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Charge-Transfer Mechanism for Electrophilic Reactions. S_E2 Cleavage of Alkylmetals with Iodine

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Abstract: The absorption spectra of transient charge transfer (CT) complexes are observed immediately upon mixing iodine and various organometals RM, where M = tin, lead, and mercury. The formation constants K_{CT} and the transition energies $h\nu_{CT}$ of these CT complexes vary with the ionization potentials and the steric properties of the alkylmetals. The subsequent disappearance of the CT absorption band is accompanied by the cleavage of the alkylmetal by iodine (iodinolysis). The kinetics of the iodine disappearance are consistent with a preequilibrium formation of the CT complex followed by the rate-limiting iodinolysis of the alkylmetal. The selectivity in the iodinolysis of unsymmetrical tetraalkyltin compounds is determined by product analysis and shown to be strongly dependent on the solvent polarity. The solvent effect is also shown to affect the formation constant of the CT complex and the rate constant for iodinolysis in a parallel manner. A charge-transfer mechanism is proposed for iodinolysis in which the rate-limiting step involves the unimolecular decomposition of the CT complex by electron transfer from the alkylmetal donor to the iodine moiety to form the ion pair $[RM^+ \ I_2^-]$. This activation process is akin to the charge-transfer interaction, as formulated in the Mulliken theory. Accordingly, the difference ΔE in the CT transition energy $h\nu_{CT}$ of a $[RM \ I_2]$ complex relative to that of a reference alkylmetal (either Me_4Sn or Me_2Hg) is used to evaluate the interaction energy of the ion pair. The change in the overall driving force ΔG_r for electron transfer in the CT complex is determined from ΔE and the ionization potential of the alkylmetal. The activation free energy $\Delta G_r^{\ddagger}$ for electron transfer is developed from the rate data by a similar comparative procedure, and shown to respond directly to the free-energy change, i.e., $\Delta G_r^{\ddagger} = \Delta G_r$. This linear free energy relationship, together with a pronounced macroscopic solvent effect on $\Delta G_r^{\ddagger}$ based on Kirkwood's equation, supports a highly polar transition state for iodinolysis in accord with Scheme II. The same CT formulation can be quantitatively applied to the solvent effect on the relationship between the selectivity and the rate constants for iodinolysis in Figure 8, as well as the relationship between the selectivity and the formation constant of the CT complexes in Figure 9. It correctly predicts the inverse relationship often observed between selectivity and rate. Importantly, the charge-transfer formulation provides a quantitative foundation for the description of electrophilic processes, heretofore provided only in qualitative forms.

Introduction

The cleavage of alkyl–metal bonds by halogens, or halogenolysis, is one of the most common reactions of organometals RM:

$$RM + X_2 \rightarrow RX + MX$$

where $X_2 = F_2$, Cl_2, Br_2, and I_2. Such substitution reactions effected by electrophiles are basic to our understanding of a wide variety of organic syntheses via organometallic intermediates.[1-4]

Halogenolysis of organometals may proceed by either an electrophilic or a radical-chain process. The latter, involving halogen atoms as prime intermediates, can be readily identified by its susceptibility to homolytic initiation and inhibition.[5] Despite extensive studies,[1-4] however, there is surprisingly little quantitative information known about the structural factors important in electrophilic substitution at a carbon–metal bond. The mechanism of the electrophilic pathway is still the subject of controversy, largely revolving around the depiction of the transition state—whether it is two or four centered, open, cyclic, etc. Although kinetic and stereochemical probes have been extensively employed, the mechanistic difficulties have doubtlessly been exacerbated by the implicit assumption, uniformly adopted, that electrophilic processes are concerted, involving no viable intermediates. The latter is somewhat surprising in view of earlier reports of the existence of complexes between organosilanes and halogens.[6-8]

We wish to present an alternative approach to electrophilic mechanisms based on our recent study of charge-transfer complexes between iodine and organometals, including an extensive series of dialkylmercury, tetraalkyltin, and lead compounds.[9] Importantly, the theoretical basis for charge-transfer interactions in these complexes is well provided by the Mulliken theory,[10,11] allowing us to probe the nature of the intimate interaction between alkylmetals and iodine in quantitative detail.

Results

The products and stoichiometry of the electrophilic cleavage of organometals by halogen have been well established.[12] As applied to the iodinolysis of tetraalkyltin compounds (R_4Sn) emphasized in this study, the reaction is[13]

$$R_4Sn + I_2 \rightarrow R_3SnI + RI \qquad (1)$$

When a solution of tetraethyltin in carbon tetrachloride is mixed with iodine, a transient, new absorption band with λ_{max}

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Table I. Charge-Transfer Complexes of Alkylmetals and Iodine. Relationship of the Ionization Potentials of Alkylmetals with the CT Transition Energies and the Formation Constants[a]

no.	alkylmetal	I_D,[b] eV	$h\nu_{CT}$, eV	K_{CT}, M^{-1}	no.	alkylmetal	I_D,[b] eV	$h\nu_{CT}$, eV	K_{CT}, M^{-1}
1	Me_4Sn	9.69	4.59	0.06	**16**	*sec*-Bu_4Sn	8.45	4.14	20
2	Et_4Sn	8.90	4.27	3.6	**17**	*i*-Bu_4Sn	8.68	4.22	0.57
3	*n*-Pr_4Sn	8.82	4.27	0.40	**18**	*i*-Bu_2SnEt_2		4.00	0.76
4	*n*-Bu_4Sn	8.76	4.30	0.35					
5	$EtSnMe_3$	9.10	4.49	0.12	**19**	Me_2Hg[c]	9.33	4.17	0.07
6	*n*-$PrSnMe_3$	9.10	4.50	0.16	**20**	$EtHgMe$	8.84	3.97	0.63
7	*n*-$BuSnMe_3$	9.10	4.49	0.21	**21**	*n*-Pr_2Hg	8.29	3.73	1.5
8	*i*-$BuSnMe_3$	9.05	4.54	0.092	**22**	*n*-Bu_2Hg	8.35	3.72	4.7
9	Et_2SnMe_2	9.01	4.44	0.59	**23**	*i*-Bu_2Hg	8.30	3.77	4.5
10	*n*-Pr_2SnMe_2	8.80	4.35	0.33					
11	*n*-Bu_2SnMe_2	8.80	4.35	0.76	**24**	Me_4Pb[c]	8.90		
12	*i*-Pr_2SnMe_2	8.56	4.27	1.2	**25**	$EtPbMe_3$	8.65		0.83
13	*t*-Bu_2SnMe_2	8.22	4.10	0.30	**26**	Et_2PbMe_2	8.45		1.6
14	Et_3SnMe	8.95	4.27	0.63	**27**	Et_3PbMe	8.26		2.9
15	*i*-Pr_4Sn	8.46	4.20	4.9	**28**	Et_4Pb	8.13		3.1

[a] The values of $h\nu_{CT}$ determined in carbon tetrachloride and K_{CT} in methylene chloride at 25 °C, unless stated otherwise.[9] [b] From ref 14. [c] All dialkylmercury and methylethyllead compounds in carbon tetrachloride solutions at 25 °C.

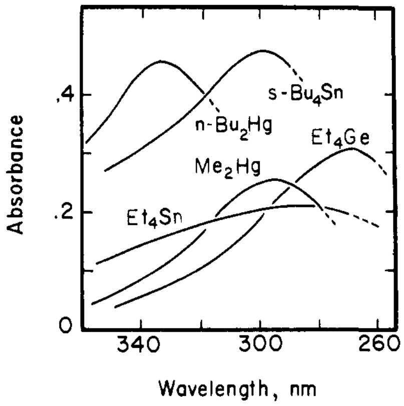


Figure 1. Charge transfer absorption bands of alkylmetal-iodine complexes in carbon tetrachloride solutions containing 1.60 × 10^{-2} M iodine and 9.40 × 10^{-3} M *n*-Bu_2Hg or 8.0 × 10^{-3} M iodine and 3.35 × 10^{-2} M Et_4Sn, 5.97 × 10^{-2} M *sec*-Bu_4Sn, 1.0 × 10^{-1} M Et_4Ge, 4.42 × 10^{-2} M Me_2Hg at 25 °C.

290 nm is immediately observed in the ultraviolet spectrum. The broad absorption band $h\nu_{CT}$ is characteristic of intermolecular charge transfer (CT) complexes, e.g.[9]

$$Et_4Sn + I_2 \overset{K_{CT}}{\rightleftharpoons} [Et_4Sn\ I_2] \qquad (2)$$

Similar spectral bands can also be observed with the other alkylmetals, as shown in Figure 1.

The formation of alkylmetal-iodine CT complexes is accompanied by a corresponding drop in the absorbance of the visible absorption band of iodine, $(A_0 - A)$, which is related to the formation constant K_{CT} according to the equation[9]

$$\frac{K_{CT}[RM]}{1 + K_{CT}[RM]} = 1 - \frac{A}{A_0} = \gamma \qquad (3)$$

The formation constants and CT energies of various alkylmetal-iodine complexes are collected in Table I, together with the ionization potentials of the alkylmetals.[9,14]

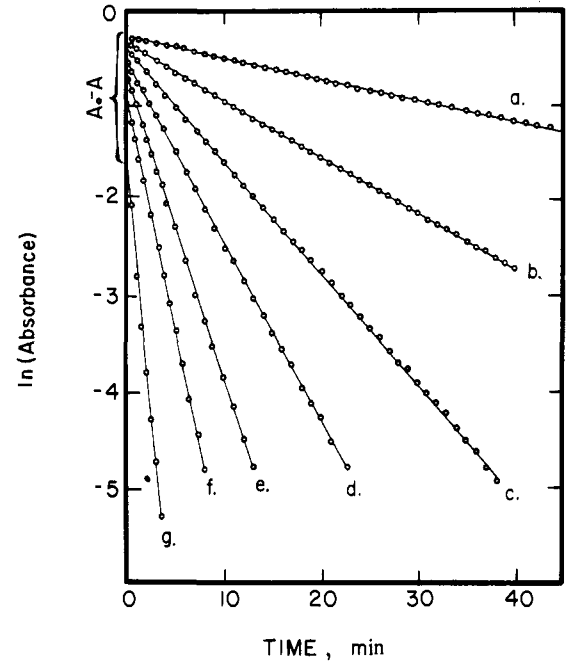


Figure 2. The initial drop in iodine absorbance $(A_0 - A)$ due to charge transfer complex formation and pseudo-first-order kinetics of iodinolysis at 25 °C in methylene chloride solutions containing 8.6 × 10^{-4} M iodine and Et_4Sn: (a) 8.4 × 10^{-3}, (b) 2.5 × 10^{-2}, (c) 5.0 × 10^{-2}, (d) 8.3 × 10^{-2}, (e) 0.13, (f) 0.20, and (g) 0.32 M.

Rates of the Iodinolysis of Alkylmetals. The kinetic studies were carried out by adding various amounts of alkylmetals in excess to serial aliquots of a standard solution of iodine in methylene chloride. The rate of reaction was followed by measuring the iodine absorption at λ_{max} 504 nm (ϵ 900 M^{-1} cm^{-1}). The time dependence of the absorbance change is illustrated in Figure 2 for reactions carried out between 8.6 × 10^{-4} M iodine and seven concentrations of tetraethyltin, as indicated in the legend. There are two features in Figure 2 which merit discussion. First, there is an immediate drop in the iodine absorbance upon the addition of tetraethyltin. The magnitude of the absorbance change $(A_0 - A)$ increases with the amount of tetraethyltin added. Secondly, the slower subsequent rate of decrease of the iodine absorbance (ln A) is linear for all concentrations of tetraethyltin employed (in excess), and it is expressed as

$$[I_2] = \gamma[I_2]_0 \exp(-k_{obsd}t) \qquad (4)$$

where $\gamma = 1 - A/A_0$ and k_{obsd} is the pseudo-first-order rate constant. The experimental pseudo-first-order rate constant corrected by the fraction of free iodine is $k_{obsd}/(1 - A/A_0)$. When this quantity (at various iodine concentrations) is plotted against the tetraethyltin concentration, a linear relationship shown in Figure 3 is obtained. Thus, the complete rate law for the disappearance of iodine is

Table II. Second-Order Rate Constants for Iodinolysis of Various Alkylmetals at 25 °C

	rate constant, k,[b] $M^{-1} s^{-1}$
tetraalkyltin[a]	
Me_4Sn	5.8×10^{-3} (6.3)
Et_4Sn	3.8×10^{-2} (1.3)
n-Pr_4Sn	1.7×10^{-2} (0.27)
n-Bu_4Sn	1.5×10^{-2} (0.27)
$EtSnMe_3$	7.9×10^{-3} (6.3)
n-$PrSnMe_3$	7.8×10^{-3} (6.6)
n-$BuSnMe_3$	8.9×10^{-3} (7.2)
i-$BuSnMe_3$	9.3×10^{-3} (–)
Et_2SnMe_2	1.5×10^{-2} (11)
n-Pr_2SnMe_2	1.3×10^{-2} (8.9)
n-Bu_2SnMe_2	1.4×10^{-2} (9.3)
i-Pr_2SnMe_2	2.2×10^{-2} (9.2)
t-Bu_2SnMe_2	6.2×10^{-3} (0.83)
Et_3SnMe	2.0×10^{-2} (10)
i-Pr_4Sn	2.2×10^{-3} (1.4×10^{-2})
sec-Bu_4Sn	6.5×10^{-4} (3.2×10^{-3})
i-Bu_4Sn	8.3×10^{-3} (0.21)
i-Bu_2SnMe_2	2.2×10^{-2} (–)
dialkylmercury[c]	
Me_2Hg	7.8×10^{-4}
$EtHgMe$	6.5×10^{-2}
n-Pr_2Hg	0.63
n-Bu_2Hg	0.62
i-Bu_2Hg	0.26
tetraalkyllead[c]	
$EtPbMe_3$	0.10
Et_2PbMe_2	0.33
Et_3PbMe	0.76
Et_4Pb	0.89

[a] In methylene chloride solutions. [b] In acetonitrile solutions in parentheses. [c] In carbon tetrachloride solutions.

$$\frac{-d[I_2]}{dt} = \frac{k_1 + k_2[Et_4Sn]}{1 + K_{CT}[Et_4Sn]} K_{CT}[Et_4Sn][I_2] \quad (5)$$

Since the second-order rate constant k_1 is of comparable magnitude to the third-order rate constant k_2 and K_{CT} is rather small,[15] at low concentrations of tetraethyltin, the rate is represented by

$$-d[I_2]/dt \simeq k[Et_4Sn][I_2] \quad (6)$$

where $k = k_1K_{CT}$. Such a second-order rate expression accords with those usually reported in previous studies (but carried out without recognizing the preequilibrium formation of charge-transfer complexes).[1-3,16]

The rates of iodinolysis of various other tetraalkyltin compounds were also measured in methylene chloride solutions, under conditions in which eq 6 is applicable. The second-order rate constants are listed in Table II. The rate constants for the analogous methylethyllead $Me_nEt_{4-n}Pb$ (where n = 1, 2, 3) and dialkylmercury compounds were measured in carbon tetrachloride, since the rates of iodinolysis were too fast to measure in methylene chloride.

At this juncture, it is important to point out the caveat that iodinolysis may also proceed via a competing radical chain process,[1,2] and care must be exercised to avoid this adventitious light-promoted complication (see Experimental Section). The problem is especially severe when studies are carried out under conditions in which the rate of the electrophilic cleavage of alkylmetals is very slow. The radical-chain iodinolysis of alkylmetals proceeding via iodine atoms differs in significant ways from that described here, and is reported separately.[17]

Selectivity in the Cleavage of Unsymmetrical Alkylmetals. In the cleavage of unsymmetrical alkylmetals such as tetraalkyltin Me_nSnR_{4-n} or dialkylmercury MeHgR, 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 competition. Thus, iodine affords a mixture of two alkyl iodides, CH_3I and RI, from R_2SnMe_2 in amounts which depend upon the relative rates of cleavage, i.e.

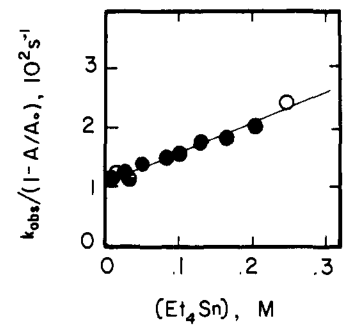
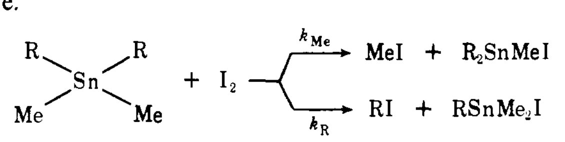


Figure 3. Pseudo-first-order rate constant for iodinolysis as a function of Et_4Sn and iodine concentrations according to eq 3 and 5. $[I_2]_0$ = ● 8.6×10^{-4}, ◑ 1.00×10^{-3}, ⊖ 1.06×10^{-3}, ○ 1.81×10^{-3} M.



(7)

(8)

The selectivity, $S(R/Me) = k_R/k_{Me}$, is obtained directly from the yields of RI and MeI. For the other tetraalkyltin compounds $RSnMe_3$ and R_3SnMe, a correction for a statistical factor must be made, i.e.

$$S(R/Me) = \frac{n}{4-n}\frac{[RI]}{[MeI]} \quad (9)$$

where n = 1, 2, 3 for Me_nSnR_{4-n} and n = 2 for MeHgR. It is noteworthy that the selectivities determined by eq 9 are rather constant for various alkyl (R) groups in Table III, independent of the value of n. In other words, S(R/Me) is a measure of the intrinsic reactivity of a given alkylmetal irrespective of the substitution patterns in a series of Me_nSnR_{4-n} compounds.

Effect of Solvent. The solvent is known to play a large, dominating role in the iodinolysis of alkylmetals, particularly with regard to the rate and selectivity.[12,16] Therefore, in order to examine the solvent effects systematically, we studied separately the variations in the formation constants of the complex K_{CT}, the rate constant k, and the selectivity S(R/Me) under a uniform set of experimental conditions.

The *formation constants* for various tetraalkyltin compounds were evaluated in different solvents by the application of eq 3 to the rapid initial drop ($A_0 - A$) in the iodine absorbance. The variation of K_{CT} with solvent polarity is included in Table IV. The latter were restricted to the less polar solvents, since the competing iodinolysis occurred too rapidly in the more polar solvents to allow accurate measurements of the initial absorbance drop, $A_0 - A$. At the other extreme, K_{CT} is too small to measure ($K_{CT} \ll 0.1\ M^{-1}$) in the least polar, carbon tetrachloride.[9]

The *second-order rate constants* for iodinolysis of tetraalkyltin compounds in acetonitrile are from 10^2 to 10^3 times faster than those obtained in methylene chloride solutions, as shown in Table V. Furthermore, the rate constants in carbon tetrachloride are from 10^{-3} to 10^{-4} times slower than those in methylene chloride. Indeed, the rates are so slow in carbon tetrachloride that the rate constants could not be reliably determined as a result of the competing radical chain process,[17] induced by the monitoring light of the spectrophotometer. In

Table III. Selectivities in the Iodinolysis of Unsymmetrical Alkylmetals in Various Solvents[a]

	solvent[b]											
alkylmetal	CH_3CN (a)	MeOH (b)	EtOH (c)	Me_2CO (d)	CH_2Cl_2 (e)	o-Br-C_6H_4Cl (f)	$CH_3C(Cl)$-$HC(Cl)H_2$ (g)	$CHCl_3$ (h)	o-Cl-$C_6H_4CH_3$ (i)	C_6H_5Cl (j)	n-Bu_2O (k)	CCl_4 (l)
$EtSnMe_3$	0.024	0.060	0.059		0.13	0.16	0.12			0.23	0.35	1.4
Et_2SnMe_2	0.020	0.051	0.059	0.045	0.08	0.15	0.08		0.17	0.15		0.8
Et_3SnMe	0.030	0.046		0.042	0.11	0.16	0.12			0.20		0.5
n-$PrSnMe_3$	0.0073	0.025	0.023	0.024	0.030			0.031		0.081		0.9
n-Pr_2SnMe_2	0.0075	0.026	0.022	0.024	0.028			0.032		0.064	0.10	0.6
n-$BuSnMe_3$	0.0040		0.019	0.019	0.035	0.037	0.040	0.025		0.065		0.9
n-Bu_2SnMe_2	0.0060	0.035	0.015	0.017	0.027		0.034	0.025		0.062		0.6
t-Bu_2SnMe_2	0.048				0.26		0.24	0.36		0.45		
EtHgMe	0.11	0.15	0.17	0.86	2.8		1.8	5.0		4.2		6.7

[a] Selectivities, $S(R/Me)$, evaluated according to eq 14. [b] Solvents identified according to letters in parentheses.

Table IV. Solvent Effect on the Formation Constants of $[R_4Sn\ I_2]$ Charge Transfer Complexes[a]

	solvent				
alkyltin	CH_2Cl_2	o-BrC_6H_4Cl	$CH_3C(Cl)HC(Cl)H_2$	o-$ClC_6H_4CH_3$	C_6H_5Cl
$EtSnMe_3$	0.12	0.081	0.12		0.030
Et_2SnMe_2	0.59	0.15	0.68	0.12	0.20
Et_3SnMe	0.63	0.25			0.15
n-$PrSnMe_3$	0.16	0.11			0.054
n-Pr_2SnMe_2	0.33	0.16			
n-$BuSnMe_3$	0.21		0.16		0.079
n-Bu_2SnMe_2	0.76		0.68		0.33

[a] Formation constants in M^{-1} at 25 °C.

Table V. Solvent Effect on the Second-Order Rate Constants for Iodinolysis of Alkyltin Compounds[a]

	solvent[b]							
alkyltin	CH_3CN (a)	EtOH (c)	Me_2CO (d)	CH_2Cl_2 (e)	o-BrC_6H_4Cl (f)	$CH_3C(Cl)$-$HC(Cl)H_2$ (g)	$CHCl_3$ (h)	C_6H_5Cl (j)
Me_4Sn	6.3			5.8×10^{-3}				1.7×10^{-4} [c]
$EtSnMe_3$	6.3	0.34	1.6×10^{-2}	7.9×10^{-3}	4.6×10^{-2}	1.4×10^{-2}	3.5×10^{-2}	9.3×10^{-4}
Et_2SnMe_2	10.9			1.6×10^{-2}	8.7×10^{-3}	1.5×10^{-2}		8.4×10^{-4}
Et_3SnMe	10.1			2.0×10^{-2}	6.5×10^{-3}	1.6×10^{-2}		1.1×10^{-3}
Et_4Sn	1.3			3.8×10^{-2}				1.0×10^{-3} [c]
n-$PrSnMe_3$	5.6	0.21		7.8×10^{-3}	4.2×10^{-3}		3.2×10^{-2}	6.8×10^{-4}
n-Pr_2SnMe_2	6.0		2.6×10^{-2}	1.3×10^{-2}	5.3×10^{-3}			7.4×10^{-4}
n-Pr_4Sn	0.27			1.7×10^{-2}				1.3×10^{-4} [c]
n-$BuSnMe_3$	7.3	0.32	2.2×10^{-2}	8.9×10^{-3}	4.5×10^{-3}	1.0×10^{-2}	3.2×10^{-2}	6.8×10^{-4}
n-Bu_2SnMe_2	9.3			1.4×10^{-2}	6.1×10^{-3}	9.8×10^{-3}		7.2×10^{-4}
t-Bu_2SnMe_2	0.82			6.2×10^{-3}		1.7×10^{-3}	4.5×10^{-4}	1.9×10^{-4}

[a] Rate constants evaluated according to eq 6 in $M^{-1}\ s^{-1}$ at 25 °C. [b] Solvents identified by letters in parentheses. Other rate constants: Et_2SnMe_2, $1.0 \times 10^{-3}\ M^{-1}\ s^{-1}$ in o-chlorotoluene; $EtSnMe_3$, $4.3 \times 10^{-5}\ M^{-1}\ s^{-1}$ in n-Bu_2O. [c] Taken from ref 16a.

addition to the large sensitivity of the rates to variations in the solvent, there is a remarkable *inversion in the relative rates of reactivity.* For example, Et_4Sn is about ten times more reactive than Me_4Sn in methylene chloride, but the order is reversed in acetonitrile. (This effect is graphically illustrated later in Figure 6.)

Finally, in the iodinolysis of all tetraalkyltin compounds, there is a marked dependence of *selectivity* on the solvent. The results in Table III show that there are even notable reversals in selectivity with solvent polarity, e.g., $S(n\text{-}Bu/Me) = 0.0040$ in acetonitrile but 1.7 in carbon tetrachloride, and $S(Et/Me) = 0.11$ in acetonitrile but 6.7 in carbon tetrachloride. In general, the selectivities in Table III for iodinolysis in chlorobenzene are comparable to those reported earlier by Boué, Gielen, and Nasielski[12] for the brominolysis of Me_3SnR, where R = Et (0.38), n-Pr (0.15), and n-Bu (0.14).

Discussion

The observation of transient charge-transfer complexes of iodine has provided us with a unique opportunity to examine quantitatively the structural and electronic effects of the alkylmetals in electrophilic processes. To do so, we first consider the role of charge-transfer complexes as viable intermediates in iodinolysis, and then discuss the nature of the activation process as it is elucidated by charge-transfer interactions based on the well-developed Mulliken theory. The charge-transfer formulation of the mechanism for electrophilic iodinolysis will be presented, and examined quantitatively in the context of solvent effects on the selectivity and the rate of iodinolysis as well as on the formation constant of the charge-transfer complexes. Finally, the relationship of the charge-transfer mechanism to the more familiar but qualitative description of electrophilic cleavage will be considered.

I. Charge-Transfer Complexes as Intermediates in the Iodinolysis of Alkylmetals. The independent, spectroscopic evidence for the formation of [alkylmetal-iodine] charge-transfer complexes must be accommodated in any mechanistic formulation for the iodinolysis of alkylmetals. Thus, the mechanism in Scheme I is consistent with the experimental rate expression in eq 5 for the iodinolysis of alkylmetals:

Table VI. The Driving Force for Electron Transfer in Tetraalkyltin-Iodine Complexes in Acetonitrile Solution

tetraalkyltin	$\Delta G_r°$, kcal mol^{-1} [a]	ΔE, kcal mol^{-1} [b]	tetraalkyltin	$\Delta G_r°$, kcal mol^{-1} [a]	ΔE, kcal mol^{-1} [b]
Me_4Sn	0	0			
Et_4Sn	−11.0	10.8	n-Pr_2SnMe_2	−12.4	15.0
n-Pr_4Sn	−12.1	12.7	n-Bu_2SnMe_2	−12.4	15.0
n-Bu_4Sn	−12.9	14.8	i-Pr_2SnMe_2	−15.7	18.7
$EtSnMe_3$	−8.2	11.3	t-Bu_2SnMe_2	−20.4	22.6
n-$PrSnMe_3$	−8.2	11.5	Et_3SnMe	−10.3	9.7
n-$BuSnMe_3$	−8.2	11.5	i-Pr_4Sn	−17.1	19.4
i-$BuSnMe_3$	−8.9	–	sec-Bu_4Sn	−17.2	18.2
Et_2SnMe_2	−9.4	12.2	i-Bu_4Sn	−14.0	14.8

[a] Calculated from the data in ref 25. [b] Calculated from eq 15 and the ionization potentials and transition energies listed in Table I.

Scheme I

$$RM + I_2 \overset{K_{CT}}{\rightleftharpoons} [RM\ I_2] \xrightarrow{k_1} RI + MI \qquad (10)$$

$$[RM\ I_2] + RM \xrightarrow{k_2} \text{products} \qquad (11)$$

where K_{CT} and k_1 are the equilibrium constant and first-order rate constant for the formation and decay, respectively, of the charge-transfer complex. The other term in the rate expression represents the second reaction (eq 11) with a rate constant k_2 for a kinetically third-order process.[18] For our immediate purposes, however, any contribution from the latter is readily dispensed with, since k_2 is sufficiently small that it can be effectively obviated at low alkylmetal concentrations.

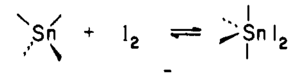
II. The Activation Process Proceeding from Charge-Transfer Complexes. We wish to show how the formulation in Scheme I provides the basis of our further description of electrophilic cleavage, by focusing on the properties of the CT complex and the unique information provided by the transition energy.[19,20] According to the well-established charge-transfer theory developed by Mulliken,[10,11] the spectral transition $h\nu_{CT}$ represents an electronic excitation from the ground state Ψ_N of the complex to the excited state Ψ_E. For weak complexes of the type described here for alkylmetals and iodine, this transition occurs essentially from the structure $\Psi_0(RMI_2)$ to the structure $\Psi_1(RM^+\ I_2^-)$, i.e., it corresponds to an intermolecular transition $h\nu_{CT}$ within the complex involving electron transfer from RM to I_2, as represented by the process

$$[RM\ I_2] \xrightarrow{h\nu_{CT}} [RM^+\ I_2^-]^* \qquad (12)$$

The asterisk identifies an excited ion pair with the same mean separation r_{DA} as that in the CT complex; i.e., eq 12 represents a vertical (Franck-Condon) transition, the energy of which is given by

$$h\nu_{CT} = I_D - E_A + \omega \qquad (13)$$

I_D is the vertical ionization potential of RM, 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_{DA} within $[RM^+\ I_2^-]^*$. In a recent study, we showed that the magnitudes of r_{DA} (and thus 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.[9] For example, the latter could arise from the distortion of the normally tetrahedral tetraalkyltin to a trigonal-bipyramidal configuration in the complex, i.e.



(14)

In order to evaluate this and other effects quantitatively, we related ω for various tetraalkyltin to ω_0 of the least sterically hindered Me_4Sn, chosen as a reference. It follows from eq 13 that the energy change, $\Delta E = \omega - \omega_0$, is given by

$$\Delta E = -\Delta I_D + \Delta h\nu_{CT} \qquad (15)$$

where ΔI_D is the difference in the ionization potentials between a particular tetraalkyltin and Me_4Sn, and $\Delta h\nu_{CT}$ is the difference in their CT energies in the iodine complexes. Thus *by choosing a reference alkylmetal, all changes in the interaction energies of these CT complexes, including steric, distortional, and other effects, can be compositely expressed in a single energy term* ΔE, which can be evaluated directly from the experimental data according to eq 15.

We now turn to the iodinolysis reaction as it proceeds from the CT complex described in Scheme I, in which the rate-limiting activation process is considered to be electron transfer, i.e.

$$[RM\ I_2] \xrightarrow{k_1} [RM^+\ I_2^-] \qquad (16)$$

(Such an electron transfer in CT complexes has been demonstrated recently in the thermal insertion reaction involving the same series of alkylmetals with tetracyanoethylene.[21,22]) The thermally formed ion pair $[RM^+\ I_2^-]$ in eq 16 is akin to the photochemically excited ion pair $[RM^+\ I_2^-]^*$ in eq 12.[23] According to this formulation, the change in the *driving force for electron transfer* derives from two factors: (1) the oxidation of the alkylmetal and (2) the interaction energy in the thermal ion pair. In order to evaluate these terms, we resort again to the comparative method, as described above for CT complexes, and relate changes in the free-energy terms relative to a reference alkylmetal. The free-energy change $\Delta G_r°$ for the oxidation of tetraalkyltin relative to Me_4Sn in solution is obtained directly from the difference in their ionization potentials in the gas phase, i.e.

$$\Delta G_r° = \alpha \Delta I_D \qquad (17)^{24}$$

where the proportionality constant α is 0.60 in acetonitrile solutions at 25 °C.[25] For the accompanying change in the interaction energy of the thermal ion pair, we equate it to ΔE determined from the CT complexes in eq 15.[26] The values of $\Delta G_r°$ and ΔE are listed in Table VI for various tetraalkyltin-iodine complexes.

The *activation free energy for electron transfer* may be evaluated for various tetraalkyltins by a similar comparative procedure, i.e.[24]

$$\Delta G_r^{\ddagger} = -2.3RT \log k/k_0 \qquad (18)$$

where k and k_0 are the rates of electron transfer in $[R_4Sn\ I_2]$ and $[Me_4Sn\ I_2]$, respectively, as tabulated in Table II. The relationship between $\Delta G_r^{\ddagger}$ and $\Delta G_r°$ includes the contribution from ΔE, and it is graphically illustrated in Figure 4.[27]

This striking correlation with a slope of 1.0 represents a linear free energy relationship expressed as[24]

$$\Delta G_r^{\ddagger} = \Delta G_r° + \Delta E \qquad (19)$$

(It is important to point out that eq 19 obtains directly from three *independent* sets of experiments by a purely operational approach.) Furthermore, the same experimental relationship

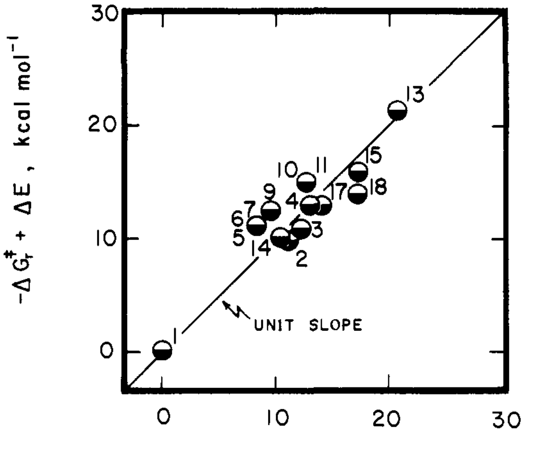


Figure 4. The correlation of the changes in the activation free energy for iodinolysis of tetraalkyltin in acetonitrile solutions at 25 °C with changes in the driving force for $[RM^+ I_2^-]$ formation. Compounds identified by numbers in Table I. Note the correlation with the line of unit slope (see text).

can be established in even nonpolar solvents in which $\Delta G_r°$ cannot be determined.[28] For example, the linear correlation in both Figures 5a and 5b for the iodinolysis of tetraalkyltin in methylene chloride and dialkylmercury in carbon tetrachloride, respectively, corresponds to the linear free energy relationship

$$\Delta G_r^{\ddagger} - \Delta E = \Delta G_r^{\circ} = \alpha \Delta I_D \qquad (20)$$

From the slopes, α is evaluated as 0.71 in methylene chloride and 0.77 in carbon tetrachloride. As expected, these values are larger than $\alpha = 0.60$ in the more polar acetonitrile.[29] Indeed, the solvent effect on the rates of iodinolysis provides an important test of this linear free energy relationship in dealing with the rather unusual inversion in the reactivities reported in Table V. Thus, the relative reactivities of various R_4Sn are obtained directly from eq 18 and 20 as

$$-\log k/k_0 = \frac{1}{2.3RT}[\alpha \Delta I_D + \Delta E] \qquad (21)$$

Since the variations in the relative reactivities with solvent are represented by changes in α, these are drawn in Figure 6 as a family of solid lines calculated from eq 21. (The values of I_D and ΔE for various R_4Sn are listed in Tables I and VI, respectively.) The fit to the available experimental rate data, indicated by the shaded circles, is unmistakable.[30] In other words, a single parameter α correctly predicts the marked alteration in reactivity order of alkylmetals, which in previous treatments could only be attributed to solvent-induced changes in mechanism.[12]

Since the charge-transfer formulation quantitatively accounts for the reactivities of alkylmetals in iodinolysis, we might inquire about the structural factors involved. In general terms, $\alpha\Delta I_D$ and ΔE correspond to the electronic and steric contributions, respectively, to the activation process.[31] The solvent effect is primarily associated with changes in the electronic effect, owing to variations in α.[31b] As the solvent increases in polarity, α decreases and steric effects become dominant—leading to $k_{Me_4Sn} > k_{Et_4Sn}$. The reverse reactivity $k_{Me_4Sn} < k_{Et_4Sn}$ obtains in nonpolar solvents in which the electronic demand is optimized as a result of the increased values of α.

The importance of solvent polarity may also be examined in another way. Thus the activation free energy, as described by the charge-transfer mechanism, relates directly to the free energy of formation of the ion pair in eq 16. Consequently, the role of the solvent on the rate is largely reduced to its effect on the ion pair. Despite the lack of knowledge regarding solvent structure, we can consider the solvation of the ion pair from a macroscopic property of the solvent.[32] Such an approach is described by the classical Kirkwood equation in which the ion pair is considered as a dipolar solute with dipole moment μ in a solvent of bulk dielectric ϵ_B. The electrostatic contribution to the chemical potential or the free energy of solvation is given by

$$\Delta G_{solv} = -(\mu^2/a^3)\varphi(\epsilon_B) \qquad (22)$$

where $\varphi(\epsilon_B) = (\epsilon_B - 1)/(2\epsilon_B + 1)$ and a is the radius of the solute considered as a sphere.[32] In the series of alkylmetal-iodine CT complexes considered here, the reactants have no dipole moment. Accordingly, in the charge-transfer reaction, the change in the solvation term relative to that in methylene chloride with solvent variation may be written as

$$\Delta E_{solv} = -\Delta\Delta G^{\ddagger}_{solv} = (\mu^{\ddagger 2}/a^3)\Delta\varphi(\epsilon_B) \qquad (23)$$

where $\mu^{\ddagger}$ is the dipole moment in the transition state.[33] The more or less linear correlation of the solvation energy and the dielectric function according to eq 23 is shown in Figure 7. It suggests that the slope $\mu^{\ddagger 2}/a^3 = 2.5$ is constant for these solvents. If, for the moment, we consider the dipolar CT solute to be approximated by a sphere, then the degree of charge separation is estimated to be between 0.8 and 1.[33b] The crude model notwithstanding, this analysis of the solvent effect provides further support for the high degree of charge separation in the rate-limiting transition state for the iodinolysis of alkylmetals. These results, together with the clean linear free energy relationship in eq 19 or its equivalent in eq 21, provide strong evidence that the transition state for electron transfer is accurately reflected by the excited ion pair in the CT complex. As such, this conclusion forms the basis for describing the activation process for iodinolysis as electron transfer in the CT complex.

III. The Charge-Transfer Mechanism for Iodinolysis of Alkylmetals. The preequilibrium formation of the alkylmetal-iodine charge-transfer complex is included in the general mechanism in Scheme II for the iodinolysis of alkylmetals.

Scheme II

$$RM + I_2 \overset{K_{CT}}{\rightleftharpoons} [RM\ I_2] \qquad (24)$$

$$[RM\ I_2] \xrightarrow{k_1} [RM^+\ I_2^-] \qquad (25)$$

$$[RM^+\ I_2^-] \xrightarrow{fast} [R\cdot\ M^+\ I_2^-] \qquad (26)$$

$$[R\cdot\ M^+\ I_2^-] \longrightarrow RI + MI \qquad (27)$$

$$[R\cdot\ M^+\ I_2^-] \xrightarrow{diffuse} R\cdot + MI + I\cdot, \text{etc.} \qquad (28)$$

The activation process for iodinolysis is represented in eq 25 for inner-sphere electron transfer from the alkylmetal donor to the iodine acceptor, as elaborated in the foregoing discussion. The subsequent sequence of reactions following the CT activation process can be readily formulated on the basis of previous studies with other acceptors such as TCNE and $IrCl_6^{2-}$,[21,34] i.e.

$$[RM\ TNCE] \rightarrow [RM^+\ TCNE^-], \text{etc.} \qquad (29)$$

$$[RM\ IrCl_6^{2-}] \rightarrow [RM^+\ IrCl_6^{3-}], \text{etc.} \qquad (30)$$

From studies of these donor-acceptor systems, it is known that the lifetime of the paramagnetic ion pair in eq 26 is exceedingly short, and RM^+ is subject to spontaneous fragmentation.[35] The cage combination of the radical pair would occur in eq 27 with essentially no activation energy.[21,36]

According to Scheme II, the selectivity in iodinolysis, i.e.,

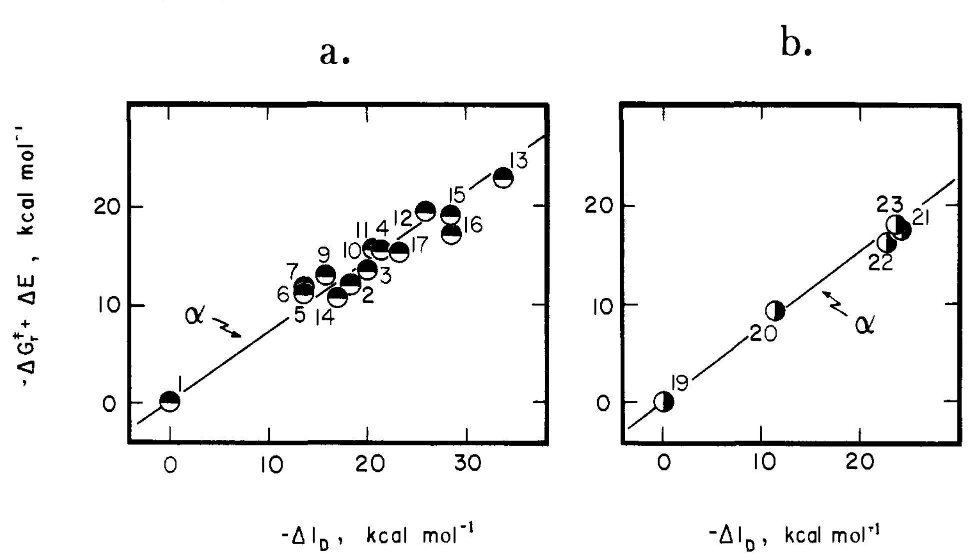


Figure 5. Linear free energy relationships established in the iodinolysis of alkylmetals in nonpolar media. Left: tetraalkyltin in CH_2Cl_2. Right: dialkylmercury in CCl_4. Numbers refer to compounds in Table I.

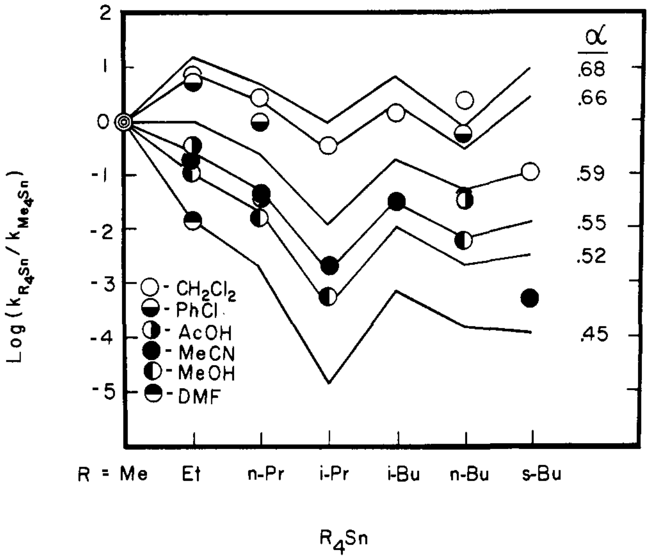


Figure 6. Prediction of the solvent effect on the relative reactivities according to the linear free energy relationship for iodinolysis. The solid lines are calculated for various α from eq 21. The experimental solvent dependences: ○, CH_2Cl_2; ⊖, PhCl; ◑, HOAc; ●, MeCN; ◐, MeOH; ○, DMF, taken from Table II and ref 16a.

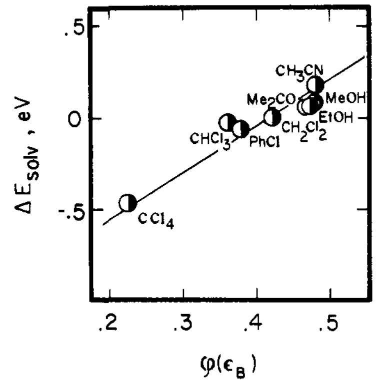
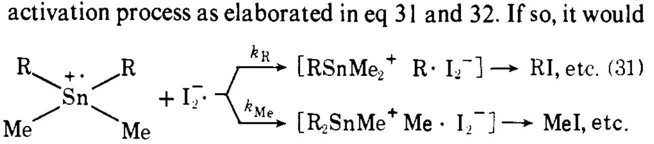


Figure 7. The correlation of the solvent parameter φ (ϵ_B) with the change in solvation energy according to eq 23.[33]

the formation of products, is determined by the fragmentation of the RM^+ moiety in eq 26, subsequent to the rate-limiting activation process as elaborated in eq 31 and 32. If so, it would



$$R_2SnMe_2^{+\cdot} + I_2^{-\cdot} \xrightarrow{k_R} [RSnMe_2^+ \; R\cdot \; I_2^-] \rightarrow RI, \text{etc.} \quad (31)$$

$$R_2SnMe_2^{+\cdot} + I_2^{-\cdot} \xrightarrow{k_{Me}} [R_2SnMe^+ Me \cdot I_2^-] \rightarrow MeI, \text{etc.} \quad (32)$$

seem that the selectivity would be independent of the acceptor. However, a direct comparison shows that the selectivity S(R/Me) is significantly higher for either TCNE or $IrCl_6^{2-}$ compared to iodine under the same reaction conditions.[21,37] In the following section we focus on the rather unusual and marked solvent effects on selectivity in Table III to describe how the acceptor may influence the products of iodinolysis in a step subsequent to the rate-limiting electron transfer.

IV. The Solvent Effect on the Iodinolysis of Alkylmetals. It has been known for some time that the nature of the solvent plays an important role in determining the selectivity as well as the rate of the electrophilic cleavage of alkylmetals with halogens.[38] For example, it is reported that the rates of halogenolysis increase with solvent polarity, accompanied generally by a decrease in the selectivity S(R/Me). Indeed the same conclusion can be drawn from our systematic study of solvent effects in Tables V and III on the rates and selectivities, respectively, in the iodinolysis of alkylmetals. However, no unified analysis of this problem has evolved heretofore,[39] largely owing to the lack of a suitable method of directly treating the solvent effect. Although the empirical and macroscopic approaches described in eq 19 and 21 may be appropriate for describing the changes in polarity of the transition state for electron transfer, they are not adequate for treating selectivity. Insight into the latter, involving microscopic changes in the ion pair, is provided by the charge-transfer formulation in which the solvent is treated as a perturbation on the interaction energy ω in eq 13.

A. Solvent Effect on the Selectivity and the Rate Constant. In the CT formulation, the perturbation by steric effects is included in the energy term ΔE in eq 15. The solvent effect may also be expressed as a perturbation in similar form, i.e.

$$\ln k_m/k_n = \frac{1}{RT}\left(\frac{e^2}{r_m} - \frac{e^2}{r_n}\right) \qquad (33)$$

where the subscripts m and n refer to different solvents as elaborated in Appendix I. Thus, the problem reduces to one of describing the solvent-induced change in the mean separation.

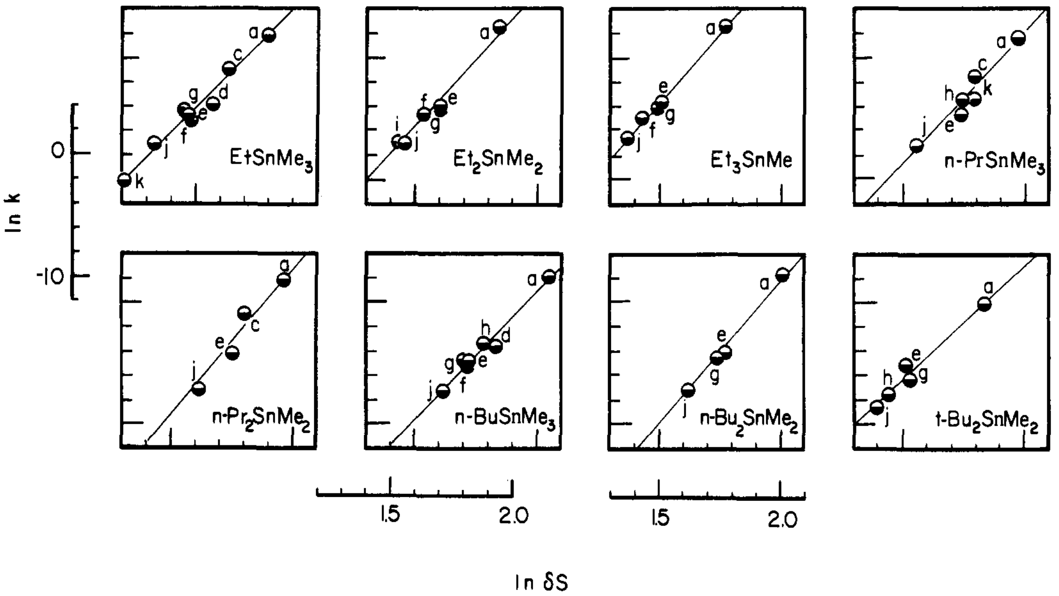


Figure 8. The solvent effect on the relationship according to eq 36 between the rate constant and selectivity in the iodinolysis of various alkylmetals, as indicated. The letters refer to solvents identified in Table III.

A direct attack on this problem lies in the measurement of the CT transition energies $h\nu_{CT}$ in various solvents. Unfortunately, this route is experimentally unavailable owing to complications arising from the rapid rates of iodinolysis in all but the least polar solvents. The alternative approach derives from the strong influence of solvent on the intramolecular selectivity reported in Table III. To carry out this analysis, we introduce the term δS as

$$\delta S = \ln S_0/S \qquad (34)$$

where S is the selectivity of a particular alkylmetal in iodinolysis and S_0 is that selectivity in a reference system (arbitrarily chosen as $IrCl_6^{2-}$).[34,37] The relationship between the changes in selectivity and mean separation, as they are affected by solvent, can be represented by

$$\delta S_m/\delta S_n = \exp(r_n - r_m) \qquad (35)$$

as described in detail in Appendix II. The relationship between the rate constants and selectivities as they are affected by solvent is then obtained from eq 33 and 35, and expressed as

$$\ln k_m/k_n = (r_m r_n RT)^{-1}[\ln \delta S_m/\delta S_n] \qquad (36)$$

First, it is important to note that eq 36 correctly predicts the inverse relationship between the rate constant and the selectivity in the iodinolysis of alkylmetals. Secondly, if eq 36 is valid, the solvent dependence of the rates of iodinolysis should be linear with the selectivity changes. Indeed, Figure 8 shows the linear correlation obtained from the rate and selectivity data for several alkylmetals in Tables V and III, respectively. The slope of the correlation is given by $(r_m r_n RT)^{-1}$, from which the mean value $\bar{r}_{mn}$, ranging from 3.7 Å for Et_2SnMe_2 to 4.1 Å for t-Bu_2SnMe_2, is evaluated.[40] The relative magnitudes of $\bar{r}_{mn}$ for Et_2SnMe_2 and t-Bu_2SnMe_2 accord with qualitative expectations based on steric effects. More interestingly, the difference (0.40 eV) in ΔE for these alkylmetals, calculated from the differences in CT transition energies and ionization potentials according to eq 15, is in surprisingly good agreement with the value (0.37 eV) evaluated from $\bar{r}_{mn}$, i.e.,[41]

$$\Delta E \simeq \Delta(e^2/\bar{r}_{mn}) \qquad (37)$$

It is important to emphasize that the linear relationship in eq 36 between the rate constant (ln k) and the selectivity (ln δS) is largely of phenomenological origin, and derived without extensive assumptions.

B. Solvent Effect on the Formation Constant and Selectivity. The formation constants K_{CT} of alkylmetal-iodine complexes also vary with solvents, as listed in Table IV. The heat of formation of the CT complex according to Mulliken theory is given by

$$-\Delta H = \beta^2/h\nu_{CT} \qquad (38)$$

where β is the resonance energy between $\Psi_0(RM\ I_2)$ and $\Psi_1(RM^+\ I_2^-)$, and it can be expressed as $\propto \exp(-r)$.[9] The solvent effect on β is then represented by

$$\beta_m/\beta_n = \exp(r_n - r_m) \qquad (39)$$

where m and n again refer to different solvents. The corresponding change in the formation constant, i.e.

$$\ln K_m/K_n = -(1/RT)(\Delta H_m - \Delta H_n) \qquad (40)$$

is obtained from eq 38 as

$$\ln K_m/K_n = -(\Delta H_n/RT)\{(\delta S_m/\delta S_n)^2 - 1\} \qquad (41)$$

assuming a constant entropy change. The solvent is shown in the plot of the formation constants and selectivities in Figure 9 using n = methylene chloride as a reference solvent. The slope yields $-\Delta H_{CH_2Cl_2} = 3.1 \pm 0.8$ kcal mol^{-1}. This compares well with experimental values in the range of 2.0–2.4 kcal mol^{-1} determined independently from the temperature dependence of K_{CT}.[9]

V. Charge-Transfer Ion Pairs and Selectivity—The Relationship to Electrophilic Mechanisms. The charge-transfer model for iodinolysis of alkylmetals correctly predicts the otherwise rather unusual inverse relationship between the selectivity and the rate constant. According to Scheme II, the selectivity is determined by the cage fragmentation of the $[RM^+\ I_2^-]$ ion pair in eq 26 subsequent to the rate-limiting step. As such, an important question which evolves is: How does the nature of the ion pair affect the fragmentation pattern of the RM^+ moiety leading to changes in selectivity? To answer this question, we refer to an earlier study,[25] in which the selectivity was shown to decrease from 25 to 11 in outer-sphere and inner-sphere mechanisms, respectively, using the inorganic oxidants FeL_3^{3+} and $IrCl_6^{2-}$ to effect electron transfer, i.e.

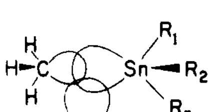
$$RM + FeL_3^{3+} \xrightarrow[\text{sphere}]{\text{outer}} [RM^+ \, FeL_3^{2+}], \text{etc.}$$

$$S(\text{Et/Me}) = 25 \quad (42)$$

$$RM + IrCl_6^{2-} \xrightarrow[\text{sphere}]{\text{inner}} [RM^+ \, IrCl_6^{3-}], \text{etc.}$$

$$S(\text{Et/Me}) = 11 \quad (43)$$

where RM = Et_nSnMe_{4-n}. Such outer-sphere and inner-sphere mechanisms are differentiated primarily by the intermolecular separation between the alkylmetal and the oxidant in the transition state for electron transfer.[42] Extending this relationship, we consider the lower selectivities in iodinolysis to arise from selective interactions between RM^+ and I_2^-, which is dictated largely by steric effects as follows. For a charge-transfer model, the alkyltin-iodine interaction can be depicted as



The extent of the resonance interaction is given by the common relationships[43]

$$\mathcal{E} = \mathcal{E}^0 S_r \quad (44)$$

$$S_r = S_r^0 \exp(-r^\ddagger) \quad (45)$$

where S_r is the overlap integral and $r^\ddagger$ is the mean separation between I_2 and alkylmetal; $\mathcal{E}^0$ and S_r^0 are constants.

The extent of the resonance interaction between I_2 and the least hindered site in the alkylmetal, i.e., the Me-Sn bond, will lead to reductions in the selectivity S(R/Me) in the following way. We first select $IrCl_6^{2-}$ as the reference acceptor in which the resonance interaction with the alkylmetal is taken as nil;[25] that is, the selectivity S_0 is determined solely by the relative bond energies D_{Me} and D_R for dissociation of Me· and R· from the alkylmetal cation radical $Me_nSnR_{4-n}^+$. The selectivity for the reference system is given by

$$RT \ln S_0 = D_{Me} - D_R \quad (46)$$

For iodinolysis, the selectivity can then be represented as

$$RT \ln S = RT \ln S_0 - \mathcal{E} \quad (47)$$

by considering that D_{Me} is reduced to $D_{Me} - \mathcal{E}$ by the resonance interaction between $Me\text{-}SnR_3^+$ and I_2^-. Equation 47 can be expressed in a form which emphasizes the relationship between the selectivity and mean separation, i.e.

$$\ln S = -A \exp(-r^\ddagger) + B \quad (48)$$

which is obtained by combining eq 44, 45, and 47. The constants are $A = \mathcal{E}^0 S_r^0/RT$ and $B = \ln S_0$. Since changes in the mean separation are a measure of the steric effect, eq 48 indicates how the selectivity may be affected by steric effects, all within the context of the charge-transfer ion pair. In other words, a strong resonance interaction in the ion pair, mediated by the mean separation, can quantitatively account for changes in selectivity with solvent variations as described above. The cleavage of an alkyl-metal bond under these circumstances is highly reminiscent of a concerted process, more commonly referred to as an electrophilic cleavage.[1-3] As a result, the two concepts become largely indistinguishable at this extreme. Indeed, the charge-transfer formulation provides new meaning to electrophilic cleavages, which has heretofore been a rather generic mechanistic description.[44]

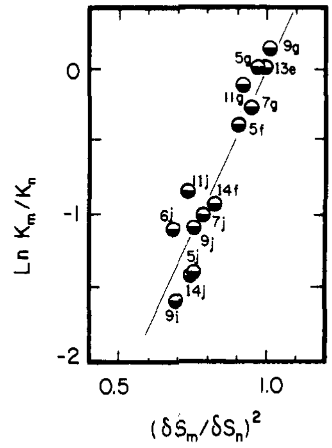


Figure 9. The solvent effect on the relationship according to eq 41 between the formation constant of the charge-transfer complex and the selectivity in the iodinolysis of various alkylmetals, identified as a number-letter referring to compounds in Table I and solvents in Table III (e.g., **7j** = n-$BuSnMe_3$ in C_6H_5Cl). The point labeled **13e** is a composite of compounds **5**, **6**, 7, **9**, **11**, and **14** in methylene chloride.

Summary and Conclusions

Charge-transfer (CT) complexes have been observed as transient intermediates in the iodinolysis of alkylmetals RM:

$$RM + I_2 \rightleftharpoons [RM \, I_2]$$

The properties of these CT complexes provide detailed information, heretofore unavailable, about the nature of the intimate interaction of alkylmetals with halogens such as iodine. Thus the charge-transfer interaction $h\nu_{CT}$ between various alkylmetals and iodine, which can be systematically probed by the proper choice of alkyl ligands with different donor and steric properties, relates the activation process for iodinolysis in Scheme II directly to the alkylmetal acting as an electron donor and iodine as an electron acceptor. This formulation allows a linear free energy relationship for halogenolysis to be established for the first time, since the magnitude of the steric effect can be quantitatively evaluated from the charge-transfer data.

According to the charge-transfer model for electrophilic cleavage, the product formation occurs subsequent to the rate-limiting charge-transfer reaction. As such, the selectivity is largely determined by the fragmentation pattern of the alkylmetal moiety in the ion pair, the mean separation being an important parameter which determines the fragmentation by controlling the magnitude of the resonance interaction between RM^+ and I_2^-. When the resonance interaction is large, the cleavage of an alkyl-metal bond is strongly influenced by the iodine acceptor. Under these circumstances the mechanistic distinction from that of a concerted electrophilic process becomes merged. Moreover, a mechanism described as electrophilic is a rather vague general description, mostly conveying a qualitative rather than a quantitative connotation, particularly with regard to the reactivity of the organometal, the selectivity in the cleavage, and the solvent effect. On the other hand, the charge-transfer formulation contains quantitative information in explicit terms. More importantly, it correctly predicts the inverse relationship between the rates and selectivity in iodinolysis insofar as they are mediated by solvent effects.

We hope that additional studies, particularly of the stereochemistry,[45-47] will provide further tests of the predictive value of the charge-transfer formulation.

Experimental Section

Materials. The preparations of the alkylmetals used in this study were described previously.[9] The solvents (chloroform, 1,2-dichloropropane, chlorobenzene, methanol, ethanol, and acetone) were reagent

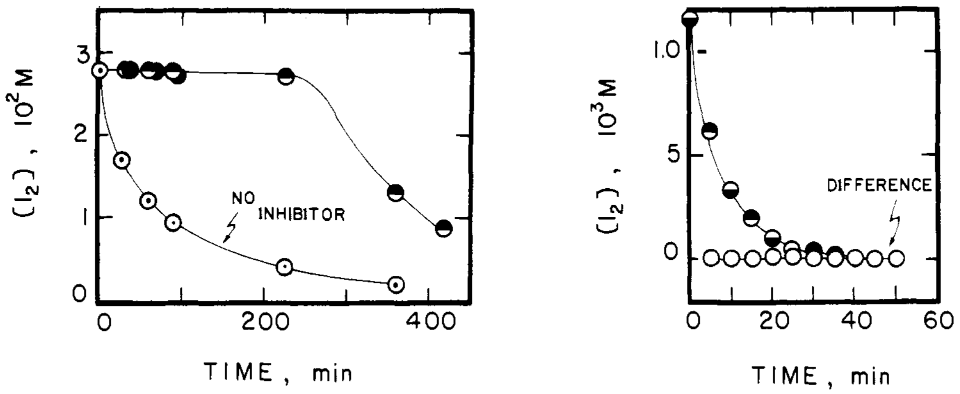


Figure 10. Effect of inhibitors on (a, left) the photochemical iodinolysis of 2.53 × 10^{-2} M *n*-BuSnMe$_3$ in CCl$_4$ [light intensity = 4.3 × 10^{-7} einstein L^{-1} min^{-1}]: ⊙, no inhibitor, ●, 2.22 × 10^{-2} M isoamyl nitrite; ○, 1.17 × 10^{-3} M galvinoxyl with 2.80 × 10^{-2} M iodine. (b, right) Thermal iodinolysis of 6.6 × 10^{-2} M *n*-BuSnMe$_3$ in CHCl$_3$ in the presence of either (◒) 2.22 × 10^{-2} M isoamyl nitrite or (○) 1.17 × 10^{-3} M galvinoxyl. The difference spectrum (see text) is given by ○.

grade materials obtained commercially and purified according to standard methods.[48] Acetonitrile (Mallinckrodt, analytical reagent) was stirred with calcium hydride overnight, filtered, treated with potassium permanganate, and then redistilled from P$_2$O$_5$ under a nitrogen atmosphere. Methylene chloride and carbon tetrachloride (Fisher Scientific Co., Spectranalyzed grade) were repurified by successive washings with concentrated sulfuric acid, followed by 5% aqueous sodium bicarbonate and distilled water. After drying over calcium sulfate they were redistilled from calcium hydride. Di-*n*-butyl ether was transferred in vacuo from a solution containing sodium benzophenone,

Kinetic Measurements. The iodinolysis of alkylmetals was carried out in a 10-mm quartz cuvette containing a solution of iodine (usually 5 × 10^{-4} to 2 × 10^{-3} M) in the appropriate solvent. After temperature equilibration in the thermostated compartment of a Cary 14 spectrophotometer, the reaction was started by injecting a known amount of alkylmetal (usually 1-100 μL) by means of a glass microsyringe. The addition was accompanied by vigorously shaking the cuvette, and carried out in the dark to avoid photochemical initiation. The course of iodinolysis was followed by the decrease in the iodine absorbance (e.g., in CCl$_4$, λ_{max} 520 nm, ϵ 900 M^{-1} cm^{-1}). Neither the organometals nor their products of iodinolysis absorb in this region.

To ensure that radical-chain reactions were not a complicating factor under these conditions, we carried out separate studies with inhibitors (galvinoxyl and isoamyl nitrite[46b]) in two ways. First, the efficiency of these inhibitors was established in the photochemical reaction of alkyltin and iodine, which is known to be a radical-chain process initiated by the photodissociation of iodine.[49] Next, the rate of the thermal reaction was compared with those in the presence of each of these inhibitors.

Inhibition of Photochemical Iodinolysis. Aliquots of a standard iodine solution (2.0 mL of 2.8 × 10^{-2} M) in carbon tetrachloride were transferred into three Pyrex tubes (10-mm i.d.). One tube contained no inhibitor, and the others contained either 2.22 × 10^{-2} M isoamyl nitrite or 1.17 × 10^{-3} M galvinoxyl. The same amount of *n*-BuSnMe$_3$ (2.53 × 10^{-2} M) was added to each tube, which was then sealed, placed in a precision merry-go-round apparatus,[50] and irradiated with a 100-W incandescent light bulb at ambient temperatures (30-35 °C). Samples (50 μL) were removed periodically and diluted to 3.0 mL and the iodine absorbance was measured. All transfers were carried out in the dark, and control experiments showed that thermal reactions were negligible in carbon tetrachloride solutions when carried out under these conditions. Figure 10a clearly shows that both galvinoxyl and isoamyl nitrite are effective inhibitors of the free radical chain iodinolysis. (Galvinoxyl reacts slowly with alkylmetals, which accounts for the induction period in Figure 10a.)

Effect of Inhibitors on the Thermal Iodinolysis. The effect of inhibitors on the thermal iodinolysis was examined in chloroform, methylene chloride, and chlorobenzene solutions by a spectral difference technique, in which the sample compartment of the spectrophotometer contained a solution of iodine and *n*-BuSnMe$_3$ with inhibitor, whereas the reference compartment contained an aliquot of the same solution without inhibitor. The optical transmission at 520 nm remained unchanged within 5% over the course in which the absolute concentration of iodine showed the characteristic exponential fall-off (Figure 10b). Thus, galvinoxyl and isoamyl nitrite do not affect the rate of iodinolysis of *n*-BuSnMe$_3$ under these thermal conditions. The same result was obtained with Et$_4$Sn in methylene chloride and chlorobenzene, using both inhibitors, as well as with *n*-Bu$_4$Sn and *i*-Bu$_4$Sn in methylene chloride, chloroform, and chlorobenzene using isoamyl nitrite as the inhibitor. The difference spectra occasionally exceeded ±10% (i.e., in the transmission) with the reactive Et$_4$Sn and *n*-Bu$_4$Sn, since it was difficult to manipulate the mixing of solutions in both compartments simultaneously. However, there was no consistent trend in the data to suggest an effect due to the presence of these inhibitors.

Selectivity Studies in the Cleavage of Alkylmetals. Selectivities in the iodinolysis of alkylmetals were obtained from the analysis of the organic iodides by gas-liquid chromatography or ^{1}H NMR spectroscopy. Typically, a solution of 0.10 M iodine was added to a 5-mL sample tube protected from light. After the tube was flushed with argon, sufficient alkylmetal was added to make a 0.12 M solution and the tube sealed. The reaction was carried out for minimal lengths of time (to ensure completion), which depended on the reactivity of the alklymetal as well as the solvent, e.g., from 10 to 60 min for alkyltin compounds in polar solvents and for alkyllead and mercury compounds in all solvents or from 10 to 20 h for alkyltin compounds in nonpolar solvents. Gas-liquid chromatography was carried out on a Varian 200 chromatograph using a tandem column consisting of a front section of 15 ft of 20% Apiezon L and 20% Carbowax on 20 60/80 Chromosorb P followed by 15 ft of 15% Apiezon L at 145 °C. Methyl iodide and the primary alkyl iodides were compared with authentic samples, and quantitative analysis was effected by the internal standard method using calibration curves as previously described.[25] Typical retention times for MeI, EtI, *n*-PrI, and *n*-BuI are 4.2, 6.0, 9.6, and 15.7 min, respectively, and vary slightly with the solvent. The ^{1}H NMR spectra of these alkyl iodides were also determined prior to analysis, which was carried out on either a Varian 220 or 60 MHz spectrometer by comparing the relative intensities of the proton resonances. The relevant proton resonances used in the analysis follow: MeI, δ 2.2 (s); EtI, δ 3.2 (q, J = 7 Hz), 1.9 (t, J = 7 Hz); *n*-PrI, δ 3.2 (t, J = 7 Hz); *n*-BuI, δ 3.2 (t, J = 7 Hz); *t*-BuI, δ 1.9 (s). For the tin products, Me$_n$SnR$_{3-n}$I: R = Me, δ 0.8 (s); Et, δ 1.3 (s), *t*-Bu, δ 1.3. The sensitivity is less than that obtained by GLC but showed good agreement when compared directly, e.g., S(Et/Me) of EtHgMe in methylene chloride is 2.85 by GLC analysis and 2.8 by ^{1}H NMR analysis. NMR analysis of *tert*-butyl iodide was necessitated owing to its thermal lability.

The cleavage of alkylmetals by hexachloroiridate(IV) was carried out at either 30 or 50 °C. Typically a solution of 0.2 M Na$_2$IrCl$_6$·6H$_2$O in acetonitrile-d_3 contained in an NMR tube was deaerated with a stream of argon, capped, and placed in a thermostated bath. An equimolar amount of alkylmetal was added and the reaction allowed to go to completion. The analysis of the alkyl chlorides from their ^{1}H NMR spectra was carried out as described previously.[25] The relevant ^{1}H resonances used in the analyses follow: MeCl, δ 3.0 (s); EtCl, δ 3.6 (q, J = 7 Hz), 1.5 (t, J = 7 Hz); *n*-PrCl, δ 3.6 (t, J = 7 Hz); *n*-BuCl, δ 3.6 (t, J = 7 Hz); *t*-BuCl, δ 1.5 (s). For the tin products, Me$_n$SnR$_{3-n}^+$: R = Me, δ 0.6 (s); Et, δ 1.2 (s); *t*-Bu, δ 1.2 (s). The values of S(R/Me) found for various alkyltins follow: EtSnMe$_3$, 10.2; Et$_2$SnMe$_2$, 11.0; Et$_3$SnMe, 10.4; *n*-PrSnMe$_3$, 9.2; *n*-Pr$_2$SnMe$_2$, 9.3; *n*-BuSnMe$_3$, 9.5; *n*-Bu$_2$SnMe$_2$, 9.7; *t*-Bu$_2$SnMe$_2$, ~25.

Spectral Measurements. The charge-transfer spectra in Figure 1 and the transition energies in Table I were reported previously.[9] All the alkylmetals were sufficiently volatile to record the photoelectron spectra in the gas phase.[14]

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Appendix I. Solvent Effects on the Rate and Mean Separation

According to Scheme II, the selectivity in iodinolysis is determined by the properties of the intimate ion pair, one of the critical factors being the mean separation r, as described above. The latter is introduced indirectly by considering the macroscopic effects of the solvent on the ion pair, as expressed by the Kirkwood formulation in eq 23. An alternative microscopic approach is to consider the solvent-induced changes as perturbations on the electrostatic potential, which are given by $\omega = -e^2/r$ in the gas phase. The same applies in solution since the effective dielectric constant saturates to a value of unity owing to the intimate nature of the ion pair. Accordingly, the change in the interaction energy for the ion pair from solvent m to solvent n is given by[31b]

$$\omega_{\mathrm{m}} - \omega_{\mathrm{n}} = -e^2/r_{\mathrm{m}} + e^2/r_{\mathrm{n}} \qquad (49)$$

The accompanying change in the activation free energy $\Delta G_{\mathrm{m}}^{\ddagger} - \Delta G_{\mathrm{n}}^{\ddagger}$ is represented in the rate constants, i.e., $-RT \ln k_{\mathrm{m}}/k_{\mathrm{n}}$. Since the iodinolysis of alkylmetals can be formulated as a linear free energy relationship in the ion pair (see eq 19 and 21), we equate these changes as

$$\Delta G_{\mathrm{m}}^{\ddagger} - \Delta G_{\mathrm{n}}^{\ddagger} = \omega_{\mathrm{m}} - \omega_{\mathrm{n}} \qquad (50)$$

or

$$RT \ln k_{\mathrm{m}}/k_{\mathrm{n}} = e^2/r_{\mathrm{m}} - e^2/r_{\mathrm{n}} \qquad (33)$$

Appendix II. Solvent Effect on the Selectivity and Mean Separation

According to eq 47, the selectivity ratio is given as

$$\delta S = \ln S_0/S = \mathcal{E}/RT \qquad (51)$$

From eq 44, 45, and 51, the mean separation $r^{\ddagger}$ is represented by

$$r^{\ddagger} = \ln(\mathcal{E}^0 S_r^0/RT) - \ln \delta S \qquad (52)$$

If the mean separations in solvents m and n are taken as r_{m} and r_{n}, respectively, the relative values from eq 52 are given as

$$r_{\mathrm{n}} - r_{\mathrm{m}} = \ln \delta S_{\mathrm{m}}/\delta S_{\mathrm{n}} \qquad (53)$$

or

$$\delta S_{\mathrm{m}}/\delta S_{\mathrm{n}} = \exp(r_{\mathrm{n}} - r_{\mathrm{m}}) \qquad (35)$$

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(19) A kinetic alternative to Scheme I should be mentioned here, since it is commonly asked whether a complex is a precursor as in eq 10 or an unrelated side reaction as in

$$[\mathrm{RM\,I_2}] \xrightleftharpoons{K_{\mathrm{CT}}} \mathrm{RM} + \mathrm{I_2} \xrightarrow{k_1} \mathrm{RI} + \mathrm{MI}$$

The difference lies in whether the rate-limiting, second-order rate constant is a product $k = K_{\mathrm{CT}}k_1$ (eq 10) or a simple bimolecular rate constant $k = k_1$, although the two processes are kinetically indistinguishable.[20] It is noteworthy that the formation constant (log K_{CT}) for alkylmetal–iodine CT complexes listed in Table I parallels the rate constant (log k) for iodinolysis in Table II. The same trend between K_{CT} and k has been observed with the analogous alkylmetal–tetracyanoethylene complexes, in which it could be shown independently by photochemical pumping that the CT complex is an intermediate in the thermal reaction (insertion).[21] Such parallel relationships show that structural properties which promote CT complex formation are essentially the same as those involved in surmounting the activation barrier, i.e., there is a linear free energy relationship between the two. In other words, factors involved in complex formation are directly reflected in the transition states for iodinolysis and TCNE insertions in basic accord with Scheme I.

(20) This mechanistic distinction is actually dubious and possibly even meaningless, as also previously pointed out by Colter, A. K.; Dack, M. R. J. In "Molecular Complexes", Foster, R., Ed.; Crane Russak & Co.: New York, 1974; Vol. 2, p 2 f.

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(24) Hereafter, for brevity we employ the notation ΔG_r° and $\Delta G_r^{\ddagger}$ to indicate free-energy changes relative to a reference, rather than the more conventional, but cumbersome, $\Delta\Delta G^\circ$ and $\Delta\Delta G^{\ddagger}$.

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(26) (a) Although this equation may appear arbitrary, it is based on the reasonable formulation that *changes* in the mean separation parameter for the charge-transfer complexes are reflected by a corresponding *change* in the activated complexes (see note 23). However, its further application does not depend on this picture, since eq 19 derives purely from a phenomenological treatment. (b) Importantly, the comparative definition of ΔE in eq 15 minimizes solvation terms by cancellation, especially as it applies to donors with similar structures as given by the series of alkylmetal used in this study.

(27) Since ΔG_r° and ΔE are both rather large quantities, the linear free energy relationships are plotted in the figure as $-\Delta G_r^{\ddagger} + \Delta E$ and $-\Delta G_r^\circ$ for clarity.

(28) As described in note 25, the measurements depend on the electron transfer reactions with iron(III) complexes which are unfortunately insoluble in nonpolar media.

(29) The effects of solvation on $\Delta G_r°$ decrease in the less polar solvents.

(30) (a) It is noteworthy that the α values for the best fit to the experimental data are $\alpha(CH_3CN) = 0.55$ and $\alpha(CH_2Cl_2) = 0.66$, which compare well with the independently determined values of $\alpha(CH_3CN) = 0.60$ in eq 17 and $\alpha(CH_2Cl_2) = 0.71$ in Figure 5a. (b) The deviations of the calculated lines for *n*-Bu$_4$Sn and *sec*-Bu$_4$Sn from the experimental points are due to errors in the determinations of either I_D or $h\nu_{CT}$, or both, since they occur by the same amounts in the same direction and considerable scatter is also found for these alkyltins in Figure 4. Indeed, a change of ΔE by only 0.03 and 0.08 eV for n-Bu$_4$Sn and *sec*-Bu$_4$Sn, respectively, is required to fit the experimental data like other R$_4$Sn in the figure. (c) Essentially the same analysis can be employed to account for the solvent effect on the *brominolysis* of these alkylmetals studied earlier.[16a] For Et$_4$Sn and *n*-Pr$_4$Sn, the values of $\Delta E(Br_2)$ are 10.2 and 11.9 kcal mol^{-1}, which compare with 10.8 and 12.7 kcal mol^{-1}, respectively, for iodinolysis [Fukuzumi, S., unpublished results].

(31) (a) The change $\Delta E = \omega - \omega_0$ is considered to be largely a steric effect since it consists mainly of Coulombic terms,[9] inversely proportional to the mean separation. The other terms in the interaction energy also probably depend on the mean separation, either directly or indirectly. (b) Solvents have relatively minor effects on ΔE (additional studies in progress).

(32) For a general theory of solvent polarities, see: Abboud, J.-L. M.; Taft, R. W. *J. Phys. Chem.* **1979,** *83*, 412.

(33) (a) The change in solvation energy is defined as $\Delta E_{solv} = RT \ln k/k_r$ where k refers to the rate constants in Table V for *n*-BuSnMe$_3$, and k_r is that in methylene chloride, chosen as a reference solvent. The rate constant in CCl$_4$ was estimated from the selectivity in Table III using eq 36. (b) The dipole moment is $\mu^{\ddagger} = -\alpha e r^{\ddagger}$ where α is the degree of charge separation in the transition state. From the slope in Figure 7, $\alpha = [(\text{slope})a^3/(er^{\ddagger})^2]^{1/2}$. The value of $r^{\ddagger}$ is taken as 3.7 Å from $\bar{r}_{mn}$ (as described in note 40) and $e^2 = 14.4$ eV Å. When $a = 1.1\bar{r}_{mn}$, $\alpha = [3.0(1.1)^3(3.75)/14.4]^{1/2} = 1$. The lower limit is obtained when $a = \bar{r}_{mn}$, and then $\alpha = 0.8$.

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(39) Compare Martino, G.; Jungers, J.-C. *Bull. Soc. Chim. Fr.* **1970,** 3392. Reference 3, p 172 ff.

(40) Since the slope is $(r_m r_n RT)^{-1}$, the mean value of r_m and r_n is $\bar{r}_{mn} = (r_m r_n)^{1/2} = a_H(RT\cdot\text{slope})^{-1/2}$, where a_H is the Bohr radius taken as 0.5292 Å and RT is in atomic units.

(41) For Et$_2$SnMe$_2$ and *t*-Bu$_2$SnMe$_2$, $\Delta E = -\Delta I_D + \Delta h\nu_{CT} = (9.01 - 8.22) - (4.49 - 4.10) = 0.40$ eV from eq 15 and Table I, and $\Delta e^2/r_{mn} = e^2(1/3.7 - 1/4.1) = 0.37$ eV. (b) It is noteworthy that the solvent effect on the iodinolysis of an alkylmetal as described in eq 23 and 36 derives from two independent approaches. (The detailed implications merit further consideration.) Both of these treatments dealing with the *absolute* reactivities of alkylmetals are to be compared with the treatment in eq 21 (Figure 6) which accounts for the solvent effects on the *relative* reactivities. Together, they should allow a general description of solvents effects (studies in progress).

(42) Such a comparison also focuses on the ion-pairing energies since the electrostatic potential in the ion pair in eq 42 is repulsive whereas it is clearly attractive in eq 43.

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Vertical and "Nonvertical" Energy Transfer Processes. A General Classical Treatment

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Abstract: A classical treatment of exchange energy transfer processes in fluid solution is given, which parallels that already used for electron transfer quenching processes. This treatment is based on a model which does not require violation of the Franck-Condon principle, nor the use of ill-defined concepts such as "nonvertical" energy transfer or "phantom" excited states. Making use of absolute reaction rate theory and of recently proposed relationships between free-energy change and free activation energy, a general equation is obtained for the experimental quenching constant. Unlike the well-known Sandros equation, the equation derived in this paper provides a unified view of the so-called vertical and nonvertical energy transfer behavior, and it can also account for the lower than diffusion rates of energy-transfer processes in the exoergonic region. The meaning and limitations of such a classical treatment are critically examined and the relationships between spectroscopic and thermodynamic parameters are discussed. The validity of the proposed treatment is tested on the literature data for energy transfer from aromatic triplets to *cis*- and *trans*-stilbene, ferrocene and ruthenocene, biacetyl and *o*-anisil, and β-diketonatoiron(III) complexes.

I. Introduction

In fluid solution, energy-transfer processes

$$*D + A \xrightarrow{k^{en}_q} D + *A \qquad (1)$$

involving exchange interaction occur with a maximum rate that is equal to the rate of encounters between excited donors and acceptors.[2a] When the donor has insufficient excitation energy to promote the acceptor to its excited state (endothermic en-

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