.4 | 0.068 | 0.028 | 23 | 19 | 0.8 | 5.4 |
| 2.4 | 0.17 | 0.071 | 44 | 15 | 2.0 | 6.8 |
| 2.4 | 0.17 | 0.071 | 52 | 17 | 3.3 | 9.8 |
| 1.6 | 0.12 | 0.075 | 33 | 15 | | |
| 2.4 | 0.24 | 0.10 | 51 | 12 | | |
| 2.4 | 0.34 | 0.14 | 75 | 12 | | |
| 1.2 | 0.17 | 0.14 | 45 | 15 | | |
| 2.4 | 0.44 | 0.18 | 110 | 14 | 1.7 | 5.8 |
| 1.2 | 0.24 | 0.20 | 80 | 19 | 2.2 | 8.9 |
| 0.4 | 0.17 | 0.43 | 61 | 20 | | |
| *t*-BuBr | *n*-$Bu_3SnD$ | | | | | |
| 2.8 | 0.24 | 0.085 | 24 | 5.7 | 1.8 | 2.4 |
| *t*-BuBr | $Me_3SnH$ | | | | | |
| 2.4 | 0.40 | 0.17 | 45 | 6.3 | | |
| 2.2 | 0.37 | 0.17 | 37 | 5.6 | | |
| 2.0 | 0.73 | 0.37 | 85 | 6.5 | | |

[a] In units of $M$ sec. [ACHN] = $3.8 \times 10^{-3}$ $M$, with full illumination $R_i = 3.2 \times 10^{-8}$ $M$ sec$^{-1}$.

case (with 0.25% by weight benzyl chloride) and benzyl chloride as the solvent in the second case (with 5% by weight cyclohexyl bromide). The products were analyzed for toluene and cyclohexane with *n*-pentane as the internal standard. The methyl iodide–cyclohexyl bromide mixture was analyzed for the iodide consumed and cyclohexane produced.

## Results

**Reaction Scheme.** The reduction of alkyl halides by organotin hydrides can be represented by the following free-radical chain process.

Initiation

$$\longrightarrow \mathrm{R}\cdot \text{ (rate } R_i) \tag{1}$$

Propagation

$$\mathrm{R}\cdot + \mathrm{R'_3SnH} \longrightarrow \mathrm{RH} + \mathrm{R'_3Sn}\cdot \tag{2}$$

$$\mathrm{R'_3Sn}\cdot + \mathrm{RX} \longrightarrow \mathrm{R'_3SnX} + \mathrm{R}\cdot \tag{3}$$

Termination

$$\left.\begin{array}{r} \mathrm{R}\cdot + \mathrm{R}\cdot \longrightarrow \\ \mathrm{R}\cdot + \mathrm{R'_3Sn}\cdot \longrightarrow \\ \mathrm{R'_3Sn}\cdot + \mathrm{R'_3Sn}\cdot \longrightarrow \end{array}\right\} \text{inactive products} \qquad \begin{array}{r} (4) \\ (5) \\ (6) \end{array}$$

This complete system of equations can be most conveniently solved in two forms

$$\frac{R_i[\mathrm{R'_3SnH}]^2}{R_s^2} = \frac{2k_4}{k_2^2} + \frac{2k_5[\mathrm{R'_3SnH}]}{k_2k_3[\mathrm{RX}]} + \frac{2k_6[\mathrm{R'_3SnH}]^2}{k_3^2[\mathrm{RX}]^2} \tag{I}$$

$$\frac{R_i[\mathrm{RX}]^2}{R_s^2} = \frac{2k_6}{k_3^2} + \frac{2k_5[\mathrm{RX}]}{k_2k_3[\mathrm{R'_3SnH}]} + \frac{2k_4[\mathrm{RX}]^2}{k_2^2[\mathrm{R'_3SnH}]^2} \tag{II}$$

where $R_s$ is the over-all rate of reaction and $R_i$ is the rate of chain initiation. If chain termination occurs predominantly by reactions 4 and 5 a plot of the left-hand side of eq I against [R$'_3$SnH]/[RX] will yield a line of slope $2k_5/k_2k_3$ and intercept $2k_4/k_2^2$. If reaction 4 is the sole terminating step then the left-hand side of I will be independent of the hydride/halide ratio and the rate expression can be simplified to the following equation (Ia).

$$\frac{R_s}{R_i^{1/2}[\mathrm{R'_3SnH}]} = \frac{k_2}{(2k_4)^{1/2}} \tag{Ia}$$

Similarly, if termination occurs solely by reaction 6 we can write

$$\frac{R_s}{R_i^{1/2}[\mathrm{RX}]} = \frac{k_3}{(2k_6)^{1/2}} \tag{IIa}$$

**Kinetics.** The kinetics of the reduction of alkyl halides by tin hydrides were generally fairly straightforward. The rate usually exhibited a first-order dependence on either the halide or the hydride concentration over a wide range of relative and absolute reactant concentrations. The rate was generally approximately proportional to the square root of the light intensity. Under certain experimental conditions the order in light intensity was slightly greater than 0.5 which suggests the presence of a kinetically first-order chain termination process competing with the normal bimolecular termination reaction. In measuring absolute rate constants the effect of the first-order termination was corrected for in the usual way.[21] The reactions behaved normally throughout their entire course[22] continuing until one of the reactants was completely consumed. The results for the different halide–hydride reactions are described in detail below.

(i) **Alkyl Bromides and Methyl Iodide.** Experimental data for the reactions of *t*-butyl bromide with triphenyl, tri-*n*-butyl, and trimethyl tin hydrides are given in Table III. Data for the reactions of cyclohexyl bromide, 1-bromohexane, and methyl iodide with tributyltin hydride are given in Table IV. In all cases the quantity $R_s/R_i^{1/2}[\mathrm{R'_3SnH}]$ is essentially independent of the hydride/halide ratio. The kinetics are therefore

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[21] G. M. Burnett and H. W. Melville, in "Technique of Organic Chemistry," Vol. VIII, Part II, S. O. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 20.

[22] This contrasts with our results on the *t*-butyl hypochlorite–toluene reaction which we examined previously in the same experimental apparatus.[10]

Table IV. The Kinetics and Rate Constants for the Reactions of Cyclohexyl Bromide, 1-Bromohexane, and Methyl Iodide with Tri-*n*-butyltin Hydride[a]

| [RX], *M* | [R′$_3$SnH], *M* | [R′$_3$SnH]/[RX] | $R_s \times 10^5$ | $R_s/\{(R_i)^{1/2} \times$ [R′$_3$SnH]$\}$ | $2k_t \times 10^{-9}$ | $k_p \times 10^{-5}$ |
|---|---|---|---|---|---|---|
| *c*-$C_6H_{11}Br$ | *n*-$Bu_3SnH$ | | | | | |
| 2.6 | 0.21 | 0.08 | 99 | 26 | 2.8 | 14 |
| 1.5 | 0.12 | 0.08 | 56 | 26 | | |
| 1.4 | 0.15 | 0.10 | 55 | 21 | 2.6 | 11 |
| 1.4 | 0.24 | 0.16 | 120 | 28 | | |
| 0.84 | 0.27 | 0.33 | 140 | 29 | | |
| $CH_3(CH_2)_4CH_2Br$ | *n*-$Bu_3SnH$ | | | | | |
| 1.6 | 0.068 | 0.043 | 29 | 24 | 1.0 | 8 |
| 1.6 | 0.17 | 0.11 | 76 | 25 | 3.1 | 14 |
| 3.2 | 0.63 | 0.20 | 220 | 20 | | |
| 1.6 | 0.34 | 0.22 | 130 | 21 | 2.0 | 9 |
| 0.63 | 0.17 | 0.27 | 68 | 22 | 2.5 | 11 |
| 2.0 | 0.81 | 0.40 | 260 | 18 | | |
| $CH_3I$ | *n*-$Bu_3SnH$ | | | | | |
| 3.9 | 0.037 | 0.0094 | 66 | 64 | 13 | 73 |
| 2.3 | 0.14 | 0.058 | 210 | 56 | | |
| 3.6 | 0.34 | 0.094 | 580 | 61 | | |
| 3.6 | 0.34 | 0.094 | 660 | 69 | 8.6 | 64 |
| 1.2 | 0.14 | 0.11 | 200 | 53 | 5.0 | 37 |

[a] In units of *M* sec. [ACHN] = $3.8 \times 10^{-3}$ *M*, with full illumination $R_i = 3.2 \times 10^{-8}$ *M* sec$^{-1}$ for the bromides and $8.0 \times 10^{-8}$ *M* sec$^{-1}$ for methyl iodide.

Table V. The Kinetics for the Reaction of *t*-Butyl Chloride with Triphenyltin Hydride[a]

| [RX], *M* | [R′$_3$SnH], *M* | [RX]/[R′$_3$SnH] | [ACHN] × $10^3$ | $R_i \times 10^8$ | $R_s \times 10^5$ | $R_s/\{(R_i)^{1/2} \times$ [RX]$\}$ |
|---|---|---|---|---|---|---|
| 0.4 | 0.34 | 1.2 | 3.4 | 3.8 | 3.3 | 0.44 |
| 1.3 | 0.60 | 2.2 | 3.4 | 3.8 | 8.4 | 0.33 |
| 1.3 | 0.60 | 2.2 | 3.4 | 3.8 | 11 | 0.43 |
| 0.9 | 0.32 | 2.9 | 3.4 | 3.8 | 6.9 | 0.38 |
| 1.6 | 0.35 | 4.6 | 3.8 | 4.2 | 15 | 0.46 |
| 1.4 | 0.30 | 4.7 | 2.4 | 2.7 | 8.9 | 0.39 |
| 1.4 | 0.30 | 4.7 | 0.68 | 0.75 | 5.5 | 0.46 |
| 1.4 | 0.30 | 4.7 | 3.4 | 3.8 | 11 | 0.40 |
| 1.4 | 0.30 | 4.7 | 3.4 | 3.8 | 8.8 | 0.32 |
| 1.4 | 0.22 | 6.5 | 3.4 | 3.8 | 11 | 0.40 |
| 1.6 | 0.25 | 6.6 | 3.8 | 4.2 | 14 | 0.43[b] |
| 2.3 | 0.27 | 8.7 | 3.4 | 3.8 | 13 | 0.29 |
| 2.9 | 0.25 | 12 | 3.8 | 4.2 | 38 | 0.64 |
| 2.9 | 0.25 | 12 | 3.8 | 4.2 | 39 | 0.65 |
| 2.9 | 0.25 | 12 | 3.8 | 4.2 | 28 | 0.47 |
| 2.9 | 0.25 | 12 | 3.8 | 4.2 | 29 | 0.49[c] |
| 2.9 | 0.22 | 13 | 3.4 | 3.8 | 19 | 0.34[d] |
| 2.9 | 0.22 | 13 | 3.4 | 3.8 | 24 | 0.42 |
| 1.5 | 0.08 | 19 | 3.4 | 3.8 | 9.8 | 0.34 |
| 7.5 | 0.30 | 25 | 3.4 | 3.8 | 46 | 0.32 |

[a] In units of *M* sec. [b] $2k_t = 2.6 \times 10^9$, $k_p = 2.2 \times 10^4$ $M^{-1}$ sec$^{-1}$. [c] $2k_t = 3.7 \times 10^9$, $k_p = 3.0 \times 10^4$ $M^{-1}$ sec$^{-1}$. [d] $2k_t = 2.2 \times 10^9$, $k_p = 1.6 \times 10^4$ $M^{-1}$ sec$^{-1}$.

described by eq Ia. Chain termination must occur by the self-reaction of two alkyl radicals and the rate-controlling propagation step is hydrogen atom abstraction from the hydride.

(ii) **Alkyl Chlorides.** The reactions of *t*-butyl chloride with the hydrides of triphenyltin (Table V), trimethyltin, di-*n*-butylchlorotin, and di-*n*-butyltin (Table VI) are all first order in chloride *over the range of concentration examined.* The reactions of cyclohexyl chloride with tri-*n*-butyltin and trimethyltin hydrides, and of 1-chloropentane with tri-*n*-butyltin hydride are also first order in chloride (Table VII). For all of these reactions, therefore, the kinetics are described by equation IIa. Chain termination must involve the self-reactions of the triorganotin radicals and the rate-controlling step of propagation must be the abstraction of chlorine by the tin radical.

In contrast to these results, the reaction of *t*-butyl chloride with tri-*n*-butyltin hydride exhibits rather more complex kinetics (Table VIII). The reaction is approximately first order in chloride and zero order in hydride at relatively low [RX]/[R′$_3$SnH] ratios (*i.e.*, $R_s/R_i^{1/2}$[RX] ~ constant) but at high [RX]/[R′$_3$SnH] ratios the reaction tends to become zero order in chloride and first order in hydride (*i.e.*, $R_s/R_i^{1/2}$[R′$_3$SnH] ~ constant). The kinetics are therefore described by eq I or II.

**Deuterium Isotope Effect.** Cyclohexyl bromide was treated with an equimolar mixture of tri-*n*-butyltin hydride and deuteride (0.38 *M* in each compound) in tridecane. The reactions were run to completion and the cyclohexane was analyzed by mass spectrometry. The yields of $C_6H_{11}D$ were 27.0% with 0.08 *M* bromide and 26.8% with 0.15 *M* bromide, which correspond to a kinetic isotope effect $k_H/k_D = 2.7$.

Direct measurement of the rate of reaction of *t*-butyl bromide with tri-*n*-butyltin hydride and deuteride (Table III) gives a kinetic deuterium isotope effect $k_H/k_D = 2.8$.

**Absolute Rate Constants.** The rate constants for chain termination ($2k_t$), and hence for chain propagation ($k_p$) were determined by the rotating-sector method (Tables III–VIII). Their measurement was generally fairly straightforward except for the extremely fast reactions. In the case of the *t*-BuBr + $Ph_3SnH$ reaction and the $CH_3I$ + *n*-$Bu_3SnH$ reaction the measured rates decreased rapidly at each succeeding light pulse owing to the rapid consumption of the tin hydrides. It was therefore difficult to obtain accurate ratios of the rates under steady and under intermittent illumination. The rate constants for these reactions are less accurate than for most of the other reactions studied.

**Relative Rate Constants.** The kinetic experiments already described give no information about the rate constants for bromine abstraction from the alkyl bromides (reaction 3) because this reaction was never

Table VI. The Kinetics and Rate Constants for the Reactions of *t*-Butyl Chloride with Some Tin Hydrides[a]

| [RX], *M* | [R'$_3$SnH], *M* | [RX]/[R'$_3$SnH] | $R_s \times 10^5$ | $R_s/(R_i)^{1/2}$[RX] | $2k_t \times 10^{-9}$ | $k_p \times 10^{-3}$ |
|---|---|---|---|---|---|---|
| *t*-BuCl | Me$_3$SnH | | | | | |
| 0.75 | 1.0 | 0.75 | 2.0 | 0.13 | 4.7 | 9.4 |
| 0.82 | 0.37 | 2.2 | 2.0 | 0.12 | | |
| 0.82 | 0.37 | 2.2 | 2.1 | 0.13 | | |
| 4.5 | 0.37 | 12 | 10 | 0.12 | 1.5 | 4.6 |
| *t*-BuCl | *n*-Bu$_2$SnClH | | | | | |
| 0.4 | 0.10 | 4 | 0.8 | 0.10 | | |
| 0.7 | 0.10 | 7 | 1.0 | 0.073 | | |
| 1.3 | 0.10 | 13 | 1.8 | 0.072 | | |
| 7.1 | 0.48 | 15 | 9.5 | 0.069 | 3.0 | 3.8 |
| 2.2 | 0.11 | 20 | 3.8 | 0.089 | 4.4 | 5.9 |
| 2.0 | 0.08 | 25 | 3.4 | 0.087 | 3.3 | 5.0 |
| *t*-BuCl | *n*-Bu$_2$SnH$_2$ | | | | | |
| 0.8 | 0.32 | 2.4 | 1.7 | 0.11 | | |
| 1.4 | 0.39 | 3.6 | 2.4 | 0.088 | 2.0 | 3.9 |
| 1.4 | 0.30 | 4.7 | 2.6 | 0.095 | | |
| 2.5 | 0.26 | 9.6 | 4.0 | 0.082 | 1.1 | 2.7 |
| 0.8 | 0.06 | 13 | 1.2 | 0.079 | | |
| 1.5 | 0.10 | 15 | 2.2 | 0.075 | | |
| 8.6 | 0.32 | 27 | 28 | 0.17 | | |

[a] In units of *M* sec. [ACHN] = 3.4 × $10^{-3}$ *M*, with full illumination $R_i$ = 3.8 × $10^{-8}$ *M* sec$^{-1}$.

Table VII. The Kinetics and Rate Constants for the Reactions of Some Alkyl Chlorides with Some Tin Hydrides[a]

| [RX], *M* | [R'$_3$SnH], *M* | [RX]/[R'$_3$SnH] | $R_s \times 10^5$ | $R_s/(R_i)^{1/2}$[RX] | $2k_t \times 10^{-9}$ | $k_p \times 10^{-3}$ |
|---|---|---|---|---|---|---|
| *c*-C$_6$H$_{11}$Cl | *n*-Bu$_3$SnH | | | | | |
| 1.0 | 0.23 | 4.3 | 1.0 | 0.052 | | |
| 2.6 | 0.44 | 5.9 | 2.3 | 0.045 | 0.5 | 1.0 |
| 2.8 | 0.23 | 12 | 2.3 | 0.042 | | |
| 4.1 | 0.24 | 18 | 4.5 | 0.056 | 1.2 | 1.9 |
| 7.9 | 0.23 | 34 | 4.5 | 0.029 | 0.5 | 0.6 |
| 2.9 | 0.08 | 36 | 2.0 | 0.035 | | |
| *c*-C$_6$H$_{11}$Cl | Me$_3$SnH | | | | | |
| 4.5 | 0.37 | 12 | 0.95 | 0.011 | | |
| 4.5 | 0.22 | 20 | 0.90 | 0.010 | | |
| CH$_3$(CH$_2$)$_3$CH$_2$Cl | *n*-Bu$_3$SnH | | | | | |
| 1.8 | 0.24 | 7.8 | 0.76 | 0.022 | | |
| 6.9 | 0.66 | 10 | 2.3 | 0.017 | 1.2 | 0.6 |
| 3.9 | 0.25 | 16 | 1.3 | 0.018 | | |
| 7.8 | 0.24 | 33 | 2.0 | 0.013 | | |
| 7.8 | 0.24 | 33 | 2.7 | 0.018 | 2.1 | 0.8 |
| 7.8 | 0.24 | 33 | 3.6 | 0.024 | 2.9 | 1.3 |
| 7.4 | 0.075 | 99 | 1.8 | 0.013 | | |

[a] In units of *M* sec. [ACHN] = 3.4 × $10^{-3}$ *M*, with full illumination $R_i$ = 3.8 × $10^{-8}$ *M* sec$^{-1}$.

Table VIII. The Kinetics and Rate Constants for the Reaction of *t*-Butyl Chloride with Tri-*n*-butyltin Hydride[a]

| [RX], *M* | [R'$_3$-SnH], *M* | [RX]/[R'$_3$-SnH] | $R_s \times 10^5$ | $R_s/\{(R_i)^{1/2} \times$ [RX]$\}$ | $R_s/\{(R_i)^{1/2} \times$ [R'$_3$SnH]$\}$ | $2k_t \times 10^{-9}$ |
|---|---|---|---|---|---|---|
| 0.4 | 0.24 | 1.7 | 2.9 | 0.35 | 0.59 | 1.8 |
| 1.6 | 0.34 | 4.8 | 12 | 0.37 | 1.7 | |
| 2.7 | 0.42 | 6.4 | 17 | 0.32 | 2.0 | |
| 2.9 | 0.24 | 12 | 16 | 0.28 | 3.3 | 1.4 |
| 2.9 | 0.24 | 12 | 19 | 0.31 | 3.8 | |
| 2.9 | 0.24 | 12 | 20 | 0.34 | 4.1 | 1.5 |
| 2.9 | 0.22 | 13 | 12 | 0.20 | 2.6 | |
| 1.4 | 0.074 | 19 | 5.6 | 0.20 | 3.7 | |
| 2.9 | 0.10 | 28 | 10 | 0.17 | 4.8 | 2.3 |
| 8.5 | 0.28 | 30 | 18 | 0.11 | 3.2 | 1.6 |
| 8.8 | 0.23 | 37 | 27 | 0.15 | 5.6 | 2.7 |
| 2.9 | 0.074 | 39 | 9 | 0.15 | 5.9 | |
| 8.7 | 0.17 | 52 | 20 | 0.11 | 5.7 | 2.9 |
| 8.9 | 0.10 | 87 | 11 | 0.058 | 5.3 | |
| 9.0 | 0.074 | 120 | 14 | 0.079 | 9.3 | |
| 9.0 | 0.069 | 130 | 7.8 | 0.042 | 5.5 | |

[a] In units of *M* sec. [ACHN] = 3.8 × $10^{-3}$ *M*, with full illumination $R_i$ = 4.2 × $10^{-8}$ *M* sec$^{-1}$.

rate determining. For this reason we have measured, in a series of competitive experiments, the relative reactivities of the alkyl halides used in this work toward the tri-*n*-butyltin radical. The relative reactivities, calculated by the method of Ingold and Shaw,[23] are given in Table IX. The results are in satisfactory agreement with our absolute rate measurements for the three alkyl chlorides and also with Menapace and Kuivila's[4c] previously determined relative reactivities for benzyl chloride and the bromides at 45°.

## Discussion

**Self-Termination.** Absolute rate constants for chain termination are summarized in Table X. The values given represent averages of all the measured termination constants from Tables III–VIII, *e.g.*, the rate constant for the self-reaction of *t*-butyl radicals was obtained from reactions of *t*-butyl bromide with the triphenyltin hydride, tri-*n*-butyltin hydride, and tri-*n*-butyltin deuteride. Our own rate constants, which are probably

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[23] C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927).

**Table IX.** The Relative Reactivities of Alkyl Halides toward the Tri-*n*-butyltin Radical

| Alkyl halide | Relative reactivity<br>This work | <br>Ref 4c[a] |
|---|---|---|
| *c*-$C_6H_{11}F$ | <0.1 | |
| 1-Chloropentane | 1[b] | |
| *c*-$C_6H_{11}Cl$ | 1.7 | |
| *t*-BuCl | 1.7 × 6.5 = 11 | |
| $PhCH_2Cl$ | 1.7 × 320 = 540 | 540[b] |
| *c*-$C_6H_{11}Br$ | 540 × 35 = 19,000 | 15,800 |
| 1-Bromohexane | 19,000 × 0.86 = 16,300 | 11,300[c] |
| *t*-BuBr | 19,000 × 3.8 = 72,200 | 75,600 |
| $CH_3I$ | 19,000 × 110 = 2,090,000 | 660,000[d] |

[a] Competitive experiments at 45°. [b] Assumed. [c] Mean of the value for 1-bromobutane and 1-bromooctane. [d] Value for 1-iodoheptane.

accurate to within about a factor of 2, are in excellent agreement with results obtained by other workers in the same medium at room temperature[24–28] (see Table X).

**Table X.** Absolute Rate Constants for Radical–Radical Reactions in Cyclohexane at 25°

| Termination reaction | $2k_t \times 10^{-9}$, $M^{-1}$ sec$^{-1}$<br>Present work | <br>Lit. |
|---|---|---|
| $CH_3\cdot + CH_3\cdot$ | 8.9 | |
| *n*-$C_6H_{13}\cdot$ + *n*-$C_5H_{13}\cdot$ | 2.2 | 2.0[a] |
| *c*-$C_6H_{11}\cdot$ + *c*-$C_8H_{11}\cdot$ | 2.7 | 2.5,[b] 2.2[c] |
| *t*-Bu· + *t*-Bu· | 2.1 | 2.2[d] |
| $PhCH_2\cdot + PhCH_2\cdot$ | | 7.2,[c] 2.0[e] |
| $Ph_3Sn\cdot + Ph_3Sn\cdot$ | 2.8 | |
| $Me_3Sn\cdot + Me_3Sn\cdot$ | 3.1 | |
| *n*-$Bu_3Sn\cdot$ + *n*-$Bu_3Sn\cdot$ | 1.4 | |
| *n*-$Bu_2(Cl)Sn\cdot$ + *n*-$Bu_2(Cl)Sn\cdot$ | 3.6 | |
| *n*-$Bu_2(H)Sn\cdot$ + *n*-$Bu_2(H)Sn\cdot$ | 1.6 | |
| *t*-Bu· + *n*-$Bu_3Sn\cdot$ | 0–4 (see text) | |

[a] Value for 1-pentyl[24] and 1-octadecyl[25] radicals *in benzene*. [b] Reference 26. [c] Reference 25. [d] Reference 27. [e] Reference 28.

The rate constants for the self-reactions of the tin radicals and of all the alkyl radicals except methyl are in the range 1.4–3.6 × $10^9$ $M^{-1}$ sec$^{-1}$. The mean termination rate constant for these radicals is 2.2 × $10^9$ $M^{-1}$ sec$^{-1}$ which is significantly smaller than the theoretical diffusion-controlled value[29] of about 8 × $10^9$ $M^{-1}$ sec$^{-1}$ in cyclohexane at 25°. It seems unlikely that the interaction of cyclohexane with radicals would be much stronger than its interaction with molecules and therefore the simple treatment used to calculate the diffusion-controlled rate constant should be generally applicable. However, it is possible that small radicals such as methyl have unusually high diffusion coefficients so that their diffusion-limited rate is greater than for larger radicals (*cf.* ref 32).

The fact that the termination constants are lower than predicted by theory is probably not due to any direct intramolecular shielding of the reaction center.[24] However, the recent results of Szwarc and coworkers on the cage combination of trifluoromethyl[33] and methyl radicals suggest that the *orientation* of the radicals may influence combinations.[34] These workers found that the probability of combination on each collision was three to five times as great for $CH_3\cdot$ as for $CF_3\cdot$ which was interpreted as being due to the faster rotation of $CH_3\cdot$ compared with $CF_3\cdot$. That is, the orientation of the radicals which is required for their combination may introduce rotational diffusion as a factor partially controlling the rate of this reaction. This effect is not normally considered in the solvent-cage model of bimolecular reactions in solution since it is usually assumed that once two radicals have entered the cage they will undergo sufficient collisions to cover essentially all orientations before they diffuse apart. For similar reasons, the spin-correction term (which allows for the fact that in the gas phase only one collision in four leads to a singlet state) is usually ignored in solution because of the fairly long duration of radical–radical encounters. The present results suggest that in order to bring theory into agreement with experiment, one or more of these assumptions (*i.e.*, that, (i) the diffusion radius is equal to the radius for reaction,[29] (ii) rotational diffusion is not a factor in the reaction, and (iii) the spin-correction term can be ignored) may require modifying.

The most direct evidence that the self-reaction of *t*-butyl radicals is essentially a diffusion-controlled process was obtained by measurements on the *t*-butyl bromide–tri-*n*-butyltin hydride reaction in *n*-pentane, cyclohexane, and *n*-tridecane. (Table XI). The termination constant decreases as the viscosity of the medium increases, $2k_t$ being approximately proportional to $\eta^{-0.8}$. This relationship is in reasonable agreement with the simple theory of diffusion-controlled rate processes (*i.e.*, $k \propto \eta^{-1.0}$).[29] The propagation rate constants are equal in the three solvents within the probable limits of experimental error.

**Cross-Termination.** The cross-termination rate constant ($2k_5$) for the *t*-butyl chloride–tri-*n*-butyltin hydride reaction can, in theory, be calculated by substituting the over-all rates (Table VIII) and the measured propagation ($k_2$ and $k_3$) and uncrossed termination ($2k_4$ and $2k_6$) rate constants into eq I or II. At [*t*-BuCl]/[*n*-$Bu_3SnH$] ratios of ~12 or lower, $R_s/R_i^{1/2}[RX]$ reaches a limiting value of ~0.34 ± 0.03. This corresponds to a propagation rate constant, $k_3 \sim 1.6 \times 10^4$ $M^{-1}$ sec$^{-1}$ if $2k_6$ is assumed to equal the mean termination rate constant (for all the radicals studied except

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(24) R. D. Burkhart, *J. Am. Chem. Soc.*, 90, 273 (1968).

(25) R. D. Burkhart, private communication.

(26) M. Ebert, J. P. Keene, E. J. Land, and A. J. Swallow, *Proc. Roy. Soc.* (London), 287A, 1 (1965).

(27) G. S. Hammond and S. A. Weiner, private communication; see also *J. Am. Chem. Soc.*, 90, 1659 (1968).

(28) R. J. Hagemann and H. A. Schwarz, *J. Phys. Chem.*, 71, 2694 (1967).

(29) That is, the observed bimolecular rate constant for a diffusion-controlled reaction is given by[30]

$$k = (4\pi N/1000)(\sigma_A + \sigma_B)(D_A + D_B)$$

where $D_A$ and $D_B$ are the diffusion coefficients of the reactants A and B in the solvent medium and $\sigma_A$ and $\sigma_B$ are molecular radii defined in terms of the distance across which reaction can take place between A and B. In the absence of diffusion coefficient data, it is common to use the Stokes-Einstein equation in the form

$$D = kT/6\pi\eta r$$

and to identify the diffusion radii $r$ with the radii for reaction.[31] Combination of these two equations gives a simple relation between the rate constant and the solvent viscosity in cyclohexane at 25° under typical reaction conditions.

$$k = 8RT/(3 \times 10^3\eta)\ M^{-1}\ \text{sec}^{-1} = 8 \times 10^9\ M^{-1}\ \text{sec}^{-1}$$

(30) A. M. North, *Quart. Rev.* (London), 20, 421 (1966).

(31) For small molecules the Stokes-Einstein diffusion coefficient should probably be replaced by $kT/4\pi\eta r$ (E. McGlaughlin, *Trans. Faraday Soc.*, 55, 28 (1959)).

(32) R. K. Lyon, *J. Am. Chem. Soc.*, 86, 1907 (1964).

(33) O. Dobis, J. M. Pearson, and M. Szwarc, *ibid.*, 90, 278 (1968); K. Chakravorty, J. M. Pearson, and M. Szwarc, *ibid.*, 90, 283 (1968).

(34) See, however, C. L. Kibby and R. E. Weston, Jr., *ibid.*, 90, 1084 (1968).

Table XI. Effect of Viscosity on the Self-Reaction of *t*-Butyl Radicals[a]

| Solvent | Viscosity, cP | $R_i \times 10^8$ [b] | $R_s \times 10^5$ | $R_s/\{(R_i)^{1/2} \times [R'_3\text{SnH}]\}$ | $2k_t \times 10^{-9}$ | $k_p \times 10^{-5}$ |
|---|---|---|---|---|---|---|
| *n*-Pentane | 0.35 | 4.5 | 56 | 11 | 5.4 | 8.1 |
| Cyclohexane | 0.92 | 3.2 | 81 | 19 | 2.2 | 8.7 |
| *n*-Tridecane | 1.3 | 3.8 | 73 | 15 | 1.8 | 6.7 |

[a] 2.8 *M* *t*-butyl bromide; 0.24 *M* tri-*n*-butyltin hydride. [b] $R_i$ values for pentane and tridecane calculated relative to cyclohexane from the values of $2ek_d$ for tetraphenylbutane as given in Table II.

Table XII. Absolute Rate Constants for Radical-Molecule Reactions in Cyclohexane at 25°

| Reaction | $k_p/(2k_t)^{1/2}$ | $k_p$,[a] $M^{-1}$ sec$^{-1}$ |
|---|---|---|
| $t$-Bu· + $Ph_3SnH$ | 66 | $3.1 \times 10^6$ |
| $t$-Bu· + $n$-$Bu_3SnH$ | 15.8 | $7.4 \times 10^5$ |
| $t$-Bu· + $n$-$Bu_3SnD$ | 5.7 | $2.7 \times 10^5$ |
| $t$-Bu· + $Me_3SnH$ | 6.1 | $2.9 \times 10^5$ |
| $c$-$C_6H_{11}$· + $n$-$Bu_3SnH$ | 26 | $1.2 \times 10^6$ |
| $c$-$C_6H_{11}$· + $n$-$Bu_3SnD$ | | $4.4 \times 10^5$ [b] |
| $CH_3(CH_2)_4CH_2$· + $n$-$Bu_3SnH$ | 22 | $1.0 \times 10^6$ |
| $CH_3$· + $n$-$Bu_3SnH$ | 61 | $5.8 \times 10^8$ [c] |
| $Ph_3Sn$· + $t$-BuCl | 0.42 | $2.0 \times 10^4$ |
| $Me_3Sn$· + $t$-BuCl | 0.125 | $5.9 \times 10^3$ |
| $n$-$Bu_2ClSn$· + $t$-BuCl | 0.082 | $3.9 \times 10^3$ |
| $n$-$Bu_2HSn$· + $t$-BuCl | 0.10 | $4.7 \times 10^3$ |
| $n$-$Bu_3Sn$· + $t$-BuCl | 0.34 | $1.6 \times 10^4$ |
| $n$-$Bu_3Sn$· + $c$-$C_6H_{11}Cl$ | 0.043 | $2.0 \times 10^3$ |
| $Me_3Sn$· + $c$-$C_6H_{11}Cl$ | 0.0105 | $4.9 \times 10^2$ |
| $n$-$Bu_3Sn$· + $CH_3(CH_2)_3CH_2Cl$ | 0.018 | $8.5 \times 10^2$ |
| $n$-$Bu_3Sn$· + $PhCH_2Cl$ | | $6.4 \times 10^5$ [d] |
| $n$-$Bu_3Sn$· + $CH_3(CH_2)_4CH_2Br$ | | $1.9 \times 10^7$ [d] |
| $n$-$Bu_3Sn$· + $c$-$C_6H_{11}Br$ | | $2.2 \times 10^7$ [d] |
| $n$-$Bu_3Sn$· + $t$-BuBr | | $8.5 \times 10^7$ [d] |
| $n$-$Bu_3Sn$· + MeI | | $2.5 \times 10^9$ [d] |

[a] From $k_p/(2k_t)^{1/2}$ taking $2k_t = 2.2 \times 10^9$ $M^{-1}$ sec$^{-1}$ unless otherwise noted. Slightly different values were reported for some of these rate constants in our preliminary communication.[2] [b] From competitive experiments with $n$-$Bu_3SnH$ and $n$-$Bu_3SnD$. [c] From $k_p/(2k_t)^{1/2}$ taking $2k_t = 8.9 \times 10^9$ $M^{-1}$ sec$^{-1}$. [d] From relative reactivities in Table IX taking $k_p = 2.0 \times 10^3$ $M^{-1}$ sec$^{-1}$ for the $n$-$Bu_3Sn$· + $c$-$C_6H_{11}Cl$ reaction.

methyl) of $2.2 \times 10^9$ $M^{-1}$ sec$^{-1}$. This propagation rate constant is in reasonable agreement with the value estimated from competitive experiments with cyclohexyl chloride (Table IX) and $k_3$ for this halide (*i.e.* $(k_3)_{t\text{-BuCl}} = 6.5 \times (k_3)_{C_6H_{11}Cl} = 6.5 \times 2.0 \times 10^3 = 1.3 \times 10^4$ $M^{-1}$ sec$^{-1}$). At high [*t*-BuCl]/[*n*-$Bu_3SnH$] ratios, $R_s/\{(R_i)^{1/2}\cdot[RX]\}$ decreases and $R_s/\{(R_i)^{1/2}[R'_3SnH]\}$ increases. However the latter quantity does not reach its expected value of ~16 (*cf.* the *t*-BuBr–*n*-$Bu_3SnH$ reaction, Table III) at any experimentally practicable [chloride]/[hydride] ratio, perhaps because of some solvent effect on the rate in neat *t*-butyl chloride. Theoretical curves of $R_i[R'_3SnH]^2/R_s^2$ *vs.* $[R'_3SnH]/[RX]$ and of $R_i[RX]^2/R_s^2$ *vs.* $[RX]/[R'_3SnH]$ were constructed for various values of $2k_5$, taking $2k_4 = 2k_6 = 2.2 \times 10^9$, $k_2/(2k_4)^{1/2} = 7.4$ (the average of the values found at the two highest [chloride]/[hydride] ratios), and $k_3/(2k_6)^{1/2} = 0.34$. The experimental points show considerable scatter but are mostly confined within boundaries defined by $2k_5 = 0$ (*i.e.*, no cross-termination) and $2k_5 = 4 \times 10^9$ (the value expected on statistical grounds). The experimental accuracy is therefore not sufficient for the cross-termination rate constant to be determined. Cross-termination probably occurs but the data do not absolutely require it.

**Propagation.** Absolute rate constants for chain propagation are listed in Table XII. The rate constants for the alkyl radical-tin hydride reactions (except $CH_3$· + *n*-$Bu_3SnH$) and for the tin radical–alkyl chloride reactions have been calculated from the average values of $k_p/(2k_t)^{1/2}$ taking $2k_t = 2.2 \times 10^9$ $M^{-1}$ sec$^{-1}$. Rate constants for abstraction by the tri-*n*-butyltin radical from benzyl chloride, the bromides, and methyl iodide have been calculated from the relative reactivity data in Table IX.

As we would expect from the well-known differences between primary, secondary, and tertiary alkyl groups, the rates of abstraction of chlorine and bromine by the tri-*n*-butyltin radical increase in the order 1-alkyl < cyclohexyl < *t*-butyl. The rates of abstraction of hydrogen from the tin hydride show a small increase in the order *t*-butyl < *n*-hexyl $\lesssim$ cyclohexyl < methyl. The *n*-hexyl radical occupies an anomalous position in this series but the difference in rate constants for *n*-hexyl and cyclohexyl is well within the limits of experimental error.

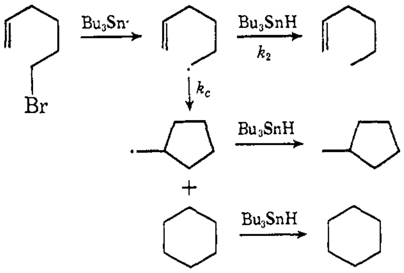
The rate of abstraction of hydrogen from the tin hydrides by the *t*-butyl radical increases by a factor of 10 along the series $Me_3SnH$ < *n*-$Bu_3SnH$ < $Ph_3SnH$. Triphenyltin hydride is therefore a significantly more reactive reducing agent than trialkyltin hydrides, as has been previously reported by Kuivila both for alkyl halide reduction,[4b] aldehyde and ketone reduction,[6] and olefin reduction.[19] The greater rate of hydrogen abstraction from triphenyltin hydride compared with trialkyltin hydrides may be due to the greater stability of the triphenyltin radical (*cf.* $Ph_3C$· *vs.* $Me_3C$·). In addition, Kuivila[19] has suggested that the electron-withdrawing inductive effect (−I effect) of the phenyl groups diminishes the hydride character of the hydrogen atom. As a result, the Sn–H bond strength will be decreased because of the decreased importance of polar contributions to the bond ($Sn^{\delta+}$–$H^{\delta-}$).

Chlorine abstraction from *t*-butyl chloride by the tin radicals depends very little on the organic groups attached to the tin, the rate increasing by only a factor of about 5 along the series *n*-$Bu_2ClSn$· $\lesssim$ *n*-$Bu_2HSn$· $\lesssim$ $Me_3Sn$· < *n*-$Bu_3Sn$· $\lesssim$ $Ph_3Sn$·. The abstraction reaction should be facilitated by inductive electron release (+I effect) from the groups attached to the tin because of increased polar contributions to the transition state of the type $R'_3Sn^{\delta+} \cdots Cl^{\delta-} \cdots R$. The first four radicals appear to be in an order consistent with this suggestion, but the relatively high reactivity of triphenyltin is unexpected. Perhaps in this case, the phenyl groups offset their −I effect by altering the local environment around the reaction center to one of higher dielectric constant than that which exists (in cyclohexane) around the other tin radicals. As a result, polar contributions to the transition state would be stabilized by a local dielectric effect.

The propagation constants listed in Table XII are consistent with the simple kinetics that are generally observed in tin hydride–alkyl halide reactions. That is, alkyl radicals generally abstract hydrogen from the tin hydrides more rapidly than the tin radicals abstract chlorine but more slowly than the tin abstracts bromine or iodine. However, there is no doubt that many compounds containing activated chlorine (such as $CCl_4$ or benzyl chloride) will behave kinetically like the bromides or, at least, like the *t*-butyl chloride–tri-*n*-butyltin hydride reaction.

It is interesting to note that the estimated rate constant for iodine atom abstraction from methyl iodide is as large as the rate constants for the termination processes. That is, this reaction is essentially diffusion controlled and it is therefore one of the fastest known abstraction reactions which involves a radical rather than an atom as the abstracting species.

**Radical Isomerization.** During the past 2 or 3 years the halide–tin hydride reaction has been used to investigate the conformational stability of a number of free radicals.[4d,5b,5d,35] The rate constants for hydrogen abstraction which have been obtained in this work are of obvious importance to the interpretation of these results. For example, Walling, *et al.*,[5c] have studied the reaction of 5-hexenyl bromide with tributyltin hydride in order to investigate the cyclization of the 5-hexenyl radical. The main products are 1-hexene and methylcyclopentane, together with a small amount of cyclohexane. The cyclization is not reversible under the experimental conditions. At 40° the ratio of the rate constants for cyclization and hydrogen abstraction, $k_c/k_2$, is 0.1. Our own results on 1-hexyl bromide give $k_2 = 1 \times 10^6\ M^{-1}\ \text{sec}^{-1}$ (at 25°) and hence, $k_c = 1 \times 10^5\ \text{sec}^{-1}$. Completely analogous results have been obtained by Struble, *et al.*,[35e] for the reduction of 4-(1-cyclohexenyl)butyl bromide with tributyltin hydride in benzene at 65°. The products are similar, *i.e.* and $k_c = k_2[\text{Bu}_3\text{SnH}]([\text{II}] + [\text{III}])/[\text{I}] \approx 4 \times 10^4\ \text{sec}^{-1}$ if $k_2$ is assumed to be $1 \times 10^6\ M^{-1}\ \text{sec}^{-1}$ (see Table XIII). These rate constants for cyclization may be compared with a great number of rate constants for radical addition to double bonds which have been obtained in polymerization studies.[36] Of more particular interest, James and Ogawa[37] have reported on the addition of ethyl radicals to heptene-1 in the gas phase measured relative to the rate of ethyl radical combination. At 40° their data give a value of about $1 \times 10^3\ M^{-1}\ \text{sec}^{-1}$ for the rate constant for addition. Thus the "effective" double bond concentration for the intramolecular cyclization is ~40–100 *M*.



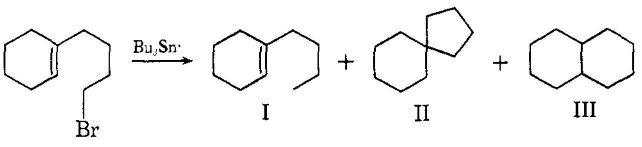


Table XIII. Cyclization of the 4-(1-Cyclohexenyl)butyl Radical[a]

| $[\text{Bu}_3\text{SnH}]$, *M* | $([\text{II}] + [\text{III}])/[\text{I}]$ | $k_c \times 10^{-4}$, sec$^{-1}$ [b] |
|---|---|---|
| 0.02 | 1.83 | 3.7 |
| 0.028 | 1.33 | 3.7 |
| 0.10 | 0.64 | 6.4 |
| 0.14 | 0.28 | 4.0 |

[a] See ref 35e. [b] $k_2 = 1 \times 10^6\ M^{-1}\ \text{sec}^{-1}$.

A further example of the rearrangement of a primary alkyl radical has been provided by Kaplan[5b] who has shown that in the reaction of 2,2,2-triphenylethyl chloride with triphenyltin hydride at 70–130° the 2,2,2-triphenylethyl radical can be trapped before it rearranges to the 1,1,2-triphenylethyl radical. The rate constant for hydrogen abstraction from the hydride by the primary $\text{Ph}_3\text{CCH}_2\cdot$ radical should be $\sim 5 \times 10^6\ M^{-1}\ \text{sec}^{-1}$ at 30° and will probably be $\sim 5 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ at 100°. The yield of $\text{Ph}_3\text{CCH}_3$ at 100° was 76% with 2.6 *M* [$\text{Ph}_3\text{SnH}$] and 40% with 0.75 *M* [$\text{Ph}_3\text{SnH}$], the other major product being $\text{Ph}_2\text{CHCH}_2\text{Ph}$. The rate constant for the isomerization

$$\text{Ph}_3\text{CCH}_2\cdot \longrightarrow \text{Ph}_2\dot{\text{C}}\text{CH}_2\text{Ph}$$

is given by

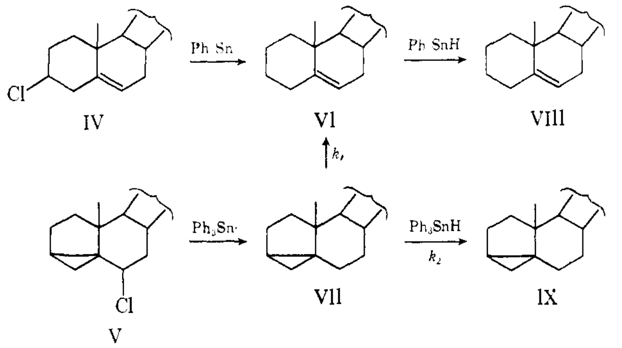
$$[\text{Ph}_3\text{SnH}]\frac{[\text{Ph}_2\text{CHCH}_2\text{Ph}]}{[\text{Ph}_3\text{CCH}_3]}(k_2)_{\text{Ph}_3\text{CCH}_2\cdot} \approx$$

$$5 \times 10^7\ \text{sec}^{-1} \text{ at } 100°$$

Christol and Barbour[35d] have studied the reduction of 3$\beta$-chlorocholest-5-ene (cholesteryl chloride, IV) and 6$\beta$-chloro-3$\alpha$,5$\alpha$-cyclocholestane (cyclocholestanyl chloride, V) with triphenyltin hydride. The chloride IV gives only 5-cholestene (VIII) but V gives both VIII and 3$\alpha$,5$\alpha$-cyclocholestane (IX). The rate constants ($k_r$) for rearrangement of the 3,5-cyclocholestanyl radical (VII) to the cholesteryl radical (VI) can be calculated from Cristol and Barbour's data using the relation

$$k_r = k_2[\text{Ph}_3\text{SnH}]([\text{VIII}]/[\text{IX}]).$$

The results are given in Table XIV, it having been assumed that $k_2 = 5 \times 10^6\ M^{-1}\ \text{sec}^{-1}$ at each temperature.



The reduction of norbornenyl bromide and chloride and of nortricyclyl bromide and chloride with tri-*n*-butyltin hydride provides the same mixture of norbornene and nortricyclene indicating the existence of common intermediates in the reaction. However, with triphenyltin hydride, nortricyclyl bromide yields a higher ratio of nortricyclene to norbornene in the absence of

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[35] (a) D. B. Denney, R. M. Hoyte, and P. T. MacGregor, *Chem. Commun.*, 1241 (1967); (b) T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 3051 (1967); (c) F. Warbertin and E. Sanford, *ibid.*, **90**, 1667 (1968); (d) S. J. Cristol and R. V. Barbour, *ibid.*, **90**, 2832 (1968); (e) D. L. Struble, A. L. J. Beckwith, and G. E. Gream, *Tetrahedron Letters*, 3701 (1968).

[36] See for example, C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

[37] D. G. L. James and T. Ogawa, *Can. J. Chem.*, **43**, 640 (1965).

**Table XIV.** Rearrangement of the 3,5-Cyclocholestanyl Radical to the Cholesteryl Radical[a]

| Temp, °C | [$Ph_3SnH$], $M$ | [VIII]/[IX] | $k_r \times 10^6$, $sec^{-1}$ [b] |
|---|---|---|---|
| 30 | ~4 | 6.25 | 125 |
| 15 | 0.4 | 25 | 50 |
| 15 | 0.04 | 100 | 20 |
| −15 | 1.0 | 2.3 | 12 |
| −20 | 0.08 | 4.5 | 1.8 |

[a] See ref 35d. [b] $k_2$ assumed = $5 \times 10^6\ M^{-1}\ sec^{-1}$.

solvent than in pentane indicating the presence of discreet nortricyclyl and norbornenyl free radicals. The rate constant for abstraction from the tin hydrides by these radicals should be similar to that for the cyclohexyl radical, *i.e.*, $\sim 1 \times 10^6\ M^{-1}\ sec^{-1}$ for tri-*n*-butyltin hydride and probably about five times as great for the triphenyltin hydride. On this basis, the rather limited data of Warner, *et al.*,[4d] suggest that the rate constant for unimolecular isomerization of these radicals to one another is $\sim 10^8\ sec^{-1}$.

A *cis* source of 9-decalyl radicals gives a short-lived radical which changes into the same radical as is obtained from a *trans* source but yields *cis* products on reaction with oxygen[38] or hypochlorite.[39] The more stable radical obtained from a *trans* source yields both *cis* and *trans* products on reaction with these reagents. The radical from a *cis* source (*cis*-9-chlorodecalin) could not be trapped by tin hydrides[5d] which is not surprising in view of the rate of hydrogen abstraction by tertiary alkyl radicals ($\leqslant 3 \times 10^6\ M^{-1}\ sec^{-1}$) relative to the estimated lifetime of the radical (*ca.* $10^{-8}$–$10^{-9}$ sec[38]).

Abstraction from tin hydrides by allyl radicals is probably even slower than abstraction by tertiary alkyl radicals. The almost complete lack of conformational stability of the allyl radicals produced in a number of allyl chloride–triphenyltin hydride reactions[35a] may be due to the slowness of the hydrogen abstractions. However, the usefulness of the tin hydrides for studying the conformational stabilities of allyl radicals is open to question because triorganotin radicals undergo a rapid reversible addition to many double bonds.[11,12] Unfortunately, there does not appear to be any suitable data available for estimating the rate constants of the addition reaction for comparison with the present abstraction rate constants.

It may be possible to determine the rates of decarbonylation of acyl radicals by absolute rate measurements on acyl halide–tin hydride systems.[40]

## Conclusion

The evaluation of both propagation rate constants and two out of three termination rate constants for some of the tin hydride–alkyl halide reactions means that, in quantitative terms, these reactions are now among the most completely understood two-step chain reactions.

**Acknowledgment.** The authors gratefully acknowledge the assistance of Mr. A. Lafortune in the later stages of this work.

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(38) P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Am. Chem. Soc.*, **87**, 2590 (1965).

(39) F. D. Greene and N. N. Lowry, *J. Org. Chem.*, **32**, 875 (1967).

(40) H. G. Kuivila and E. J. Walsh, Jr., *J. Am. Chem. Soc.*, **88**, 571 (1966).