

Mechanism of Homolytic Substitution (S_H2) Reactions. Radical Chain Cleavage of Alkylmetals by Photochemically Generated Iodine Atoms

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Homolytic substitution (S_H2) of tetramethyltin by an iodine atom is shown to be the rate-limiting step in the photochemically initiated radical chain process for iodinolysis in carbon tetrachloride solutions. The reactivities of various tetraalkyltin compounds with different electronic and steric properties are measured from the kinetics of the iodinolysis. The activation energy, ΔG^\ddagger , for the S_H2 process is found to be quantitatively related to the driving force for ion-pair formation, i.e., $R_4Sn + I \cdot \rightarrow [R_4Sn^+ \cdot I^-]$, by evaluating (1) the free-energy change, ΔG° , for the oxidation of the tetraalkyltin compound and (2) the interaction energy, ΔE , of the ion pair. The latter is obtained independently from the charge-transfer interaction of the alkyltin compound with iodine. The formation of the ion pair as a reactive intermediate in S_H2 reactions is supported by selectivity studies, in which intramolecular competition in the homolytic displacement of alkyl ligands from unsymmetrical tetraalkyltin compounds is found to be the same as that observed in the fragmentation of the cation radical $R_4Sn^+ \cdot$ generated independently by electron transfer to hexachloroiridate(IV). Solvent studies support a rather polar transition state for the S_H2 iodinolysis of alkylmetals, in accord with the charge-transfer mechanism in Scheme II. The direct comparison of the activation energies for the cleavages of alkylmetals by an iodine atom and molecular iodine in the same solvent allows parallels to be drawn for homolytic S_H2 and electrophilic S_E2 mechanisms.

Chain transfer reactions play an important role in free-radical chemistry. Among these, the bimolecular process, designated as S_H2 , is ubiquitous.¹ When it is observed at a terminal univalent atom, commonly hydrogen or halogen, it is usually referred to as an abstraction process. When it occurs at a multivalent center, it is of particular interest because it is conceptually related to the heterolytic equivalents, i.e., the bimolecular nucleophilic and electrophilic substitution processes, S_N2 and S_E2 , respectively.

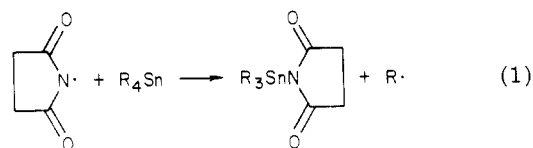
Despite the widespread involvement of S_H2 processes, surprisingly little is quantitatively known about how they occur, let alone the driving force for substitution. Whether the S_H2 reaction is synchronous or stepwise or whether it occurs with stereochemical inversion or retention has not been well established. Part of the difficulty is associated with inadequate information about the nature of the activation process for the S_H2 reaction.

The S_H2 reaction with organometals, RM, is particularly useful for mechanistic studies since it can be rapid.



In some cases the paramagnetic intermediates and products have been observed.¹⁻⁵ More importantly, the tetraalkyl derivatives of the group 4A metals, silicon, germanium, tin, and lead (which bear a direct structural relationship to alkanes), are substitution stable, and by changing the alkyl ligands, electronic and steric effects can be examined systematically.⁶ The latter is especially important since S_H2 reactions of tetraalkyltin compounds have been reported to show complex reactivity patterns.^{7,8}

For example, the mixing of electronic and steric effects is apparent in the reaction of succinimidyl radical (eq 1), in



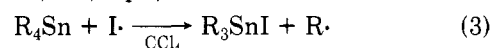
which Me_4Sn is more reactive than Et_4Sn ,⁷ in contrast to the reaction of bromine atom (eq 2), in which the reverse order, Me_4Sn less reactive than Et_4Sn , has been reported.⁸



The photochemically induced halogenolysis of tetraalkyltin occurs by an S_H2 reaction (compare eq 2) as a propagation step in the radical chain sequence.^{8,9} We have now examined the kinetics of iodinolysis and related it to the rate of the S_H2 reactions of various tetraalkyltin compounds with an iodine atom. This study has also enabled us to compare directly the S_H2 process with an iodine atom with the recently reported S_E2 process with molecular iodine,¹⁰ using a common substrate.

Results

Three series of symmetrical and unsymmetrical tetraalkyltin compounds were examined in this study, viz., R_4Sn , $RSnMe_3$, and R_2SnMe_2 , where R is an alkyl ligand. The homolytic cleavage of these tetraalkyltin compounds by iodine atoms, i.e., eq 3, was carried out at 25 °C in



carbon tetrachloride solutions. The latter allowed molecular iodine to be used as the precursor, since photodissociation in this medium is known to proceed with a quantum yield of 0.14 with 436-nm light¹¹ (eq 4). More



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Table I. Photochemical Cleavage of Me_4Sn by Iodine. Dependence on Light Intensity^a

actinometer ^b 10^{10} M s^{-1}	$10^{10} I_n$, ^c einstein $\text{L}^{-1} \text{ s}^{-1}$	$10^7 R_{\text{init}}$, ^d M s^{-1}	Φ , mol einstein ⁻¹
4.0	3.4	2.8	850
14.9	12.4	5.0	400
35.7	29.7	9.5	320
85.5	71.3	14.5	200

^a $[\text{Me}_4\text{Sn}]_0 = 7.28 \times 10^{-2} \text{ M}$ and $[\text{I}_2]_0 = 2.57 \times 10^{-2} \text{ M}$ in carbon tetrachloride solution at 25 °C. ^b 0.143 M in potassium ferrioxalate in water. ^c Light intensity. The quantum yield for ferrioxalate taken as 1.20. ^d Initial rate.

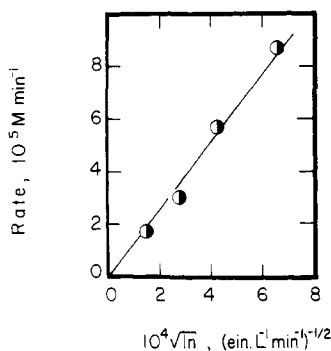
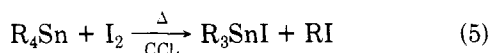


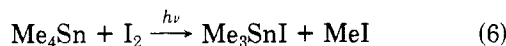
Figure 1. Rate of photochemical iodolysis as a function of the square root of the light intensity in carbon tetrachloride at 25 °C; $[\text{I}_2]_0 = 2.57 \times 10^{-2} \text{ M}$; $[\text{Me}_4\text{Sn}]_0 = 7.28 \times 10^{-2} \text{ M}$.

importantly, any competition from the electrophilic cleavage of the tetraalkyltin compounds by molecular iodine (eq 5) is too slow to be a significant complication



in this solvent at this temperature.¹⁰

Kinetics of the Photochemical Cleavage of Tetramethyltin by Iodine. A solution of tetramethyltin and molecular iodine in carbon tetrachloride is thermally stable at 25 °C for prolonged periods. However, irradiation of the solution with even weak actinic light readily induces the decoloration of iodine ($\lambda_{\text{max}} 520 \text{ nm}$) according to the stoichiometry in eq 6. The rate of tetramethyltin cleavage



was followed by the disappearance of the iodine absorbance at 520 nm ($\epsilon_{\text{max}} 900$) at the various light intensities listed in Table I. The quantum yields for iodine disappearance measured by ferrioxalate actinometry¹² (last column) were much larger than unity, showing the photochemical cleavage to be a chain process. Moreover, the initial rate follows a half-order dependence on the light intensity in Figure 1. At a constant light intensity, the rate is first-order in Me_4Sn and independent of the iodine concentration, as shown in Figure 2. The initial rate of the photochemical iodolysis of tetramethyltin is thus given by eq 7, where I_n is the incident light intensity and k_i is the iodine-independent rate constant.

$$d[\text{I}_2]/dt = k_i I_n^{1/2} [\text{Me}_4\text{Sn}] \quad (7)$$

The radical chain nature of the photochemical iodolysis is also demonstrated by inhibition studies. A typical rate of iodolysis at a constant light flux is shown for

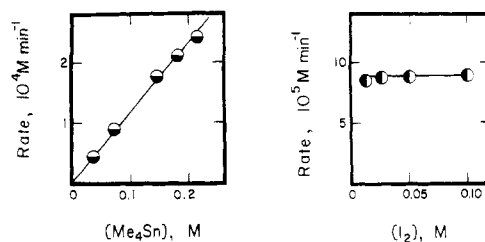


Figure 2. Rate of the photochemical iodolysis in carbon tetrachloride as a function of (left) Me_4Sn concentration with $[\text{I}_2]_0 = 2.5 \times 10^{-2} \text{ M}$ and (right) iodine concentration with $[\text{Me}_4\text{Sn}]_0 = 7.28 \times 10^{-2} \text{ M}$ and with a light flux $I_n = 4.28 \times 10^{-7} \text{ einstein L}^{-1} \text{ min}^{-1}$.

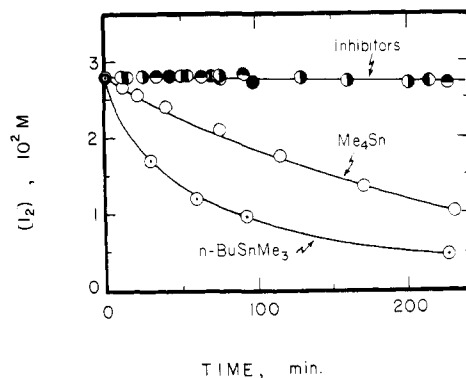


Figure 3. Inhibition of the photochemical iodolysis of $8.00 \times 10^{-2} \text{ M}$ tetramethyltin and $2.53 \times 10^{-2} \text{ M}$ *n*-butyltrimethyltin with $I_n = 4.3 \times 10^{-7} \text{ einstein L}^{-1} \text{ min}^{-1}$ in carbon tetrachloride at 25 °C. Me_4Sn : ○, no inhibitor; ●, $2.22 \times 10^{-2} \text{ M}$ isoamyl nitrate; ○, $1.17 \times 10^{-3} \text{ M}$ galvinoxyl. *n*-BuSnMe₃: ○, no inhibitor; ●, $2.22 \times 10^{-2} \text{ M}$ isoamyl nitrate; ○, $1.17 \times 10^{-3} \text{ M}$ galvinoxyl.

Table II. Reactivities of Various Tetraalkyltin Compounds in the Photochemical Iodolysis in Carbon Tetrachloride Solutions^a

no.	tetraalkyltin	rel rate ^b	$h\nu_{\text{CT}}$, ^c eV	I_D , ^d eV
1	Me_4Sn	1 (0)	4.59	9.69
2	Et_4Sn	51 (1.71)	4.27	8.90
3	<i>n</i> -Pr ₄ Sn	49 (1.69)	4.27	8.82
4	<i>n</i> -Bu ₄ Sn	51 (1.71)	4.30	8.76
5	EtSnMe_3	9.2 (0.96)	4.49	9.10
6	<i>n</i> -PrSnMe ₃	10.6 (1.03)	4.50	9.10
7	<i>n</i> -BuSnMe ₃	11.7 (1.07)	4.49	9.10
8	<i>i</i> -BuSnMe ₃	9.0 (0.95)	4.54	9.05
9	Et_2SnMe_2	42 (1.62)	4.44	9.01
10	<i>n</i> -Pr ₂ SnMe ₂	41 (1.61)	4.35	8.80
11	<i>n</i> -Bu ₂ SnMe ₂	40 (1.60)	4.35	8.80
12	<i>i</i> -Pr ₂ SnMe ₂	38 (1.58)	4.27	8.56
13	<i>t</i> -Bu ₂ SnMe ₂	30 (1.48)	4.10	8.22
14	Et_2SnMe	58 (1.76)	4.27	8.95
15	<i>i</i> -Pr ₄ Sn	38 (1.58)	4.20	8.46
16	<i>s</i> -Bu ₄ Sn	48 (1.68)	4.14	8.45
17	<i>i</i> -Bu ₄ Sn	10.3 (1.01)	4.22	8.68

^a At 25 °C with $[\text{R}_4\text{Sn}]_0 = 3.00 \times 10^{-2} \text{ M}$ and $[\text{I}_2]_0 = 2.57 \times 10^{-2} \text{ M}$ with a light intensity of $4.28 \times 10^{-7} \text{ einstein L}^{-1} \text{ min}^{-1}$. ^b Rates measured relative to that of Me_4Sn . Logarithms in parentheses. ^c Charge-transfer transition energies of $[\text{R}_4\text{Sn I}_2]$ complexes in CCl_4 taken from ref 15. ^d Ionization potentials from ref 14.

tetramethyltin and *n*-butyltrimethyltin by the open circles in Figure 3. However, no iodolysis of either alkylmetal occurs in the presence of galvinoxyl or isoamyl nitrate, which are known to inhibit similar chain processes.¹³ The

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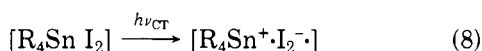
Table III. Selectivities in the Iodinolysis of Unsymmetrical Tetraalkyltin Compounds in Carbon Tetrachloride. Comparison of the Photochemical and Thermal Processes

tetraalkyltin	S(R/Me)		
	$I_2, h\nu^a$	I_2, Δ^b	$IrCl_6^{2-} c$
EtSnMe ₃	10.2	1.4 (1.5 ^d)	10.2
<i>n</i> -PrSnMe ₃	9.1	0.9	9.2
<i>n</i> -BuSnMe ₃	9.9	0.9	9.5
<i>i</i> -BuSnMe ₃	7.7	0.5	7.3
(Et) ₂ SnMe ₂	10.5	0.8 (1.0, ^d 0.9 ^e)	11.0
(<i>n</i> -Pr) ₂ SnMe ₂	9.3	0.6 (0.8, ^d 0.6 ^e)	9.3
(<i>n</i> -Bu) ₂ SnMe ₂	9.0	0.6 (0.9, ^d 0.8 ^e)	9.7
(<i>i</i> -Pr) ₂ SnMe ₂	15		15
(<i>t</i> -Bu) ₂ SnMe ₂	22		25
(Et) ₃ SnMe	10.5	0.5 (0.6 ^{d,e})	10.4
(<i>i</i> -Bu) ₂ SnEt ₂	2.0 ^f	3.3 ^f	2.1 ^f

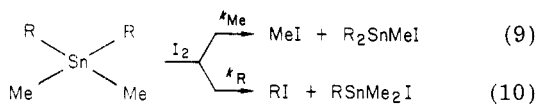
^a At 25 °C with $[I_2]_0 = 0.10$ M and $[R_4Sn]_0 = 0.12$ M at a light intensity of $\sim 10^{-4}$ einstein L⁻¹ min⁻¹. ^b At 50 °C with $[I_2]_0 = 0.10$ M and $[R_4M]_0 = 0.15$ M. ^c At 25 °C with $[IrCl_6^{2-}]_0 = 0.12$ or 0.20 M and $[R_4Sn]_0 \approx 0.12$ –0.20 M in acetonitrile.¹⁶ ^d In the presence of 1.17×10^{-3} M galvinoxyl. ^e In the presence of 2.22×10^{-2} M isomyl nitrite added as inhibitor. ^f S(Et/*i*-Bu).

kinetic chain length is estimated to be roughly 10³ (see Experimental Section).

Reactivities of Tetraalkyltin Compounds. The rates of photochemical iodinolysis of the various tetraalkyltin compounds listed in Table II were carried out under a standard set of conditions by using the same tetraalkyltin and iodine concentrations as well as a constant light intensity. The rates are tabulated relative to that of Me₄Sn. The ionization potentials, I_D , of the tetraalkyltin compounds¹⁴ are also included in Table II, together with the transition energies, $h\nu_{CT}$, of the charge-transfer complexes between tetraalkyltin and iodine determined previously¹⁵ (see eq 8).



Selectivity in the Cleavage of Unsymmetrical Tetraalkyltin Compounds. In the cleavage of unsymmetrical tetraalkyltin compounds Me_nSnR_{4-n}, the selectivity, S(R/Me), determines the relative rates of scission of the relevant bonds (i.e., an alkyl–tin bond vs. a methyl–tin bond), as an intramolecular comparison. Thus, iodine affords a mixture of two alkyl iodides, CH₃I and RI, from R₂SnMe₂ in amounts which depend on the relative rates of cleavage (i.e., eq 9 and 10). The selectivity, S(R/Me)



$= k_R/k_{Me}$, is obtained directly from the yields of RI and MeI. For the other unsymmetrical tetraalkyltin compounds, RSnMe₃ and R₃SnMe, a statistical correction is made (i.e., eq 11, where $n = 1, 2,$ and 3). It is noteworthy

$$S(R/Me) = \frac{n [RI]}{4 - n [MeI]} \quad (11)$$

that the selectivities determined by the use of eq 11 are rather constant for various alkyl (R) groups in Table III,

Table IV. Solvent Effect on the Rates of Photochemical and Thermal Iodinolysis^a

solvent	ϵ_B^b	iodinolysis rate $\times 10^6$ M s ⁻¹	
		$h\nu$	Δ^c
carbon tetrachloride	2.24	1.5	~ 0.1
<i>n</i> -butyl ether	3.06	20.7	43
chlorobenzene	5.62	25.8	930

^a At 25 °C, $[Me_4Sn]_0 = 7.28 \times 10^{-2}$ M, $[I_2]_0 = 5.00 \times 10^{-3}$ M, $In = 4.28 \times 10^{-7}$ einstein L⁻¹ min⁻¹. ^b Dielectric constant from ref 17. ^c Thermal (electrophilic) rate constant for Me₃SnEt in units of 10^6 M⁻¹ s⁻¹ from ref 10.

Table V. Solvent Effect on Selectivity for Various Tetraalkyltin Compounds. Comparison Between Photochemical and Thermal Processes

tetraalkyltin	S(R/Me)				
	CCl ₄	PhCl	PhBr	<i>m</i> -Cl ₂ Ph	CHCl ₃
	Photochemical ^a				
EtSnMe ₃	10.2 (10.7)	10.5	10.4	10.2	(10.1)
<i>n</i> -PrSnMe ₃	9.1 (9.6)	8.4	9.3	9.4	(8.3)
<i>n</i> -BuSnMe ₃	9.9 (9.5)	9.5	9.8	9.7	(8.0)
<i>i</i> -BuSnMe ₃	7.7	7.0	7.8	7.2	(6.5)
<i>i</i> -Bu ₂ SnEt ₂	2.0 ^b	2.1 ^b	2.1 ^b	2.2 ^b	(2.0) ^b
	Thermal ^c				
EtSnMe ₃	1.4	0.23			
<i>n</i> -PrSnMe ₃	0.9	0.081			0.031
<i>n</i> -BuSnMe ₃	0.9	0.065			0.025

^a Iodinolysis carried to completion (30–90 s) at 25 °C by using $[R_4Sn]_0 = 0.12$ M, $[I_2]_0 = 0.10$ M, and $In = 3.6 \times 10^{-6}$ einstein L⁻¹ s⁻¹. Values in parentheses obtained at –10 °C with $In = 5.7 \times 10^{-6}$ einstein L⁻¹ s⁻¹ and completed in ~ 60 s. ^b S(Et/*i*-Bu). ^c From ref 10.

independent of the value of n . Moreover, the selectivity is unaffected by the energy of the incident light, since $S(n\text{-Bu/Me}) = 9.9$ for *n*-BuSnMe₃ is essentially unchanged from that (9.2) obtained by the use of an interference filter transmitting at 546 ± 10 nm.

The selectivity in the photochemical iodinolysis of tetraalkyltin compounds by iodine atoms differs significantly from that observed in the electrophilic iodinolysis by molecular iodine.¹⁰ The latter is also included in Table III for comparison. Similarly, the selectivities listed in column four of Table III represent alkylmetal cleavages by hexachloroiridate(IV).¹⁶

Solvent Effects on the Rates and Selectivities of Photochemical Iodinolysis. The rates of the photochemical iodinolysis of tetramethyltin were also measured in other solvents. Unfortunately the choice was severely restricted to a limited number of nonpolar solvents,¹⁷ since the electrophilic process (eq 5, which is highly solvent dependent) became too competitive even in such solvents as methylene chloride and chloroform.¹⁰ This limitation notwithstanding, the trend in the rates in Table IV indicates that the solvent effect on the photochemical process is similar but somewhat attenuated relative to that observed in the thermal (electrophilic) process.

The selectivities in the photochemical cleavage of unsymmetrical tetraalkyltin compounds are relatively

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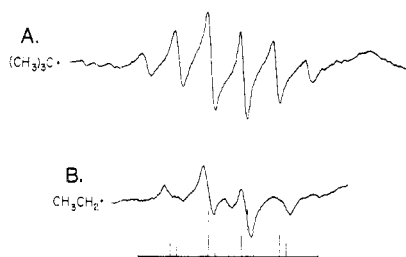


Figure 4. ESR spectra of alkyl radicals obtained during irradiation of solutions of alkylmetals and iodine in carbon tetrachloride frozen at -180°C : (A) *tert*-butyl radicals from $t\text{-Bu}_2\text{SnMe}_2$; (B) ethyl radicals from Et_4Ge . The stick spectrum is constructed with isotropic hyperfine splittings of $a_{\text{H}\alpha} = 22.4$ G and $a_{\text{H}\beta} = 26.9$ G.¹⁸

unaffected by changes in the solvent. Thus the variations in $S(\text{R}/\text{Me})$ in Table V are significantly less than the changes in the rates listed in Table IV. Furthermore, these selectivities are also less sensitive to solvent changes compared to the selectivities previously obtained in the thermal (electrophilic) process,¹⁰ relisted at the bottom of Table V for comparison. (The photochemical selectivities in chloroform solution were not investigated at the same temperature since the competing thermal iodinolysis could not be completely obviated. Therefore, these selectivities in Table V were measured at -10°C .) Contribution from the thermal process could be minimized by using a rather high light flux emitted from a 100-W Hg lamp to preferentially promote the photochemical process.^{8,9}

Direct Observation of Alkyl Radicals During Photochemical Iodinolysis of Tetraalkyltin Compounds. When a solution of tetraalkyltin and iodine is irradiated directly in the cavity of the ESR spectrometer, the chain reaction is too rapid, even at -45°C , to allow the spectrum of the transient radicals to be recorded. However, the latter could be immobilized by first cooling a solution of di-*tert*-butyldimethyltin and iodine in carbon tetrachloride to -180°C and then irradiating the frozen matrix. The ESR spectrum in Figure 4 is clearly that of the *tert*-butyl radical ($a_{\text{H}} = 22.6 \pm 0.1$ G, $g = 2.0026$).¹⁸ No other paramagnetic species was observed under these conditions. Similarly, a solution of tetraethylgermane and iodine in carbon tetrachloride afforded the broadened but clearly identifiable spectrum of the ethyl radical in Figure 4B. Indeed, the accompanying stick diagram centered at $g = 2.0026$ represents the isotropic hyperfine splittings of the ethyl radical with $a_{\text{H}\alpha} = 22.38$ G and $a_{\text{H}\beta} = 26.87$ G obtained in solution.¹⁸ The same ESR spectrum is also obtained from Et_2SnMe_2 and I_2 , although with somewhat diminished amplitude. ESR spectra of alkyl radicals are not observed in the absence of iodine. Furthermore, no definite ESR signal is discerned unless a tetraalkyltin compound is present.¹⁹

The intensity of the spectrum of the *tert*-butyl radical in Figure 4A increased with irradiation time, and the spectrum persisted at -180°C upon shuttering of the light.

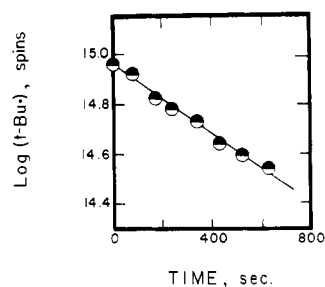


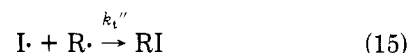
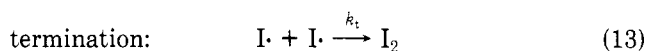
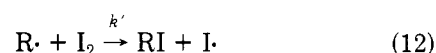
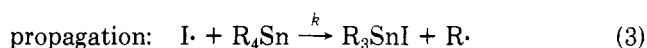
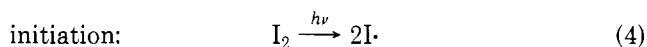
Figure 5. First-order decay of the ESR signal of *tert*-butyl radicals in a carbon tetrachloride matrix at -163°C .

However, if the matrix is annealed, even at temperatures as low as -163°C , the spectrum disappeared with a half-life of roughly 7 min. The first-order decay ($k_d = 1.57 \times 10^{-3} \text{ s}^{-1}$) is plotted in Figure 5.

Discussion

The high quantum yields in Table I together with the complete inhibition of the photochemical iodinolysis of the tetraalkyltin as shown in Figure 3 clearly indicate a radical chain mechanism for the cleavage process in eq 6. Earlier, Gielen, Nasielski, and co-workers⁸ also observed a similar chain reaction in the photochemically induced cleavage of tetraalkyltin by bromine. They proposed the homolytic substitution step involving bromine atom attack on the tetraalkyltin, similar to eq 3, in the propagation sequence. As applied to the photochemical iodinolysis, the chain mechanism is as shown in Scheme I.⁹ Scheme I forms the basis for our study of homolytic substitution on alkylmetals. However, before focussing on the $\text{S}_{\text{H}}2$ reaction in eq 3, we must first show by a kinetic analysis that it represents the rate-limiting step in the photochemical iodinolysis of tetraalkyltin compounds in carbon tetrachloride solutions.

Scheme I



Homolytic Substitution by an Iodine Atom as the Rate-Limiting Step in the Photochemical Iodinolysis of Tetraalkyltin Compounds. The rate of disappearance of iodine in Scheme I is determined by the propagation steps when the kinetic chain length is long. Since the latter is shown to be the case in Table I, we utilized the steady-state assumption to describe the rate of iodine disappearance by eq 16, where R_i is the rate of initiation,

$$-\frac{d[\text{I}_2]}{dt} \simeq k[\text{R}\cdot][\text{I}_2] = k' \left[R_i \left/ \left[k_t' + k_t'' \left(\frac{k[\text{I}_2]}{k[\text{R}_4\text{Sn}]} \right) + k_t \left(\frac{k[\text{I}_2]}{k[\text{R}_4\text{Sn}]} \right)^2 \right] \right]^{1/2} [\text{I}_2] \quad (16)$$

as detailed in the Appendix. Equation 16 can be reduced to either of two simple limiting formulations, depending upon which propagation step, eq 3 or 12, is rate-limiting.

(18) (a) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147. (b) Ayscough, R. B.; Thomson, C. *Trans. Faraday Soc.* **1962**, *58*, 1477.

(19) For example, the ESR spectrum of iodine atom is not observed, probably owing to the strong interaction of the matrix field and the orbital angular momentum which leads to shortening of the spin-spin relaxation time and broadening of the ESR signal below the level of detection. Indeed, there are no definitive reports of the ESR spectrum of iodine atom in the condensed phase, even in polycrystalline material.²⁰ The report of the ESR spectrum of iodine atom by Bailey (*J. Chem. Phys.* **1973**, *59*, 1599) was later disputed.

(20) (a) Atkins, P. W.; Symons, M. C. R. "The Structure of Inorganic Radicals"; Elsevier: Amsterdam, 1967. (b) Jen, C. K. "Formation and Trapping of Free Radicals"; Academic Press: New York, 1960.

Case i. If eq 3 is rate-limiting, then $k' \gg k$, and the self-combination of iodine atom is likely to be the termination step, since all termination rate constants are about the same, i.e., diffusion controlled. Thus, $k_t(k[I_2])/k[R_4Sn]^2 \gg k_t'$ or $k_t'k[I_2]/k[R_4Sn]$ and eq 16 reduces to eq 17.

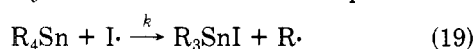
$$-d[I_2]/dt = k[R_4Sn](R_i/k_t)^{1/2} \quad (17)$$

Case ii. If eq 12 is rate-limiting, then $k \gg k'$, and the bimolecular interaction of alkyl radicals is important in termination. If so, $k_t' \gg k_t'k[I_2]/k[R_4Sn]$ or $k_t(k[I_2])/k[R_4Sn]^2$ and eq 16 reduces to eq 18.

$$-d[I_2]/dt = k[I_2](R_i/k_t)^{1/2} \quad (18)$$

The experimental rate expression in eq 7 is consistent with case i, since R_i is proportional to the light intensity and independent of the iodine concentration when all the light is absorbed.²¹ Under these circumstances, the relative reactivities of the various tetraalkyltin compounds in Table II should relate directly to the relative rate constants for the S_H2 reaction with an iodine atom in eq 3. Before discussing these relative rates in terms of the intrinsic rate constants, we must be assured that k is not affected by diffusional processes, since there are numerous examples in which fast radical reactions are so limited. The rate of recombination of iodine atoms is reported to be $7.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in carbon tetrachloride solution.²² With this value for the termination rate constant, k_t , the absolute rate constant, $k = 5.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, can be calculated from eq 17 and the data in Table I.²³ The rate of this S_H2 reaction is thus far from diffusion controlled, and it is confirmed that $k \ll k'$ (independently measured as $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at 23 °C in cyclohexane²⁴).

Stemming thus from the kinetics of the photochemical iodolysis in eq 17, the relative rates in Table II directly reflect the ratios of second-order rate constants k/k_0 for the pair of homolytic substitution reactions eq 19 and 20.



By comparison of the rate constant, k , for homolytic substitution relative to that, k_0 , of the reference Me_4Sn , it is possible to evaluate the structural and steric effects of various tetraalkyltin compounds, as described in the following section.

Structural and Steric Effects of Tetraalkyltin Compounds on the Rates of Homolytic Substitution.

The activation free energy, ΔG^\ddagger , for homolytic substitution in eq 19 may be evaluated for various tetraalkyltin compounds by a comparative procedure, i.e., eq 21, where ΔG_0^\ddagger

$$\Delta G^\ddagger - \Delta G_0^\ddagger = -2.3RT \log k/k_0 = \Delta G_r^\ddagger \quad (21)$$

is the activation free energy for the reference Me_4Sn and the subscript r refers to the relative change.

In order to probe the nature of the activated complex for this S_H2 process, we now construct various linear free-energy relationships. Consider the ease of oxidation of the tetraalkyltin as a factor in the driving force for homolytic substitution, i.e., the standard free energy

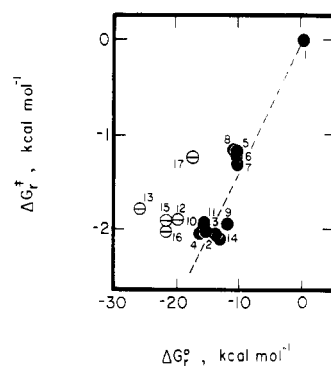


Figure 6. Linear free-energy relationship between the activation free energy, ΔG_r^\ddagger , for photochemical iodolysis and the driving force ΔG_r° for oxidation of tetraalkyltin compounds containing the following: ●, methyl and *n*-alkyl ligands; ⊖, branched alkyl ligands, as identified by the numbers in Table I. The dashed line is drawn only through the methyl and *n*-alkyltin derivatives (●) as described in the text.

change ΔG_r° as referred to in solution relative to Me_4Sn .⁶ In order to evaluate this term, we utilize the direct relationship previously established, between the gas-phase ionization potential, I_D , of tetraalkyltin compounds and ΔG_r° , i.e., eq 22, where the constant α is a property of the

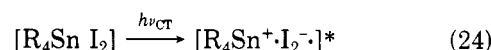
$$\Delta G_r^\circ = \alpha \Delta I_D \quad (22)$$

solvent ($\alpha_{CCl_4} = 0.77$).¹⁰ Indeed, a reasonable linear correlation is described as in eq 23 for the dashed line in

$$\Delta G_r^\ddagger \approx 0.15 \Delta G_r^\circ + \text{constant} \quad (23)$$

Figure 6, which includes only those tetraalkyltin compounds (1, 2–7, 9–11, 14) containing methyl and *n*-alkyl ligands. Other derivatives with branched alkyl ligands (compounds 12, 13, 15–17) react substantially slower than their less sterically hindered counterparts, the deviation from the line being the greatest with the highly branched *i*-Bu₄Sn (17), *t*-Bu₂SnMe₂ (13), and *i*-Pr₄Sn (15). The latter suggests that steric factors must also be included in the driving force for homolytic substitution.

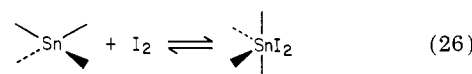
Steric factors were previously evaluated for the interaction of iodine and tetraalkyltin compounds from their charge-transfer transitions representing the process shown in eq 24.¹⁵ The asterisk identifies an excited ion pair with



the same mean separation, r , as that in the charge-transfer complex; i.e., eq 24 represents a vertical (Franck–Condon) transition, the energy of which is given by the Mulliken equation²⁵ (eq 25). I_D is the vertical ionization potential

$$h\nu_{CT} = I_D - E_A + \omega \quad (25)$$

of R_4Sn , E_A is the vertical electron affinity of I_2 , and ω is the interaction energy and mainly consists of the coulombic attraction, e^2/r , within $[R_4Sn^+ \cdot I_2^-]^*$. In a recent study, we showed that the magnitudes of r (and thus, of ω) can vary in a series of $[R_4Sn I_2]$ complexes as a result of changes in the steric properties of the alkyl ligands.¹⁵ For example, the latter could arise from the distortion of the normally tetrahedral tetraalkyltin to a trigonal-bipyramidal configuration in the complex, i.e., eq 26. In order to



(21) For the reaction conditions in Table I, $\exp(-2.3 \epsilon[I_2]d) \ll 1$, where d , the mean path length, is 0.5 cm.

(22) Marshall, R.; Davidson, N. *J. Chem. Phys.* 1953, 21, 2086.

(23) From the quantum yield for iodine dissociation in carbon tetrachloride ($\Phi = 0.14$), the rate of initiation is $R_i = \Phi I_n$. Then, $-d[I_2]/dt = (8.7 \times 10^{-5})/60 = k_1(7.28 \times 10^{-2})[(4.28 \times 10^{-7} \times 0.14)/(0.72 \times 10^{10} \times 60)]^{1/2}$, or $k_1 = 5.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for Me_4Sn .

(24) Foldiak, G.; Schuler, R. H. *J. Phys. Chem.* 1978, 82, 2756. In this paper, they concluded that the rate constant ($R \cdot + I_2$) is controlled by diffusion.

(25) (a) Mulliken, R. S. *J. Am. Chem. Soc.* 1952, 74, 811. (b) Mulliken, R. S. *J. Phys. Chem.* 1952, 56, 801. (c) Mulliken, R. S.; Person, W. B. "Molecular Complexes"; Wiley-Interscience: New York, 1969.

Table VI. Driving Force and Steric Effects in Tetraalkyltin Compounds with Iodine

tetraalkyltin	ΔG_r° , kcal mol ⁻¹	ΔE , kcal mol ⁻¹	tetraalkyltin	ΔG_r° , kcal mol ⁻¹	ΔE , kcal mol ⁻¹
Me ₄ Sn	0	0	<i>n</i> -Pr ₂ SnMe ₂	-15.8	15.0
Et ₄ Sn	-14.0	10.8	<i>n</i> -Bu ₂ SnMe ₂	-15.8	15.0
<i>n</i> -Pr ₄ Sn	-15.4	12.7	<i>i</i> -Pr ₂ SnMe ₂	-20.1	18.7
<i>n</i> -Bu ₄ Sn	-16.5	14.8	<i>t</i> -Bu ₂ SnMe ₂	-26.1	22.6
EtSnMe ₃	-10.5	11.3	Et ₃ SnMe	-13.1	9.7
<i>n</i> -PrSnMe ₃	-10.5	11.5	<i>i</i> -Pr ₃ Sn	-21.8	19.4
<i>n</i> -BuSnMe ₃	-10.5	11.5	<i>s</i> -Bu ₄ Sn	-22.0	18.2
Et ₂ SnMe ₂	-12.1	12.2	<i>i</i> -Bu ₄ Sn	-17.9	14.8

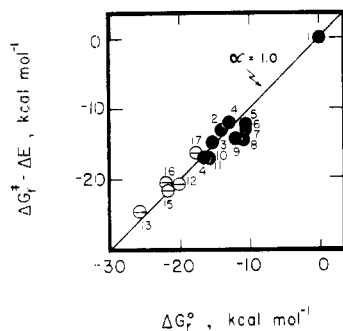


Figure 7. Inclusion of steric effects, ΔE , in the linear free-energy correlation of the activation free energy and the driving force for oxidation of tetraalkyltin compounds containing (●) methyl and *n*-alkyl ligands and (⊖) branched alkyl ligands, as identified by the numbers in Table I. Note the fit to the line drawn arbitrarily with a Brønsted slope of unity.

evaluate this and other steric effects quantitatively, we related ω for various tetraalkyltin compounds to ω_0 of the least hindered Me₄Sn, chosen as a reference. It follows from eq 25 that the energy change, $\Delta E = \omega - \omega_0$, is given by eq 27, where ΔI_D is the difference in the ionization

$$\Delta E = -\Delta I_D + \Delta h\nu_{CT} \quad (27)$$

potentials between a particular tetraalkyltin and Me₄Sn and $\Delta h\nu_{CT}$ is the difference in their CT energies in the iodine complexes. Thus by choosing a reference alkylmetal, one can compositely express all changes in the interaction energies of these charge-transfer complexes, including steric, distortional, and other effects, in a single energy term, ΔE .²⁶ The values of ΔE from eq 27 are tabulated in Table VI for various tetraalkyltin compounds by using the data listed in Table I. The correction of the driving force ΔG_r° for homolytic substitution by an amount ΔE (corresponding to the steric effect) is illustrated in Figure 7.²⁷ The striking linear correlation of all the rate data can be expressed as eq 28. The correlation in eq 28

$$\Delta G_r^{\circ*} = \Delta G_r^\circ + \Delta E \quad (28)$$

represents a linear free-energy relationship with a slope of unity. It is important to point out that eq 28 obtains directly from three independent sets of experiments by a purely operational methodology.

(26) Since the comparative definition of ΔE minimizes solvation terms by cancellation, it can also be applied directly to estimate changes in the interaction energies of thermal ion pairs.

(27) In this treatment, the use of ΔE as a steric correction is based on the reasonable formulation that changes in the mean separation between R₄Sn and I· in the activated complex for homolytic substitution are reflected by a corresponding change in the charge-transfer complex of R₄Sn and I₂. See footnote 26 and ref 10 for further elaborations of this point.

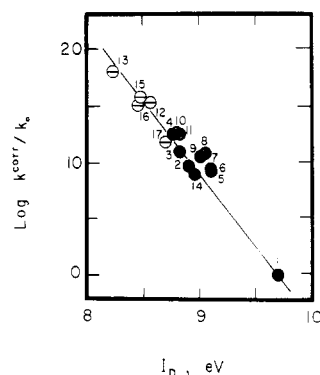


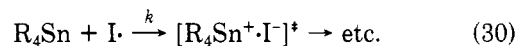
Figure 8. Correlation of the sterically corrected rate constants for S_H2 reactions between an iodine atom and tetraalkyltin compounds [containing (●) methyl and *n*-alkyl ligands and (⊖) branched alkyl ligands] with the ionization potentials. The line is not a correlation of the points but is merely drawn with a Brønsted slope of unity to emphasize the fit to eq 28.²⁹

Since the Brønsted slope in eq 28 is unity,²⁸ the steric term can also be considered as a correction factor on the rate of homolytic substitution, i.e., eq 29, where k is the

$$\log k^{\text{cor}} = \log k + \Delta E/2.3RT \quad (29)$$

experimental rate constant. Viewed in this way, $\log k^{\text{cor}}$ represents the rate constant under hypothetical conditions of constant steric effect, i.e., relative to that of the chosen reference Me₄Sn. Stated alternatively, $\log k^{\text{cor}}$, or its equivalent $\Delta G_r^{\circ*} - \Delta E$, is the form to be related to the driving force, ΔG_r° , for homolytic substitution in the absence of steric effects. Figure 8 shows the correlation of all the rate data with the ionization potentials of the tetraalkyltin compounds.

Activation Process for Homolytic Substitution. The linear free-energy relationship described in eq 28, or its kinetic equivalent in eq 29, indicates that the activated complex for homolytic substitution is accurately represented by the driving force for ion-pair formation, i.e., eq 30. In other words, the Brønsted slope of unity relates



the activated complex directly to the ion pair. The driving force for ion-pair formation is ascribed to (1) the free energy change, ΔG_r° , for electron transfer, which is derived from the ionization potentials of the tetraalkyltin compounds, and (2) the interaction energies of the ion pair, which are equated to ΔE determined from the charge-transfer transition energies in eq 27. The latter implies that the thermally formed ion pair [R₄Sn⁺·I⁻] in eq 30 is akin to the photochemically excited ion pair [R₄Sn⁺·I₂⁻]^{*} in eq 8.³⁰ Indeed, there is a strong implication that the

(28) The free-energy change for ion-pair formation, ΔG_r° , should be distinguished from the standard free-energy charge, ΔG_r° , for electron transfer, $\Delta G_r^\circ = \Delta G_r^\circ + \Delta E$. See: Marcus, R. A. *J. Phys. Chem.* 1968, 72, 891.

(29) Equation 28 is equivalent to $\log k^{\text{cor}}/k_0 = -\alpha \Delta I_D/2.3RT$, which is obtained by combining eq 29 with eq 21 and 22.

(30) (a) We have taken the charge-transfer interaction in [R₄Sn I₂]^{*} which is experimentally measurable to be a reasonable model for steric effects in [R₄Sn I·], which is too transient to study. The similarity between I₂ and I· in charge-transfer interactions has been examined with alkyl iodides as donors [Strong, R. L. et al. *J. Am. Chem. Soc.* 1976, 98, 5460; *Chem. Phys. Lett.* 1977, 46, 546]. The detailed comparison of the charge-transfer transition energies between [RI I₂] and [RI I·] support this assumption.¹⁵ (b) Furthermore, the comparative definition of ΔE in eq 27 minimizes solvation terms by cancellation. This is an important point since the absolute values of the interaction energies for the photoexcited charge-transfer state (vertical process) and the thermally excited ion pair (adiabatic process) differ (see: Fukuzumi, S.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* 1979, 101, 5961).

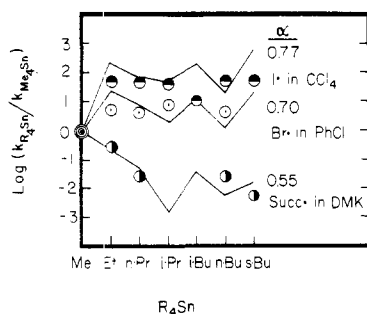
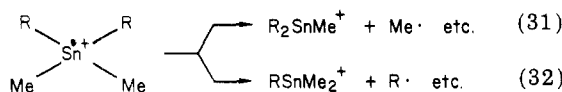


Figure 9. Solvent effect on the reactivities of tetraalkyltin compounds relative to Me_4Sn in $\text{S}_{\text{H}2}$ iodinolysis. The lines are calculated for various α in eq 36. The experimental points are for the following: \bullet , iodine atom in CCl_4 ; \circ , bromine atom in chlorobenzene from ref 8; \ominus , succinimidyl radical in acetone from ref 7. Note the predicted inversion in the relative reactivities with decreasing values of α .

ion pair in eq 30 is a reactive intermediate.

If such an ion pair were an actual intermediate, the selectivity, $S(\text{R}/\text{Me})$, would be deduced from the unimolecular fragmentation pattern of the tetraalkyltin cation moiety, i.e., eq 31 and 32. As such, the selectivity is



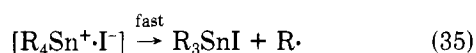
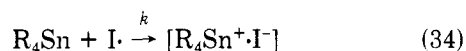
expected to be (1) largely independent of the mode of formation of the cation radical and (2) highly dependent on the relative strengths of the R-Sn and Me-Sn bonds.³¹ Indeed, the selectivities for photochemical iodinolysis in column two of Table III are strikingly similar to those listed in column four for the hexachloroiridate(IV) cleavage which has previously been shown to proceed via a rate-limiting electron transfer, i.e., eq 33.¹⁶ Moreover, the



photochemical iodinolysis always favors the cleavage of the weaker alkyl-tin bond, irrespective of the steric limitations of the ligand. The results in Figure 4, which clearly show the ESR spectra of only *tert*-butyl and ethyl radicals from *t*- Bu_2SnMe_2 and Et_2SnMe_2 , respectively, and the absence of methyl radicals, support the conclusion based on selectivity that the ion pair is an intermediate.³²

According to this formulation, homolytic substitution is a two-step process in which the activation process is represented by an electron transfer from the tetraalkyltin to iodine atom (Scheme II).

Scheme II



The rate-limiting formation of the ion pair for the $\text{S}_{\text{H}2}$ process in Scheme II is supported by solvent effects on the rate. Indeed, the solvent effect on the rates can provide an important test of the linear free energy relationship in eq 28, especially in dealing with the rather unusual inversions in the reactivities described in eq 1 and 2. Thus

(31) For a further discussion of these points, see: Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593.

(32) The alternative possibility that alkyl radicals are formed from the charge-transfer excited state of $[\text{R}_4\text{SnI}_2]^*$ is unlikely since such a process should lead to methyl not *tert*-butyl radicals from *t*- Bu_2SnMe_2 , i.e.,¹⁰ $[t\text{-Bu}_2\text{SnMe}_2\text{I}_2]^* \xrightarrow{\text{fast}} [t\text{-Bu}_2\text{SnMe}_2^+\text{I}_2^-] \xrightarrow{\text{fast}} [t\text{-Bu}_2\text{SnMe}^+\text{MeI}_2^-]$.

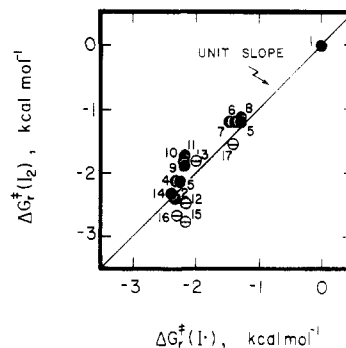


Figure 10. Comparison of the change in the activation free energy, $\Delta G_{\text{T}}^{\ddagger}$, for the $\text{S}_{\text{H}2}$ and $\text{S}_{\text{E}2}$ iodinolysis of tetraalkyltin compounds with an iodine atom and molecular iodine, respectively. Note the fit to the line representing an equal sensitivity to structural changes in the alkyl ligands.

the relative reactivities of various R_4Sn are obtained directly from eq 22 and 28 as eq 36. Since the variations

$$-\log k/k_0 = \frac{1}{2.3RT}(\alpha\Delta I_{\text{D}} + \Delta E) \quad (36)$$

in the relative reactivities with solvent are represented by changes in α , these are drawn in Figure 9 as a family of solid lines calculated from eq 21. (The values of I_{D} and ΔE for I_2 and various R_4Sn are listed in Tables II and VI, respectively.) With the value $\alpha = 0.77$ for carbon tetrachloride from eq 22, the fit of the $\text{S}_{\text{H}2}$ rate data from Table I is reasonable. Furthermore, the fit of the brominolysis data in chlorobenzene from the extant literature⁸ is also included, showing a good agreement with $\alpha = 0.70$. The rate data for the $\text{S}_{\text{H}2}$ reaction by succinimidyl radical was obtained in acetone solution,⁷ for which $\alpha = 0.55$ was employed. Despite the rather crude assumptions made,³³ Figure 9 clearly shows that solvent-induced changes of reactivity in $\text{S}_{\text{H}2}$ processes, even inversions in rates, can be readily accommodated by a single mechanism. In this formulation, $\alpha\Delta I_{\text{D}}$ and ΔE correspond to the electronic and steric contributions, respectively, to the activation process.³⁴ The solvent effect is primarily associated with changes in the electronic effect, owing to variations in α .³⁵ As the solvent increases in polarity, α decreases, and steric effects become dominant, leading to $k_{\text{Me}_4\text{Sn}} > k_{\text{R}_4\text{Sn}}$. The reverse reactivity, $k_{\text{Me}_4\text{Sn}} < k_{\text{R}_4\text{Sn}}$, obtains in nonpolar solvents in which the electronic demand is optimized as a result of increased values of α .

Comparison of Electrophilic and Homolytic Iodination of Alkylmetals. The cleavage of tetraalkyltin compounds by both molecular iodine and iodine atoms offers a unique opportunity to compare the electrophilic substitution ($\text{S}_{\text{E}2}$) examined earlier¹⁰ with a homolytic substitution ($\text{S}_{\text{H}2}$) on a common substrate and in a common solvent. The comparison of the activation processes for the $\text{S}_{\text{H}2}$ and $\text{S}_{\text{E}2}$ reactions of $\text{I}\cdot$ and I_2 , respectively, with the structural effects of the tetraalkyltin is particularly

(33) (a) Since the charge-transfer data for the bromine atom and succinimidyl radical are unknown, the values of ΔE for these systems were simply equated to that of iodine, without any attempt for justification. (b) For chlorobenzene, $\alpha = 0.66$ – 0.68 from ref 10 is in reasonable agreement with $\alpha = 0.70$ in Figure 9. (c) For acetonitrile $\alpha = 0.55$ and for acetic acid $\alpha = 0.59$. Judging solely from the values of the dielectric constants, MeCN (37.5), HOAc (6.2), and acetone (20.7), a value of $\alpha \approx 0.55$ may not be a bad guess for acetone.

(34) The change ΔE is considered to be largely a steric effect since it consists mainly of coulombic terms,¹⁵ inversely proportional to the mean separation. The other terms in the interaction energy also probably depend on the mean separation, either directly or indirectly.

(35) Solvents have relative minor effects on ΔE (additional studies in progress).

noteworthy. The relationship is illustrated in Figure 10, in which the same response of the activation free energy change, ΔG_r^\ddagger , for the S_{H2} and S_{E2} processes is shown by the fit to the line drawn with a slope of unity. This correlation is even more remarkable if cognizance is taken of the large difference in the absolute rates of the reactions. For example, with Me_4Sn the rate constants are $k(I\cdot) = 5.3 \times 10^4 M^{-1} s^{-1}$ at 25 °C and $k(I_2) = 2.3 \times 10^{-5} M^{-1} s^{-1}$ at 50 °C,³⁶ which correspond to a difference of activation free energy, $\Delta G^\ddagger(I_2) - \Delta G^\ddagger(I\cdot) = 14.6 \text{ kcal mol}^{-1}$. Indeed the common response of the S_{H2} and S_{E2} processes to tetraalkyltin structure is consistent with the charge transfer mechanism in Scheme II, since the same basic formulation was deduced in the earlier study for electrophilic iodinolysis.^{10,37}

Summary and Conclusions

Kinetic analysis of the photochemically induced iodinolysis of a series of symmetrical and unsymmetrical tetraalkyltin compounds with iodine in CCl_4 solutions shows it to be a radical chain process with a long kinetic chain length. The photochemical iodinolysis is strongly inhibited by galvinoxyl and isoamyl nitrite. The kinetics are consistent with homolytic substitution (S_{H2}) of a tetraalkyltin by an iodine atom as the rate-limiting step. It is supported by the direct observation of alkyl radicals by ESR spectroscopy carried out by photolysis of a frozen solution.

The reactivities of various tetraalkyltin compounds toward an iodine atom can be measured from the kinetics of the iodinolysis process. A linear free-energy relationship (eq 28) is derived in which the change in activation free energy, ΔG_r^\ddagger , is equal to the sum of the driving force, ΔG_r° , for the oxidation of the tetraalkyltin compound and the interaction energy, ΔE , of the ion pair, when all are evaluated relative to a Me_4Sn reference. Values of ΔE are obtained independently from the charge-transfer interaction of alkylmetals with iodine. The S_{H2} process is described as a two-step mechanism in Scheme II, in which the ion pair $[R_4Sn^+ \cdot I^-]$ is an intermediate.

Selectivities in the S_{H2} iodinolysis of tetraalkyltin according to Scheme II derive from the unimolecular fragmentation of the tetraalkyltin cation-radical moiety and occur subsequent to the rate-limiting step. This mechanism is supported by the absence of a direct relationship between the activation process and the selectivity in S_{H2} processes. Indeed, the preferential displacement of branched alkyl ligands in the order $t\text{-Bu} > i\text{-Pr} > Et > Me$ follows the trend in bond strengths, consistent with a fragmentation process. The latter is supported by ESR studies of the displaced alkyl radicals, showing a preferential loss of *tert*-butyl radical from $t\text{-Bu}_2SnMe_2$, despite steric factors which should favor direct attack on the methyl-tin bond. Finally, the selectivity in the S_{H2} reaction is the same as that observed with hexachloroiridate(IV), shown in previous studies to involve prior electron transfer. The solvent studies, though as yet restricted in number, support a polar transition state for the S_{H2} reaction in accord with the charge-transfer mechanism.

(36) Taken from Table VII. Temperature dependences are not available.

(37) (a) It is interesting to note that the difference in rates of alkylmetal cleavage with $I\cdot$ and I_2 can be accounted for by their relative electron affinities [$E_A(I\cdot) - E_A(I_2) \approx 33 \text{ kcal mol}^{-1}$].¹⁵ (b) Since the selectivity is determined subsequent to this rate-limiting step, there is no direct relationship between the rate and the selectivity. This situation in the homolytic iodinolysis of tetraalkyltin compounds represents an interesting contrast to the electrophilic cleavage of the same tetraalkyltin compounds with molecular iodine.¹⁰ We will elaborate on this difference in selectivity at a later time.

Table VII. Kinetics of Thermal Iodinolysis of Tetraalkyltin Compounds^a

tetraalkyltin	$k_{th}, M^{-1} s^{-1}$	tetraalkyltin	$k_{th}, M^{-1} s^{-1}$
Me_4Sn	2.3×10^{-5}	$n\text{-Pr}_2SnMe_2$	3.8×10^{-4}
Et_4Sn	9.6×10^{-4}	$n\text{-Bu}_2SnMe_2$	3.2×10^{-4}
$n\text{-Pr}_4Sn$	6.1×10^{-4}	$i\text{-Pr}_2SnMe_2$	1.1×10^{-3}
$n\text{-Bu}_4Sn$	6.1×10^{-4}	$t\text{-Bu}_2SnMe_2$	4.0×10^{-4}
Et_2SnMe_3	1.5×10^{-4}	Et_3SnMe	8.0×10^{-4}
$n\text{-PrSnMe}_3$	1.4×10^{-4}	$i\text{-Pr}_4Sn$	1.9×10^{-3}
$n\text{-BuSnMe}_3$	1.4×10^{-4}	$s\text{-Bu}_4Sn$	1.5×10^{-3}
$i\text{-BuSnMe}_3$	1.3×10^{-4}	$i\text{-Bu}_4Sn$	2.6×10^{-4}
Et_2SnMe_2	4.2×10^{-4}		

^a In carbon tetrachloride solutions with 0.10 M iodine and 0.12 M tetraalkyltin compound at 50 °C. k_{th} is the second-order rate constant.

The mechanistic formulation in Scheme II provides a quantitative basis for describing the activation process in homolytic substitution. Thus other S_{H2} reactions should be considered in a similar framework, which will provide tests for the generality of the charge-transfer concept.³⁸⁻⁴⁰

Experimental Section

Materials. The series of symmetrical and unsymmetrical tetraalkyltin compounds used in this study were prepared by standard procedures and analyzed as described previously.^{15,41} Iodine (Mallinckrodt reagent grade) was repurified by sublimation. Carbon tetrachloride (Fisher purified grade) was repurified by successive washing with concentrated sulfuric acid, 5% aqueous sodium bicarbonate, and distilled water, followed by drying over calcium sulfate and distillation from calcium hydride. Potassium ferrioxalate was synthesized according to the procedure of Hatchard and Parker¹² and recrystallized three times from hot water. The other materials used are described in ref 10 and 15.

Kinetics of the Photochemical Iodinolysis of Tetraalkyltin Compounds. Aliquots (2.0 mL) of a standard $2.57 \times 10^{-2} M$ iodine solution in CCl_4 were transferred into Pyrex tubes (10 mm i.d.), and the same amounts of tetraalkyltin ($3 \times 10^{-2} M$) were added to each sample. The tubes were placed in a precision merry-go-round apparatus and irradiated with a 100-W incandescent light bulb. Samples (50 μL) were removed periodically, diluted to 3.0 mL with CCl_4 , and analyzed spectrophotometrically at 520 nm ($\epsilon 900 M^{-1} cm^{-1}$). All transfers were effected in the dark. Control experiments showed that the thermal reactions were negligible under these conditions. The light intensity was measured under the same conditions with 0.142 M potassium ferrioxalate in water as the actinometer.¹² When the iodine concentration was greater than $10^{-2} M$, all the incident light was absorbed, i.e., the absorbance, $\exp(-2.3\epsilon[I_2]d) = 0.1$, is much less than unity.

Inhibition Experiments. To a 2.0-mL aliquot of a standard $2.8 \times 10^{-2} M$ iodine solution was added either $2.22 \times 10^{-2} M$ isoamyl nitrite or $1.17 \times 10^{-3} M$ galvinoxyl. The same amount of either $8.0 \times 10^{-2} M Me_4Sn$ or $2.53 \times 10^{-2} M n\text{-BuSnMe}_3$ was added to each tube. A reference was made up in the same way without inhibitor. Both solutions were irradiated under the same conditions. Only after 250 min did the iodine concentration in

(38) Judging by the values of their ionization potentials, alkyl radicals range from being good (Me , 9.85 eV) to excellent ($t\text{-Bu}$, 6.90 eV) electron donors.³⁹ The S_{H2} reaction of alkyl radicals on peroxides could similarly involve strong charge-transfer interactions.⁴⁰ Other examples¹ may be considered in a similar manner.

(39) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

(40) (a) Tokumaru, K.; Simamura, O. *Bull. Chem. Soc. Jpn.* 1963, 36, 333. Tokumaru, K. *Nippon Kagaku Zasshi* 1971, 92, 1. (b) For peroxides as acceptors see ref 39 (pp 517-22) and: Silbert, L. S. "Organic Peroxide"; Swern, D., Ed.; Wiley-Interscience: New York, 1971; Vol. 2, p 637; Yonezawa, T.; Kato, H.; Yamamoto, O. *Bull. Chem. Soc. Jpn.* 1967, 40, 307. (c) Kikuchi, O.; Suzuki, K.; Tokumaru, K. *Ibid.* 1979, 52, 1086. (d) Charge-transfer complexes of alkylperoxy radicals have been suggested. See: Fukuzumi, S.; Ono, Y. *Ibid.* 1977, 50, 2063; *J. Chem. Soc., Perkin Trans. 2* 1977, 625.

(41) Ingham, R. K.; Rosenberg, S. D.; Gilman, H. *Chem. Rev.* 1960, 60, 459 and references cited therein.

Figure 3 change in the presence of galvinoxyl. The lower limit of the kinetic chain length was calculated from the ratio of the reaction rate (1.03×10^{-3}) and the initiation rate (4.7×10^{-6}) to be 220. The upper limit of the kinetic chain length, based on the light intensity (4.28×10^{-7} einstein $L^{-1} \text{ min}^{-1}$) and the quantum yield (0.14) for photodissociation of iodine, is 2×10^4 .

Kinetics of the Thermal Iodinolysis of Tetraalkyltin Compounds. Aliquots (1.0 mL) of a standard 0.10 M iodine solution in carbon tetrachloride were placed in 3-mm Pyrex cuvettes wrapped with aluminum foil. A known amount of the tetraalkyltin was added to the cell, and the mixture was vigorously shaken and placed in a thermostated oil bath at 50 °C. The course of iodinolysis was followed by the decrease in the iodine absorbance at 625 nm (ϵ 64). Alternatively, the formation of alkyl iodide was followed by changes in the ^1H NMR spectra. The rates of iodinolysis followed by both methods yielded the same rate constants as listed in Table VII. Inhibitors, either 1.17×10^{-3} M isoamyl nitrite or 2.22×10^{-2} M galvinoxyl, had no effect on the thermal iodinolysis of either *n*-Bu₄Sn or EtSnMe₃.

Selectivity in the Cleavage of Tetraalkyltin Compounds. Photochemical Iodinolysis. Selectivities in the photochemical iodinolysis of unsymmetrical tetraalkyltin compounds were obtained from the analysis of the alkyl iodides by gas chromatography or from their ^1H NMR spectra. In a typical example, a CCl₄ solution of iodine (0.10 M) was placed in an NMR tube, and 0.12 M tetraalkyltin compound was added after the tube was flushed with a stream of nitrogen. The sample was immediately photolyzed with the aid of a 100-W medium-pressure Hg lamp. (The light flux from this lamp was greater than that used for the kinetic studies.) In most cases, the reaction was complete within 60 s, judging by the decoloration of iodine. NMR analyses of the alkyl iodide were carried out either at 60 MHz or 220 MHz. The relevant proton resonances used in the analyses are as follows: MeI, δ 2.2 (s); EtI, δ 3.2 (q, $J = 7$ Hz), δ 1.9 (t, $J = 7$ Hz); *n*-PrI, δ 3.2 (t, $J = 7$ Hz); *n*-BuI, δ 3.2 (t, $J = 7$ Hz); *i*-PrI, δ 4.3 (septet, $J = 7$ Hz); *i*-BuI, δ 3.1 (d, $J = 7$ Hz); *t*-BuI, δ 1.9 (s). For the tin products, Me₃SnR_{3-n}I, the resonances were as follows: R = Me, δ 0.8 (s); Et, δ 1.3 (s); *t*-Bu, δ 1.3 (s).

The gas chromatographic analyses of alkyl iodides were carried out with a tandem column consisting of a 15-ft column of 20% Apiezon L and 20% Carbowax 5000 M on 60/80 Chromosorb P. For Et₃SnMe, the selectivity of 11.1 was in good agreement with the value of 10.5 determined from the NMR spectra.

The selectivities in carbon tetrachloride were independent of the light intensity which was varied by moving the light source from the sample tube. In chloroform solution, the selectivities were determined at -10 °C by using a 1-kW mercury-xenon lamp (Hanovia 977B-1) to minimize competition from the thermal iodinolysis. The presence of an interference filter (546 ± 10 nm) had no effect on the selectivity of *n*-BuSnMe₃.

Thermal Iodinolysis. Typically, a CCl₄ solution of 0.1 M iodine was added to an NMR tube protected from light. After the tube was flushed with a stream of argon, sufficient tetraalkyltin compound was added to make a 0.12 M solution. The thermal iodinolysis required approximately 2–3 days for completion. The effect of inhibitors was also examined to ensure the absence of adventitious homolytic reactions (see Table V) in this slow process.

Hexachloroiridate(IV). A solution of 0.20 M Na₂IrCl₆ in CD₃CN (400 μL) was treated with tetraalkyltin compound as previously described.⁶

Electron-Spin Resonance Measurements. The appropriate tetraalkyltin was added to an ESR sample tube containing an iodine solution in carbon tetrachloride and the mixture quickly degassed by successive freeze-pump-thaw cycles before sealing. The tube was placed in a Dewar flask, cooled to -180 °C, and irradiated with a 1-kW high-pressure mercury lamp with a Pyrex filter. The ESR spectrum was recorded on a Varian E112 X-band spectrometer and calibrated with an NMR field marker. The radical concentration was determined by double integration of the derivative spectrum using DPPH as a standard. After the signal intensity attained a maximum, the light was turned off, and the signal stability examined for 1 h at this temperature. The sample was then annealed at -163 °C and the decay of the signal monitored periodically.

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Appendix. Kinetics of Photochemical Iodinolysis of Tetraalkyltin

According to Scheme I and the steady-state approximation

$$d[\text{I}_2]/dt = -R_i - k[\text{R}\cdot][\text{I}_2] + k_t[\text{I}\cdot]^2 \quad (37)$$

$$d[\text{I}\cdot]/dt = 2R_i - k[\text{I}\cdot][\text{R}_4\text{Sn}] + k[\text{R}\cdot][\text{I}_2] - 2k_t[\text{I}\cdot]^2 - k_t'[\text{R}\cdot][\text{I}\cdot] \quad (38)$$

$$d[\text{R}\cdot]/dt = k[\text{I}\cdot][\text{R}_4\text{Sn}] - k[\text{R}\cdot][\text{I}_2] - 2k_t'[\text{R}\cdot]^2 - k_t''[\text{R}\cdot][\text{I}\cdot] \quad (39)$$

For a long kinetic chain length, i.e., the propagation rates being much greater than the termination rates, the relationships of eq 40 and 41 hold.

$$[\text{I}\cdot] \approx k[\text{I}_2][\text{R}\cdot]/k[\text{R}_4\text{Sn}] \quad (40)$$

$$d[\text{I}_2]/dt \approx -k[\text{R}\cdot][\text{I}_2] \quad (41)$$

The addition of eq 38 and 39 yields eq 42.

$$d([\text{I}\cdot] + [\text{R}\cdot])/dt = 2(R_i - k_t'[\text{R}\cdot]^2 - k_t[\text{I}\cdot]^2 - k_t''[\text{R}\cdot][\text{I}\cdot]) \quad (42)$$

Since $d([\text{I}\cdot] + [\text{R}\cdot])/dt = 0$ from the steady-state approximation, the combination of eq 40 and 42 affords eq 43.

$$[\text{R}\cdot] \approx \left[\frac{R_i}{k_t' + k_t'' \left(\frac{k[\text{I}_2]}{k[\text{R}_4\text{Sn}]} \right) + k_t \left(\frac{k[\text{I}_2]}{k[\text{R}_4\text{Sn}]} \right)^2} \right]^{1/2} \quad (43)$$

Substitution of eq 43 into eq 41 produces the rate of iodine disappearance as eq 16 in the text.

Registry No. 1, 594-27-4; 2, 597-64-8; 3, 2176-98-9; 4, 1461-25-2; 5, 3531-44-0; 6, 3531-45-1; 7, 1527-99-7; 8, 1118-10-1; 9, 4282-05-7; 10, 56535-52-5; 11, 1528-00-3; 12, 66363-02-8; 13, 35569-11-0; 14, 2097-60-1; 15, 2949-42-0; 16, 6031-41-0; 17, 3531-43-9; iodine, 14362-44-8.