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Electron-Transfer Activation in Electrophilic Mechanisms. Cleavage of Alkylmetals by Mercury(II) Complexes

S. Fukuzumi and J. K. Kochi*

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405. *Received May 16, 1980*

Abstract: The disappearance of the transient charge-transfer (CT) absorption bands coincides with the electrophilic (S_E2) cleavage of a homologous series of alkyltin compounds by various mercury(II) halides, cyanide, and carboxylates. The second-order kinetics for $HgCl_2$ cleavages afford rate constants which vary in a rather unaccountable way with the structure of the alkyltin compound and with the polarity of the solvent. Furthermore, the relative reactivities of these alkyltin compounds in the analogous electrophilic cleavage by I_2 or Br_2 show poor correlations with $HgCl_2$ cleavages, in different solvents. However, the description of the activation process as an electron transfer in the precursor complex, e.g., $[R_4Sn\ HgCl_2] \rightarrow [R_4Sn^+\ HgCl_2^-]$, stems from the CT transition energy and leads to a linear free energy relationship in which the activation free energy is equal to the driving force for the formation of the ion pair. The latter is readily dissected by eq 18 into separate changes in electronic, steric and solvation energies. With this mechanistic formulation, the reactivities of various alkyltin compounds follow a remarkably simple linear correlation with the ionization potentials and the solvent effects, in the comparison with I_2 and Br_2 cleavages. Moreover, the reactivities of the various mercury(II) derivatives relate directly to differences in their electron affinities.

Introduction

A wide variety of both organic and inorganic reactions involving substitution, addition, displacement, etc., proceed by what are commonly referred to as electrophilic mechanisms. This designation is highly qualitative, and there are few viable measures of an *electrophilic* mechanism, although empirical relationships have been developed. In particular, there is surprisingly little quantitative information known about either the structural factors or the solvent effects important in the activation process for any electrophilic process.

Alkylmetals offer a number of advantages as prototypes for the study of electrophilic cleavage reactions. As electron-rich species they are susceptible to a wide variety of electrophiles, and the per-alkyl derivatives of the group 4A elements are substitution inert and well behaved in solution for kinetic studies.

Mercury(II) derivatives are commonly considered to effect the cleavage of alkyl–metal bonds by electrophilic pathways,[1,2] the descriptions of which are still the subject of controversy, largely revolving around the depiction of the transition states—whether they are two or four centered, open, cyclic, etc.

We wish to present an alternative approach to the study of electrophilic mechanisms, which focuses on the quantitative evaluation of the activation barrier. The phenomenological method relies on the charge-transfer (CT) transition energy in the electron donor–acceptor complex which precedes the rate-limiting activation process. Thus the observation of the novel CT absorption bands between mercury(II) complexes and tetraalkyltin compounds described in the foregoing study[3] offers an excellent opportunity to develop more mechanistic insight of an electrophilic process.

Results

The products and stoichiometry of the electrophilic cleavage of organometals by various mercury(II) derivatives have been well established.[1,2] As applied to the reactions of tetraalkyltin compounds and mercuric chloride, the heterolysis is represented by eq 1. A careful spectral examination of the mercury(II) cleavage

$$HgCl_2 + R_4Sn \rightarrow RHgCl + R_3SnCl \qquad (1)$$

in eq 1 revealed the growth of a *transient* charge-transfer band immediately upon mixing the components.[3] The absorption maximum λ_{max} varied between 230 and 260 nm, depending on the tetraalkyltin compound in accord with the properties of the electron donor–acceptor complexes in eq 2, as shown in Figure 1. The absorbance $\mathcal{A}$ of the CT absorption band, which is

$$HgCl_2 + R_4Sn \overset{K_{DA}}{\rightleftharpoons} [HgCl_2\ R_4Sn] \qquad (2)$$

proportional to the concentration of each component, is given by eq 3, where ϵ is the extinction coefficient. The decay of this transient CT absorption band coincides with the electrophilic cleavage in eq 1, as described below.

$$\mathcal{A} = \epsilon K_{DA}[R_4Sn][HgCl_2] \qquad (3)$$

Kinetics of Mercury(II) Cleavage of Alkyltin. The rate studies were carried out by following the disappearance of mercury(II) derivative which was analyzed by converting it quantitatively to the triiodomercurate(II) ions. Thus aliquots, periodically extracted from the reaction mixture, were quickly quenched with a solution containing excess potassium iodide, and the HgI_3^- determined spectrophotometrically at 301.5 nm according to the method described by Abraham and co-workers.[4] This kinetic technique compares favorably with that involving the direct observation of the CT band (vide supra). As an example, for the system consisting of $HgCl_2$ and excess n-Bu_4Sn, the pseudo-first-order rate of disappearance of the CT band at λ_{max} 255 nm with a constant of $5.8 \times 10^{-5}\ s^{-1}$ is essentially the same as that ($5.6 \times 10^{-5}\ s^{-1}$) measured by following the decrease in the $HgCl_2$ concentration. Since λ_{max} of the CT band was somewhat complicated by the absorbance from the products of the cleavage reaction, the kinetic studies were usually carried out by following the disappearance of $HgCl_2$. As shown in Figure 2 (left), the disappearance of $HgCl_2$ in the presence of excess Et_4Sn follows first-order kinetics for several half-lives. The pseudo-first-order rate constants obtained from the slopes are proportional to the initial concentrations of the tetraalkyltin compounds examined in Figure 2 (right). (It is noteworthy that there is no perceptible curvature in Figure 2 (right), similar to the plots of the CT absorbance as a function

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[1] (a) Matteson, D. S. "Organometallic Reaction Mechanisms"; Academic Press: New York, 1974. (b) Reutov, O. A.; Beletskaya, I. P. "Reaction Mechanism of Organometallic Compounds"; North-Holland Press: Amsterdam, 1968. (c) Jensen, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials"; McGraw-Hill: New York, 1968. (d) Kochi, J. K. "Organometallic Mechanism and Catalysis"; Academic Press: New York, 1978; Chapter 18, p 542.

[2] (a) Abraham, M. H. In "Comprehensive Chemical Kinetics", Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1973; Chapter 6, p 70. (b) Gielen, M.; Nasielski, J. In "Organotin Compounds"; Sawyer, A. K., Ed.; Marcel Dekker: New York, 1972; Vol. 3, p 653. (c) Seyferth, D. *J. Organomet. Chem.* **1979**, *176*, 137; *177*, 141. (d) For a recent review see: *Organomet. Chem.* **1978**, *7*.

[3] Fukuzumi, S.; Kochi, J. K., *J. Phys. Chem.*, submitted for publication.

[4] Abraham, M. H.; Johnston, G. F.; Spalding, T. R. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2167.

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Table I. Reactivity of Tetraalkyltin Compounds in Electrophilic Cleavages by Mercuric Chloride in Different Solvents[a]

				second-order rate constant, M^{-1} s^{-1}		
no.	R_4Sn	I_D,[d] eV	$h\nu_{CT}$,[e] eV	CH_3CN	CH_2Cl_2	MeOH
1	Me_4Sn	9.69	5.27	2.4	6.6×10^{-2}	1.6[b]
2	Et_4Sn	8.90	5.08	1.6×10^{-2}	1.7×10^{-3}	3.3×10^{-3} [b]
3	n-Pr_4Sn	8.82	5.10	3.7×10^{-3}	9.0×10^{-4}	6.3×10^{-4} [b]
4	n-Bu_4Sn	8.76	5.12	3.8×10^{-3}	1.4×10^{-3}	6.2×10^{-4} [b,c]
5	n-$BuSnMe_3$	9.10	5.17	1.1	0.10	1.0
6	n-Bu_2SnMe_2	8.80	5.02	0.50	0.15	0.64
7	i-Pr_2SnMe_2	8.56	4.98	2.5	0.13	0.23
8	t-Bu_2SnMe_2	8.22	4.86	4.6×10^{-2}	2.6×10^{-2}	1.4×10^{-3}
9	i-Bu_4Sn	8.68	5.10	5.6×10^{-4}	3.7×10^{-4}	8.0×10^{-5} [b]
10	i-Pr_4Sn	8.46	5.14	5×10^{-6}	3×10^{-6}	2×10^{-8} [b]
11	s-Bu_4Sn	8.45	5.12	7×10^{-7}	8×10^{-7}	

[a] At 25 °C. [b] Taken from ref 5. [c] Under our conditions, $k = 7.0 \times 10^{-4}$ M^{-1} s^{-1}. [d] From ref 7. [e] From ref 3.

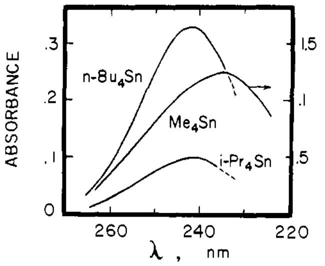

Figure 1. Charge-transfer spectra of mercury(II) chloride complexes with some tetraalkyltin compounds in acetonitrile at 25 °C: $[Me_4Sn]_0 = 4.90 \times 10^{-3}$ M, $[HgCl_2]_0 = 2.50 \times 10^{-3}$ M; $[n\text{-}Bu_4Sn]_0 = 2.02 \times 10^{-2}$ M; $[HgCl_2]_0 = 5.00 \times 10^{-3}$ M; $[i\text{-}Pr_4Sn]_0 = 1.00 \times 10^{-2}$ M, $[HgCl_2]_0 = 1.00 \times 10^{-2}$ M. See ref 3 for details.

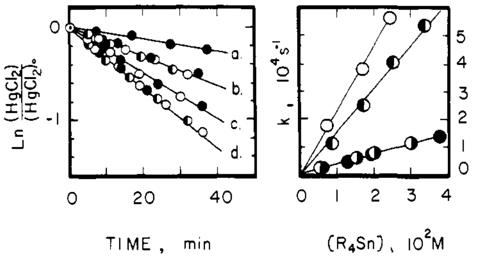

Figure 2. Left: Kinetics of the electrophilic mercury(II) cleavage of tetraalkyltin compounds in acetonitrile at 25 °C containing $[HgCl_2]_0$ (●, 1.00×10^{-2} M; ○, 5.00×10^{-3} M; ◐, 3.30×10^{-3} M) and $[Et_4Sn]_0$ (a, 8.40×10^{-3} M; b, 1.68×10^{-2} M; c, 2.51×10^{-2} M; d, 3.35×10^{-2} M). Right: Pseudo-first-order rate constant as a function of the initial alkyltin concentration at 25 °C. Symbols: ●, n-Pr_4Sn in MeCN; ◑, n-Bu_4Sn in MeCN; ◐, Et_4Sn in MeCH; ○, t-Bu_2SnMe_2 in CH_2Cl_2.

of the initial concentrations of the alkyltin given in eq 3). The kinetics of the electrophilic cleavage of alkyltin is well described by the second-order expression in eq 4. The rate constants were also measured under actual second-order conditions by using equimolar amounts of the tetraalkyltin compound and the mercury(II) derivative, as described further in the Experimental Section.

$$\frac{-d[HgCl_2]}{dt} = k[R_4Sn][HgCl_2] \qquad (4)$$

Reactivities for a Series of Tetraalkyltin Compounds. The second-order rate constants k are tabulated in Table I for the cleavage of various tetraalkyltin compounds with $HgCl_2$, for which the charge transfer data are available from the preceding study.[3] The rate constants obtained in methylene chloride and methanol are also included, together with some data reported earlier by Abraham and Johnston in methanol.[5] The rate constants in the polar acetonitrile (ϵ_B 37.5[6]) are somewhat larger than those in methanol (ϵ_B 32.65) and significantly larger than those in the least polar methylene chloride (ϵ_B 9.08). This trend in the solvent effect is also observed in dioxane as well as in a mixed solvent consisting of 2:1 v/v n-hexane and methanol in which the second-order rate constants are $<10^{-7}$ and 3.2×10^{-4} M^{-1} s^{-1}, respectively, for the cleavage of n-Bu_4Sn by $HgCl_2$ at 25 °C.

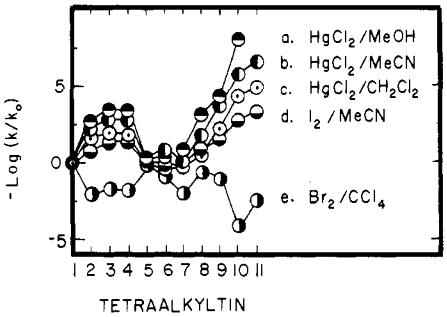

Figure 3. The reactivity patterns in the electrophilic cleavage of tetraalkyltin compounds with various electrophiles in different solvents: (a) $HgCl_2$ in methanol, (b) $HgCl_2$ in acetonitrile, (c) $HgCl_2$ in methylene chloride, (d) iodine in acetonitrile,[8] (e) bromine in carbon tetrachloride.[9] Alkyltin compounds as numbered in the abscissa are identified in Table I.

The reactivities of the tetraalkyltin compounds toward $HgCl_2$ cleavage in acetonitrile span a range of almost 10^7 in rates and are somewhat attenuated in methylene chloride. In order to compare these tetraalkyltin compounds, we describe the *relative reactivity* as the ratio of the second-order rate constants k/k_0 for a given alkyltin relative to that of the reference Me_4Sn. The relative reactivity $-(\log k/k_0)$ for $HgCl_2$ cleavage in various solvents is plotted in parts a–c of Figure 3 for various tetraalkyltin compounds. For comparative purposes, the relative reactivities for the electrophilic cleavage of the same series of alkyltin compounds with iodine[8] and bromine[9] are also included in Figure 3. The complex reactivity patterns of alkyltin compounds depend on both the acceptor as well as the solvent, and no easily definable trend can be discerned in this plot of the data. Furthermore the trends in the relative reactivities of the alkyltin compounds change markedly, even undergoing inversions from system to system. For example, i-Pr_4Sn can be 10^8 times *less* reactive than Me_4Sn toward $HgCl_2$ cleavage in Figure 3a, but i-Pr_4Sn is 10^3 times *more* reactive than Me_4Sn for bromine cleavage in Figure 3e. Moreover, a change in solvent from methylene chloride to methanol is sufficient to alter the relative reactivity of i-Pr_4Sn by a factor of 10^4. Clearly, the acceptor as well as the solvent have important, but apparently unpredictable, bearing on the relative reactivities of the various tetraalkyltin compounds. Such a complex pattern for the reactivities of various tetraalkyltin compounds is further emphasized

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(5) Abraham, M. H.; Johnston, G. F. *J. Chem. Soc. A* **1970**, 193.

(6) The dielectric constants ϵ_B are from: Koppel, I. A., Palm, U. A. "Advances in Linear Free Energy Relationships", Chapman, N. B., Shorter, Y. Eds.; Plenum Press: London, 1972, Chapter 5.

(7) Wong, C. L.; Mochida, K.; Gin, A.; Weiner, M. A.; Kochi, J. K. *J. Org. Chem.* **1979**, *44*, 3979.

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(10) Since the rate constants for R_4Sn (no. **7–10**) with I_2 are not available, the rate constants in EtOH(O) are used here from ref 17.

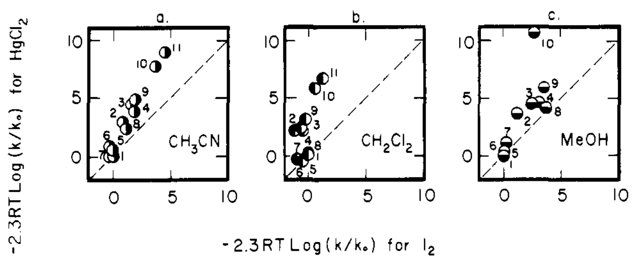


Figure 4. Comparison of the relative reactivities of tetraalkyltin compounds in cleavage by $HgCl_2$ and in iodinolysis[8] in (a) acetonitrile, (b) methylene chloride, and (c) methanol.[10] The dashed lines are drawn with slopes of unity to emphasize the deviations.

Table II. Reactivity of Various Mercury(II) Derivatives in the Electrophilic Cleavage of Me_4Sn and n-Bu_4Sn[a]

	second-order rate constant, $M^{-1}\,s^{-1}$	
mercury(II) derivative	Me_4Sn	n-Bu_4Sn
(a) $HgCl_2$	6.6×10^{-2}	1.4×10^{-3}
(b) $HgBr_2$	1.2×10^{-2}	4.8×10^{-4}
(c) $Hg(CN)_2$	0.48	2.5×10^{-3}
(d) $Hg(O_2CMe)_2$	0.33	7.4×10^{-3}
(e) $Hg(O_2CCHMe_2)_2$	5.4×10^{-2}	9.1×10^{-3}
(f) $Hg(O_2CCMe_3)_2$	3.5×10^{-2}	5.9×10^{-2}
(g) $Hg(O_2C$-n-$Bu)_2$	8.2×10^{-2}	3.8×10^{-2}
(h) $Hg(O_2CCH_2Cl)_2$	1.6	8.9×10^{-3}
(j) $Hg(O_2CCHCl_2)_2$	4.8×10^{-2}	8.3×10^{-4}
(k) $Hg(O_2CCHF_2)_2$	40	50
(l) $Hg(O_2CCF_3)_2$	2.6×10^{2}	1.6×10^{2}

[a] In CH_2Cl_2 solution at 25 °C.

by the solvent effect in the comparison of $HgCl_2$ cleavage to I_2 cleavage. Thus parts a–c of Figure 4 show that the relative reactivity of tetraalkyltin to $HgCl_2$ cleavage is different from that in iodine cleavage, even for reactions carried out in the same solvent, as indicated by the deviations from the dashed lines drawn with a slope of unity. The degree to which deviations occur from the unit slopes in the figures also depends on the solvent, appearing to be the most pronounced in CH_2Cl_2.

Reactivity of Various Mercury(II) Electrophiles. The influence of the ligand X on the reactivity of mercury(II) derivatives HgX_2 as electrophiles was examined in the cleavage of two tetraalkyltin compounds

$$HgX_2 + R_4Sn \rightarrow R_3SnX + RHgX \tag{5}$$

where R = methyl and n-butyl. The mercury(II) electrophiles consisted of a series of halo, cyano, and carboxylate derivatives listed in Table II. The reactions with the iodo derivative were complicated by metathesis of the product in eq 6[11] and were not examined further.

$$R_3SnI + HgI_2 \rightleftharpoons R_3Sn^+\ HgI_3^- \tag{6}$$

With each mercury(II) derivative, the rate of the electrophilic cleavage measured by the disappearance of Hg(II) followed the second-order kinetics in eq 4 (see Experimental Section). The immediate, initial increase in the absorbance was observed in each case, but the maximum λ_{max} of the CT band was obscured by its overlap with the tail of the HgX_2 absorption band (except for $HgCl_2$).

The second-order rate constants for the cleavage of Me_4Sn and n-Bu_4Sn span a range of more than 10^5 and depend on the mercury(II) electrophile—$HgBr_2$ being the least reactive and $Hg(O_2CCF_3)_2$ the most reactive in qualitative accord with their Lewis acidity.[12] In order to quantitatively evaluate the relationship

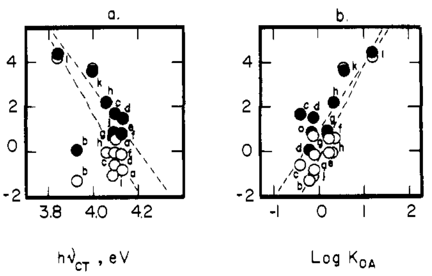
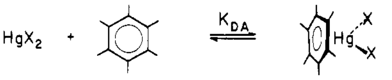


Figure 5. Relationship of the rate constants (log k) for the cleavage of alkyltin compounds by $HgCl_2$ with (a) the CT transition energy and (b) the formation constant of the $[HgX_2\ HMB]$ complex. Letters refer to the HgX_2 derivatives in Table II with (●) Me_4Sn and (○) n-Bu_4Sn. For the significance of the lines, see text.

between reactivity of a mercury(II) electrophile and its acceptor ability, we compared the rate constants (log k) with (1) the charge-transfer transition energies $h\nu_{CT}$ and (2) the formation constants K_{DA} of the donor–acceptor complexes with hexamethylbenzene[3] in parts a and b of Figure 5, respectively (see eq 7). If only the related family of mercury(II) carboxylates $Hg(O_2CR)_2$ are considered, the least-squares treatment of the data yields a correlation with the transition energies as



(7)

$$\log k = -ah\nu_{CT} + b \tag{8}$$

where $a = 14$ and $b = 56$ for Me_4Sn with $\rho = 0.82$ and $a = 17$ and $b = 70$ for n-Bu_4Sn with $\rho = 0.90$. Similarly, the least-squares treatment of the data in Figure 5b for the formation constants is

$$\log k = c \log K_{DA} + d \tag{9}$$

where $c = 3$ and $d = -1$ for Me_4Sn with $\rho = 0.82$ and $c = 4$ and $d = -2$ for n-Bu_4Sn with $\rho = 0.90$. Although these correlation coefficients ρ are not high, they are sufficient to point out the qualitative trend for log k to parallel both $-h\nu_{CT}$ and log K_{DA}, as evaluated for the donor–acceptor complexes.

Discussion

Any mechanism for electrophilic cleavage must resolve not only the complex reactivity patterns of the series of alkyltins presented in Figure 3, but it must also accommodate the relationship between the reactivity of various mercury(II) derivatives and the properties of the donor–acceptor complex shown in Figure 5. Furthermore, if this mechanistic description is to have any general value, it must also relate to the mechanism of halogen cleavage, e.g.

$$R_4Sn + Br_2 \rightarrow R_3SnBr + RBr$$

which is another common example of an electrophilic process.[1,2] Indeed our earlier charge-transfer formulation for the halogenolysis of alkylmetals[8] coincides with the observation of similar spectral transitions with mercury(II) electrophiles. In the following discussion, we wish to show how the incorporation of charge-transfer concepts can resolve the difficult problems of reactivity and solvent effects in electrophilic cleavages quantitatively. Moreover the method allows the mercury(II) cleavages and halogenolysis to evolve naturally from a single, unifying point of view.

Charge-Transfer Transition Energies and the Activation Process for Electrophilic Cleavage. In an early attempt to codify electrophilic mechanisms, Abraham and Hill[13] described a S_EC process (subsitution, electrophilic via coordination), although it was recognized that the existence of the complex by kinetic techniques was not possible—some attempts notwithstanding.[13,14] Our ap-

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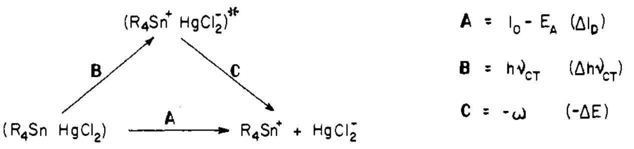
(11) Abraham, M. H.; Spalding, T. R. *J. Chem. Soc. A* **1968**, 2530.

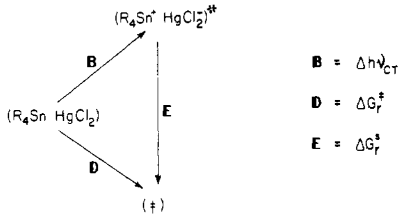
(12) (a) Qualitatively, the acceptor ability of the mercury carboxylate derivatives can be estimated by the acidity of the corresponding carboxylic acid. The acidity of the carboxylic acid in the gas phase defined as $\Delta G°$ $(RCOOH \rightarrow RCOO^- + H^+)$ is the lowest for CH_3CO_2H and the highest for CF_3CO_2H (25.2 kcal mol^{-1} higher than CH_3CO_2H). (b) McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 3399.

(13) (a) Abraham, M. H.; Hill, J. A. *J. Organomet. Chem.* **1967**, *7*, 11. (b) Abraham, M. H.; Sedaghat-Herati, M. R. *J. Chem. Soc., Perkin Trans. 2* **1978**, 729. (c) Hashimoto, H.; Morimoto, Y. *J. Organomet. Chem.* **1967**, *8*, 271. (d) Bott, R. W.; Eaborn, C.; Waters, J. A. *J. Chem. Soc.* **1963**, 681.

Scheme I



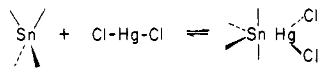
Scheme II



proach to the mechanism stems from the observation of the charge-transfer absorption spectra, since it demonstrates for the first time the actual existence of $[R_4Sn\ HgCl_2]$ complexes. According to the Mulliken formulation, the relationship between the charge-transfer transition and the energetics of the redox processes for the electron donor and acceptor pair [i.e., $R_4Sn \xrightarrow{-e^-} R_4Sn^+$ and $HgCl_2 \xrightarrow{+e^-} HgCl_2^-$, as measured in the gas phase by the ionization potential I_D and the electron affinity E_A, respectively] is expressed by Scheme I.[15] (The energy change in parentheses refers to the comparative method to be described later.) The asterisk identifies an excited ion pair arising from a vertical (Franck–Condon) excitation, which involves essentially no change in either the mean separation r_{DA} or the solvent coordination extant in the neutral ground-state complex. It follows from the energetics of paths **A** and **B** in the cyclic scheme (Scheme I) that the interaction energy ω in the excited ion pair (path **C**) is given by eq 10. For weak

$$h\nu_{CT} = I_D - E_A + \omega \tag{10}$$

complexes of the type $[R_4Sn\ HgCl_2]$, the interaction energy consists mainly of the Coulombic attraction $-e^2/r_{DA}$ within the excited ion pair $[R_4Sn^+\ HgCl_2^-]^*$. In a recent study we showed that the magnitude of r_{DA} can vary in a series of $[R_4Sn\ HgCl_2]$ complexes as a result of changes in the steric properties of the alkyl ligands, most likely owing to the distortion of the normally tetrahedral tetraalkyltin to a trigonal-bipyramidal configuration and the bending of the linear $HgCl_2$ in the complex, i.e., eq 11.[3]



(11)

In order to evaluate these and other effects quantitatively, we employ the *comparative method* and relate ω for various alkyltin compounds to ω_0 of the least sterically hindered Me_4Sn, chosen as a reference. According to eq 10, the energy change $\Delta E = \omega - \omega_0$ is then given by eq 12, where ΔI_D is the difference in the

$$\Delta E = -\Delta I_D + \Delta h\nu_{CT} \tag{12}$$

ionization potentials between a particular tetraalkyltin and Me_4Sn and $\Delta h\nu_{CT}$ is the difference in the CT energies in the $HgCl_2$ complexes listed in Table I. By utilizing the comparative method, all changes in the interaction energies of these complexes, including steric, distortional, and other effects, are compositely expressed in a single energy term ΔE which can be evaluated directly from the experimental data according to eq 12.[16]

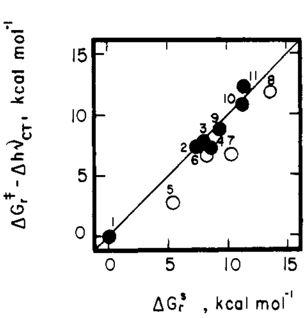


Figure 6. Relationship between $(\Delta G_r^{\ddagger} - \Delta h\nu_{CT})$ for $HgCl_2$ cleavages with the changes in the relative solvation energies of various alkyltin compounds identified in Table I. The line is drawn with a slope of unity for emphasis only.

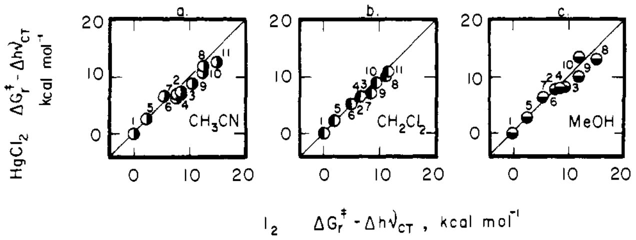


Figure 7. Correlation of the activation free energy for the electrophilic cleavage of various alkyltin compounds by $HgCl_2$ and by I_2, after the inclusion of the CT transition energy for the corresponding complexes in (a) acetonitrile, (b) methylene chloride, and (c) methanol. Note the fit to the lines arbitrarily drawn with slopes of unity. Compare with Figure 4.

We now examine the relationship between the relative rates of electrophilic cleavages of various alkyltin by $HgCl_2$ in eq 1 and the charge-transfer transition within the complex as described by path **B** in Scheme I. The relative activation free energy is expressed in eq 13, where k refers to the rate constant in eq 4 and

$$\Delta G_r^{\ddagger} = -2.3RT \log k/k_0 \tag{13}$$

k_0 to that for the Me_4Sn reference. The subscript r emphasizes that all energy changes are evaluated relative to this reference alkyltin. The thermal path **D** to the transition state for the electrophilic cleavage, denoted as $(\ddagger)$,[18c] is then related to the charge-transfer transition in path **B** by a second thermochemical cycle, represented as Scheme II. Since path **E** in Scheme II relates the charge-transfer state and the transition state, it follows that the energetics are described by the difference between path **D** and path **B**, viz., $(\Delta G_r^{\ddagger} - \Delta h\nu_{CT})$. Figure 6 shows that the energetics of path **E** are identical with the relative solvation energies ΔG_r^{s}

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[14] (a) The question of whether such complexes are intermediates along the reaction pathway, or some extraneous artifact, has been treated at length in ref 8 and 21a. It is important to emphasize that the following mechanistic treatment does not depend on whether such complexes can be proved as being the reactive intermediates. (b) In these weak complexes, values of $\Delta G_{CT}°$ are negligible.[3]

[15] (a) Mulliken, R. S.; Person, W. B. "Molecular Complexes"; Wiley-Interscience: New York, 1969. (b) Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: New York, 1969. (b) For an elaboration see ref 8. (c) The heat of formation of the complex is omitted in path **A** since it is negligible.[3]

[16] (a) For previous applications of the steric effect in electron transfer reactions, see: Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928 and ref 9. (b) Such a correction is tantamount to equating the *relative* steric effects in the EDA complex to those in the activated complex for electrophilic cleavage. (c) Although the CT transition energies are measured in solution, the possible solvent effects on ω are cancelled out in the comparative method for the determination of ΔE, especially since they are insensitive to solvent effects in these electron donor–acceptor complexes.[3]

[17] (a) Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* **1980**, *84*, 2254; Part II. (b) This paper also describes the procedure for evaluating $\Delta G_r°$ for various alkyltin compounds from outer-sphere oxidation data.

[18] (a) It is important to note that the use of the comparative procedure in eq 15 (and in eq 12) allows us to focus only on those energy changes which directly relate the various alkyltin compounds to the reference Me_4Sn, forcing other factors common to both to drop out by cancellation. For example, the formulation in Scheme II does not mean that the energy change in path **E** is due wholly to solvation changes, but only that all those extraneous factors not directly associated with the alkylmetal moiety solely (e.g., differences in the mean separation r_{DA} and $r_{\pm}$) are largely cancelled out in the comparative procedure. Accordingly, the contribution from the relatively large changes in solvation in the alkylmetal moiety represents the most important residual factor for the energy change in path **E**. (b) Since this important point has also been previously elaborated for electrophilic iodinolysis, the reader is referred to the discussion in ref 8. (c) Complex formation ($\Delta G_{CT}°$) is neglected in relating the rate of electrophilic cleavage to path **D** since it is small.[3,14b] (d) Equation 16 is independent of $\Delta G_{CT}°$, which is cancelled out between paths **A** and **D** in Scheme III.

Table III. Evaluation of Steric Effects and Solvent Effects in the Electrophilic Cleavages of Alkyltin Compounds

	mercuric chloride				iodine		bromine	
		RR[e]						
tetraalkyltin compd	$\Delta E^{a,b}/2.3RT$	CH_3CN	CH_2Cl_2	MeOH	$\Delta E^{a,c}/2.3RT$	RR[e] CH_3CN	$\Delta E^{a,d}/2.3RT$	RR[e] CCl_4
Me_4Sn	0	0	0	0	0	0	0	0
Et_4Sn	10.1	13.3	13.4	12.8	7.9	12.6	8.3	13.5
n-Pr_4Sn	11.9	15.0	15.4	14.4	9.3	13.8	9.6	14.8
n-Bu_4Sn	13.1	16.6	17.2	16.0	10.9	15.8	10.6	16.0
n-$BuSnMe_3$	8.3	12.0	12.2	12.1	8.4	12.5	8.8	11.4
n-Bu_2SnMe_2	10.8	16.1	16.7	16.4	11.0	17.2	11.3	15.7
i-Pr_2SnMe_2	14.2	21.8	21.4	21.0	13.7	21.5	12.8	19.1
t-Bu_2SnMe_2	18.0	26.3	26.7	25.0	16.6	25.7	17.8	24.2
i-Bu_4Sn	14.2	17.4	18.2	16.7	10.9	16.2	11.7	16.7
i-Pr_4Sn	18.6	21.2	21.9	19.0	14.2	19.9	12.7	20.6
s-Bu_4Sn	18.4	20.3	21.2		13.3	18.4	12.3	19.6

[a] In kcal mol^{-1} from eq 12 using $h\nu_{CT}$. [b] From ref 3. [c] Reference 8. [d] Reference 9. [e] RR represents the left side of eq 16 using values of ΔG_r^s in Table IV, and rate constants k in Table I for $HgCl_2$, in ref 8 for I_2, and in ref 9 for Br_2.

determined by an independent method described in the Experimental Section for various tetraalkyltin compounds.[17] Furthermore, such an assignment of path **E** as a solvation change can be corroborated, since values of ΔG_r^s apply only to the alkyltin moiety and should be independent of the acceptor moiety which is cancelled out in the comparative method[18] used in this study. Indeed the excellent correlations in Figure 7 show that the energetics of path **E** evaluated as $(\Delta G_r^\ddagger - \Delta h\nu_{CT})$ for the $HgCl_2$ cleavages are identical with those evaluated for the iodine cleavage of the same series of alkyltin compounds examined in the earlier investigation,[8] i.e.,

$$[\Delta G_r^\ddagger - \Delta h\nu_{CT}]_{HgCl_2} = [\Delta G_r^\ddagger - \Delta h\nu_{CT}]_{I_2} \qquad (14)$$

Importantly the striking equivalence of path **E** for $HgCl_2$ cleavage and iodinolysis in eq 14, as shown by the uniform fit of the data to lines of unit slope in Figure 7, applies to all solvents—as structurally diverse as methylene chloride, acetonitrile, and methanol are. Thus, the bizarre and unaccountable reactivity patterns shown by $HgCl_2$ and I_2 in Figure 4 become identical after the correction by $\Delta h\nu_{CT}$ is included in Figure 7.

The correlation in Figure 6 represents the linear free energy relationship

$$\Delta G_r^\ddagger = \Delta h\nu_{CT} + \Delta G_r^s \qquad (15)$$

In other words, the activation process $(\Delta G_r^\ddagger)$ for the electrophilic cleavage of alkyltin by $HgCl_2$ is akin to that $(\Delta h\nu_{CT})$ of the vertically excited ion pair $[R_4Sn^+\ HgCl_2^-]^*$ in Scheme I, except for an important difference in their solvation energies (ΔG_r^s).[18] Accordingly, the linear free energy relationship in eq 15 strongly suggests that the formation of the thermal ion pair in path **D** is an appropriate model for the activation process for the electrophilic cleavage of alkyltin with $HgCl_2$. As such, eq 15 states that the activation free energy is equivalent to the driving force for the formation of the thermal ion pair $[R_4Sn^+\ HgCl_2^-]$.[19]

Quantitative Evaluation of Alkyltin Reactivities and Solvent Effects in Electrophilic Cleavages. The charge-transfer formulation in eq 15 can now be applied directly to the straightforward resolution of the complex reactivity patterns illustrated in Figure 3, which includes three independent variables—namely, the changes in the donor (various alkyltin), the acceptor ($HgCl_2$, I_2, Br_2), and the solvent (CCl_4, CH_2Cl_2, CH_3CN, CH_3OH). Since the ionization potential is commonly applied to electron-transfer processes, it is plotted against the alkyltin reactivity with different acceptors in Figure 8, in various solvents. No clear correlation between I_D and $\log k/k_0$ can be discerned in any of the systems undergoing electrophilic cleavage. The latter is not surprising since the plot in Figure 8 is tantamount to a direct comparison of path **A** in Scheme I (which is only dependent on the alkyltin donor) with path **D** in Scheme II (which includes the solvent as well as steric effects). In order to interrelate paths **A** and **D**, we combined now directly Schemes I and II to yield the resultant thermochemical cycle shown in Scheme III. This scheme shows that any direct correlation of paths **A** and **D** must include the contribution from path **F**, the energetics of which are given by $\Delta E + \Delta G_r^s$, since path **F** is simply the difference between paths **E** and **C**. Figure 9 shows the new correlations of the relative reactivities after inclusion of path **F** by the amount $(\Delta E + \Delta G_r^s)$, the values of which are listed in Tables III and IV.

Scheme III

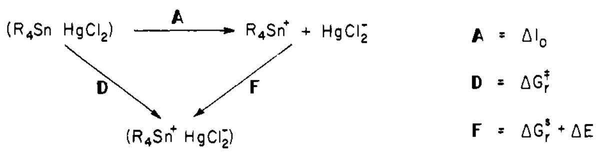

Table IV. Solvation Energy of R_4Sn^+ Relative to Me_4Sn^+

	$\Delta G_r^s/2.3RT^a$			
R_4Sn	CH_3CN	MeOH	CH_2Cl_2	CCl_4
Me_4Sn	0	0	0	0
Et_4Sn	5.4	5.4	4.9	3.1
n-Pr_4Sn	5.9	5.9	5.4	3.4
n-Bu_4Sn	6.3	6.3	5.8	3.6
n-$BuSnMe_3$	4.0	4.0	3.7	2.3
n-Bu_2SnMe_2	6.0	6.0	5.5	3.4
i-Pr_2SnMe_2	7.6	7.6	6.9	4.3
t-Bu_2SnMe_2	10.0	10.0	9.1	5.7
i-Bu_4Sn	6.8	6.8	6.2	3.9
i-Pr_4Sn	8.3	8.3	7.6	4.7
s-Bu_4Sn	8.4	8.4	7.7	4.8

[a] In kcal mol^{-1} for use in Table III.

The striking linear correlations in Figure 9 show a remarkable transformation of the relative reactivities severely scattered in Figure 8. This corresponds to the linear free energy relationship in eq 16.[18d] *Indeed if all the experimental points in Figure 9*

$$\underbrace{\log \frac{k}{k_0}}_{\text{path D}} + \underbrace{\frac{\Delta E + \Delta G_r^s}{2.3RT}}_{\text{path F}} = \underbrace{\frac{-\Delta I_D}{2.3RT}}_{\text{path A}} \qquad (16)$$

were plotted on a single figure, they would all lie on a single line with a slope of −16.9, which corresponds to −1/2.3RT in the units used here.[20] It is noteworthy that eq 16 from Scheme III is equivalent to eq 15 in Scheme II, since eq 16 derives from eq 15 by using eq 12 and 13. In other words, the activation process for electrophilic cleavage as represented by an electron transfer in the complex

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(19) For a thermodynamic description of ion-pair formation from inner-sphere complexes, see discussions in ref 8, 9, 16a, and 17. See also footnote 14b.

(20) At 25 °C the slope is −16.9 when I_D is expressed in eV.

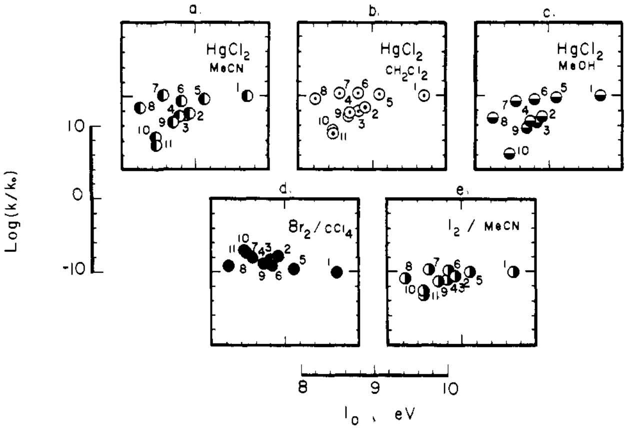

Figure 8. Relative reactivities (log k/k_0) of tetraalkyltin compounds. Top row: Solvent effect on $HgCl_2$ cleavages in (a) acetonitrile, (b) methylene chloride, and (c) methanol. Bottom row: Solvent effect on halogenolysis with (d) I_2 in acetonitrile and (e) Br_2 in carbon tetrachloride from ref 8 and 9, respectively. Alkyltin compounds identified by numbers in Table I.

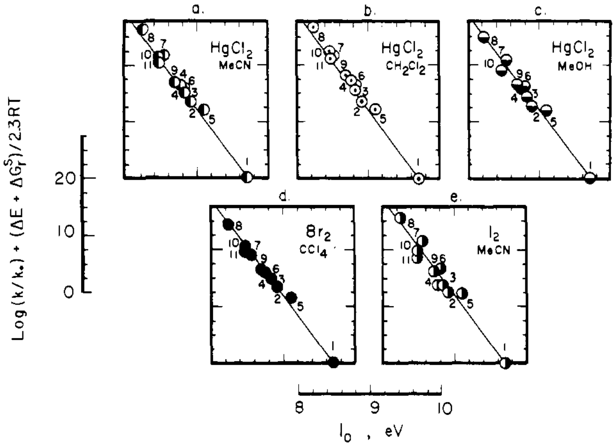

Figure 9. Linear correlations of the relative reactivities including steric and solvation effects according to eq 16, with the ionization potentials of various alkyltin compounds identified by numbers in Table I. Electrophilic cleavage with $HgCl_2$ in (a) acetonitrile, (b) methylene chloride, and (c) methanol, with (d) I_2 in acetonitrile, and (e) Br_2 in carbon tetrachloride. The solid lines are all drawn arbitrarily with the slope predicted by eq 16 to emphasize the coincidence of the data to the equation. Compare with Figure 8.

$$[R_4Sn\ HgCl_2] \xrightarrow{D} [R_4Sn^+\ HgCl_2^-] \qquad (17)$$

can be evaluated in two independent ways—either as the sum of paths **B** and **E** in Scheme II or as the sum of paths **A** and **F** in Scheme III. Since the energetics of each path are determined from three independent measurements, viz., the ionization potential, the charge-transfer transition, and the solvation energy, they are sufficient to determine completely the three variables affecting the rate of electrophilic cleavage, viz., the donor, the acceptor, and the solvent. Such a fit to the experimental data is represented by the general expression (eq 18),[18d] as illustrated in Figure 9 which can hardly be fortuitous but must be taken as compelling support for the charge-transfer formulation in eq 17.

$$-RT \ln k/k_0 = \Delta I_D + \Delta E + \Delta G_r^s \qquad (18)$$

Charge-Transfer Mechanism for Electrophilic Cleavage of Alkylmetals by Mercury(II) Derivatives. The preequilibrium formation of alkylmetal–mercury(II) complexes is included in the general mechanism in Scheme IV for electrophilic cleavage. The activation process for mercury(II) cleavages is represented in eq 20 by the formation of the ion pair. It is supported by the excellent linear correlations in Figures 6, 7, and 9 resulting from the application of eq 18 which directly equates the activation process for electrophilic cleavage with changes in the electronic, steric, and solvation energies for ion-pair formation.

Scheme IV

$$RM + HgX_2 \xrightleftharpoons{K_{DA}} [RM\ HgX_2] \qquad (19)$$

$$[RM\ HgX_2] \xrightarrow{k_E} [RM^+\ HgX_2^-] \qquad (20)$$

$$[RM^+\ HgX_2^-] \xrightarrow{\text{fast}} RX + RHgX \qquad (21)$$

In Scheme IV, the products arise subsequent to the rate-limiting electron-transfer step and are largely associated with the spontaneous fragmentation of the alkylmetal cation and recombination in the solvent cage.[21] The lability of HgX_2^- [formally a mercury(I) intermediate] accords with the facile dissociative electron capture by $HgCl_2$ to afford Cl^- and $HgCl$.[22]

Correlation of the Reactivity of Various Mercury(II) Electrophiles. The rather pronounced effects of various mercury(II) electrophiles on the rates of cleavage of Me_4Sn and n-Bu_4Sn in Table II may also be accommodated by the charge-transfer formulation for electrophilic cleavage in Scheme IV. Since we were unable to measure the CT absorption bands for the mercury(II) carboxylates with either Me_4Sn or n-Bu_4Sn owing to the overlapping spectral bands, the values of ΔE and ΔG_r^s are unavailable for the quantitative determination of the steric and solvation effects for these electrophiles. However, the examination of the CT absorption bands of the series of mercury(II) electrophiles in Table II with an alkyl aromatic donor such as hexamethylbenzene suggests that the steric effects are rather constant. If for the moment we assume that $\Delta E = \Delta G_r^s = 0$, eq 16 may be rewritten as eq 22.[23] Under these conditions a plot in Figure 5 of the rate constant (log k) for mercury(II) cleavage should be linear with the CT transition energies in the corresponding hexamethylbenzene complexes. The predicted slope of the correlation is 16.9, which compares rather favorably with a = 14 and 17 in eq 8 for the cleavage of Me_4Sn and n-Bu_4Sn, respectively, by the mercury(II) carboxylates. The deviations in Figure 5, especially with $HgBr_2$, are no doubt a result of the simplifying assumptions that steric and solvation changes are negligible.

$$\log k = -h\nu_{CT}/2.3RT + \text{constant} \qquad (22)$$

Summary and Conclusions

The rates of mercury(II) cleavage of alkyltin show complex reactivity patterns (Figure 3), which are strongly influenced by solvent. The evaluation of solvation energies allows the separation of the activation free energy ΔG_r^* for the electrophilic cleavage into three separate effects—electronic, steric, and solvation, as shown in Figure 9. The relationship is quantitatively expressed by three *independent* experimental observables as

$$\Delta G_r^* = \Delta I_D + \Delta E + \Delta G_r^s \qquad (23)$$

where the electronic effect ΔI_D is obtained directly from the ionization potential of the alkyltin, the steric effect ΔE derives from the CT transition energies, and the solvation change ΔG_r^s is evaluated from the oxidation of the alkyltin in solution. An equivalent linear free energy relationship is expressed as

$$\Delta G_r^* = \Delta h\nu_{CT} + \Delta G_r^s \qquad (24)$$

where $\Delta h\nu_{CT}$ is the relative transition energies of the alkyltin–mercury(II) complex. Solvation of the ion pair leads to diminution of the activation free energy, generally in parallel with the polarity of the solvent. These formulations emphasize the strong similarity between the CT excited state, i.e., the photochemically excited

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[21] (a) For an elaboration of these processes see: Fukuzumi, S.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5961 and ref 8. (b) See also: Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 2460; Chen, J. Y.; Gardner, H. C.; Kochi, J. K. *Ibid.* **1976**, *98*, 6150.

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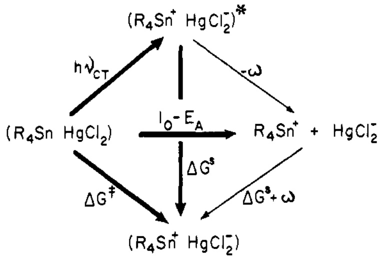
[23] The constant in eq 22 is log k_0 + $h\nu_{CT}^0/2.3RT$ for the reference mercury(II) electrophile, neglecting solvation and steric changes.

Scheme V



ion pair $[R_4Sn^+ HgCl_2^-]^*$, and the transition state, or the thermal ion pair $[R_4Sn^+ HgCl_2^-]$, in the electrophilic cleavage by mercury(II). The relationship between these ion pairs relative to the hypothetical free ions is schematically illustrated in the general Scheme V. The *heavy bar lines* in Scheme V represent those paths in which the energetics are determined directly from independent measurements. As such, they are sufficient to evaluate the energetics of the remaining paths which are represented by the lighter lines. This general scheme is simply a composite of Schemes I, II, and III, and thus the energetics of each step is appropriately labeled to show the interrelationships among the electronic (I_D and E_A), the charge transfer ($h\nu_{CT}$), and the solvation (ΔG^s) to the activation process ($\Delta G^\ddagger$).[24] In this way the complex reactivity patterns for electrophilic cleavage can be clearly dissected into its component parts, and the subtle balance among the electronic, steric, and solvation effects determines the reactivities of alkylmetals with variations in the solvent and acceptor. Importantly, the charge-transfer formulation clearly points out that mercury(II) electrophiles and halogen electrophiles (iodine and bromine) share a strikingly common reactivity pattern toward various alkyltin compounds, despite variations in the strong perturbing effects of the solvent (note the slopes of unity in Figure 7). As chemically and structurally diverse as these classes of electrophiles are, the CT formulation provides a straightforward basis from which a unified view of electrophilic cleavages evolves naturally. There are numerous other examples in the extant literature showing varying degrees of correlation between the rate constants and the ionization potentials or electron affinities of one or more of the reactants, especially as they are affected by the solvent.[25] The detailed consideration of such processes within this mechanistic framework will provide tests for the generality of the charge-transfer concept as it applies to reaction dynamics.

Experimental Section

Materials. The tetraalkyltin compounds as well as the mercury(II) derivatives used in this study were described previously.[3] The solvents (acetonitrile, methanol, methylene chloride, dioxane, and hexane) were reagent grade materials obtained commercially and purified according to standard methods.[26] Dioxane was refluxed with concentrated HCl and water for 12 h, accompanied by a slow passage of nitrogen to remove acetaldehyde. After successive treatments with KOH pellets, the mixture was refluxed for 12 h with sodium. It was finally distilled from sodium and stored under argon. The concentrations of the standard solutions of mercury derivatives in various solvents were frequently checked. Fresh aliquots were made up for each kinetic study to avoid possible solvolysis, especially in CH_3CN.[27]

Kinetic Measurements. The electrophilic cleavage of tetraalkyltin compounds with mercury(II) electrophiles was carried out in 10-mm quartz cuvettes placed in the thermostated compartment of a Cary 14 spectrophotometer. The reaction was initiated by injecting a known amount of tetraalkyltin compound with the aid of a glass microsyringe. The addition was accompanied by a vigorous shaking of the cuvette. The kinetics were followed mainly by the quenching method described by Abraham et al.[4] Aliquots of the reaction mixture (20–50 μL) were withdrawn periodically and added to another 10-mm quartz cuvette containing 2.5×10^{-3} M potassium iodide in aqueous methanol, of such a composition that the final solution for analysis had a mole fraction for MeOH of 0.91. Under these conditions, the mercury(II) derivatives used in this study were all quantitatively converted to triiodomercurate(II), HgI_3^-, instantaneously. The concentration of HgI_3^- was determined from its absorbance at 301.5 nm, using the calibrated equation presented by Abraham and Johnston.[28]

For the reactions of R_4Sn with $HgCl_2$, the kinetics in each solvent were examined in the presence of excess R_4Sn, except for the reactions of Me_4Sn in CH_3CN and MeOH. The concentrations of $HgCl_2$ and R_4Sn were 3.3×10^{-3} M, 5.0×10^{-3} M, and 1.0×10^{-2} M for $HgCl_2$, and in the range from 10^{-2} to 10^{-1} M for R_4Sn. In polar solvents such as acetonitrile and MeOH, the maximum concentrations of R_4Sn were limited because of their low solubility. Under these conditions, the kinetics for i-Pr_4Sn and s-Bu_4Sn were followed for as long as 10 days owing to their slow reaction rates.

For the reactions of Me_4Sn with $HgCl_2$ in CH_3CN and MeOH, the rates were followed with equimolar amounts of each reactant. From the linear plots of $1/C$ with time, the second-order rate constants k were determined as

$$1/C = 2kt + 1/C_0 \tag{25}$$

where C and C_0 are the concentrations of the reactant at time t and the initial time respectively. For the reactions of mercury(II) electrophiles listed in Table II with Me_4Sn and n-Bu_4Sn, the second-order rate constants were also determined from eq 25. However, the reactions of n-Bu_4Sn with $HgCl_2$, $HgBr_2$, $Hg(O_2CCH_2Cl)_2$, and $Hg(O_2CCHCl_2)_2$ were followed under pseudo-first-order conditions with excess n-Bu_4Sn. Since the reactions of $Hg(O_2CCHF_2)_2$ and $Hg(O_2CCF_3)_2$ are much faster than the others, they were followed with more dilute solutions of the reactants, i.e., 5.0×10^{-4} M and 1.0×10^{-3} M.

Some reactions were also followed by the temporal change of the UV band of the mercury(II) electrophiles. For example, the decay of the absorbance of $Hg(O_2CCHF_2)_2$ (2.5×10^{-3} M) at 260 nm from the reaction with 2.5×10^{-3} M Me_4Sn was measured in CH_2Cl_2. The same rate constant was determined from the quenching method employed above, as listed in Table II.

Although the temperature dependence of the rate constants was not examined systematically in this study, the rates of reaction of 5.0×10^{-3} M $HgCl_2$ with excess n-Bu_4Sn (0.243 M) in CH_2Cl_2 were measured at two temperatures (8 and 25 °C). The rate was followed by the decay of the CT band at 255 nm as well as the disappearance of $HgCl_2$ by the quenching method. The second-order rate constants at 8 °C determined by both methods were in good agreement, viz., $(2.35 \pm 0.05) \times 10^{-4}$ M^{-1} s^{-1}. The activation enthalpy, $\Delta H^\ddagger$, is estimated to be 17 kcal mol^{-1} from the data in Table I. The value of $\Delta H^\ddagger$ for the reaction of n-Bu_4Sn and $HgCl_2$ in CH_2Cl_2 is slightly higher than the reported value in MeOH of 15 kcal mol^{-1}.[5]

Evaluation of Steric Effects. The steric effect ΔE required for path F in Scheme III was calculated from eq 12 by using the data for the ionization potentials of the alkyltin compounds and the charge-transfer transition energies of the $[R_4Sn\ HgCl_2]$ complexes listed in Table I. The energetics for path D plus path F represented as RR in Table III (i.e., the left side of eq 16) were determined from the rate constants in Table I.

Evaluation of Solvation Energies. The change in the solvation energies for alkyltin compounds attendant upon electron-transfer oxidation is given by the difference between the ionization potential in the gas phase and the oxidation in solution, i.e.

$$\Delta G_r^s = \Delta G_r^\circ - \Delta I_D$$

where ΔG_r° is the standard free energy change for the oxidation of R_4Sn relative to that of tetramethyltin. Since the lifetime of the alkyltin cation is very short, the latter was obtained by a kinetic technique utilizing the outer-sphere oxidations in acetonitrile, as described earlier.[17] The values of ΔG_r^s in other solvents were then evaluated relative to those in acetonitrile with the aid of the modified Born equation (26),[29] where α is a

$$\Delta G^s = -\alpha(1 - 1/\epsilon)f(r_\pm) \tag{26}$$

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[24] Note: the activation free energy $\Delta G^\ddagger$ in Scheme V corresponds to $\Delta G_r^\ddagger$ in the comparative method employed in Schemes II and III. Similarly, $h\nu_{CT}$ corresponds to $\Delta h\nu_{CT}$, ω to ΔE, ΔG^s to ΔG_r^s, and $(I_D - E_A)$ to ΔI_D in Schemes I, II, and III.

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constant given as $Ne^2/2$ and $f(r_\pm)$ is a function of the radius of both ions in solution.[30] As applied to the solvation energy of R_4Sn^+ relative to Me_4Sn^+ important in this study, the anionic contribution cancels out, and the relative solvation energy is given by eq 27. Since ΔG_r^s in acetonitrile

$$\Delta G_r^s = -\alpha(1 - 1/\epsilon)\Delta f(r_+) \qquad (27)$$

is available from a previous study,[17] the value of ΔG_r^s in other solvents can be evaluated as in eq 28, where ΔG_r^{s0} is the solvation energy in

$$\Delta G_r^s = \beta \Delta G_r^{s0} \qquad (28)$$

acetonitrile as the reference solvent and $\beta = (1 - \epsilon^{-1})/(1 - \epsilon_0^{-1})$. From the known values of the dielectric constants,[6] β is obtained as 1.0 for MeOH, 0.91 for CH_2Cl_2, and 0.57 for CCl_4. The values of ΔG_r^s for various alkyltin compounds evaluated by eq 28 are listed in Table IV. [Note: the radial function $\Delta f(r_+)$ in eq 27 is cancelled out in the conversion to eq 28.]

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(30) $f(r_\pm)$ is given as $[(r_+ + r_+')^{-1} + (r_- + r_-')^{-1}]$, where r_+ (or r_-) and r_+' (or r_-') correspond to the crystal radius of the cation (or anion) and their correction factor applied to solution, respectively. In the present case, the usage of eq 28 does not rely on these values, since they cancel out.

Transition-State Effects in the Divalent Metal Ion Catalyzed Hydrolysis of Esters. Hydrolysis of 2-Pyridylmethyl Hydrogen Phthalate

Thomas H. Fife* and Theodore J. Przystas[1]

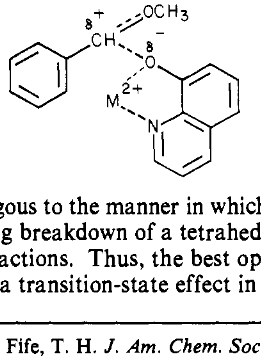
Contribution from the Department of Biochemistry, University of Southern California, Los Angeles, California 90033. *Received April 28, 1980*

Abstract: Rate constants have been obtained for hydrolysis of 2-pyridylmethyl hydrogen phthalate, an ester with a poor leaving group, at 90 °C in the pH range 6-11. The pH-rate constant profile shows hydroxide ion catalysis at high pH and a plateau due to nucleophilic carboxyl group participation. Divalent metal ions (Ni^{2+}, Co^{2+}, Zn^{2+}) exert a large catalytic effect, although binding to the substrate is weak. Saturation effects were not observed even at 0.01 M metal ion (>100-fold excess over ester). Catalysis is dependent upon the presence of the pyridine nitrogen in the 2-position; metal ions are without effect in hydrolysis of the 4-pyridyl analogue. The metal ion catalyzed reactions are pH independent (pH 4.74–7.15 at 50 °C). Therefore, metal ion catalysis in reactions of the phthalate ester is associated with carboxyl group participation. Since breakdown of a tetrahedral intermediate must be rate determining in the carboxyl nucleophilic reactions of esters with poor leaving groups, the metal ions must exert their effect in the transition state by stabilization of the leaving group. In contrast, the metal ion effects observed in hydrolysis of 2-pyridylmethyl benzoate represent metal ion promoted OH^- catalysis.

Carboxypeptidase A is a Zn(II)-requiring enzyme, catalyzing the hydrolysis of ester and peptide substrates.[2] X-ray crystallographic analysis at 2-Å resolution has shown the zinc ion to be chelated to the carbonyl oxygen of poor peptide substrates.[2-4] The carboxyl group of glutamic acid-270 has also been implicated in the catalytic process, and mechanisms have been suggested involving nucleophilic attack and classical general base catalysis (proton transfer in the transition state from a water molecule).[3,4] The role of the complexed metal ion in these mechanisms has been to provide polarization of the carbonyl group. However, this should not be a catalytic factor in the case of a carboxyl nucleophilic reaction because breakdown of a tetrahedral intermediate would be rate determining when the pK_a of the leaving group greatly exceeds that of the nucleophile. A tetrahedral intermediate might be greatly stabilized by metal ion binding. An alternative proposal is that Zn(II) exerts a transition-state effect in which the leaving group is stabilized,[5] but there have not been any assessments of the efficiency or chemical feasibility of the latter mechanism.

Chelated divalent metal ions have not been found to enhance the intramolecular carboxyl nucleophilic reactions of esters[6,7] or amides.[6,8] The reactions of amides can in fact be strongly inhibited by metal ion chelation to the carbonyl oxygen.[8] There are no metal ion effects in the carboxyl group nucleophilic reactions of phenolic esters, even though rate enhancements of up to 10^9 can be obtained in the metal ion promoted OH^--catalyzed reaction.[6,7] When the metal ion is strongly chelated to the substrate, nucleophilic attack by a carboxylate anion cannot compete with the metal ion promoted OH^- reaction.[7]

We have recently found that divalent metal ions will markedly enhance the rates of hydrolysis of benzaldehyde methyl 8-quinolyl acetals by binding to the leaving group in the transition state.[9] In those reactions the catalytic effectiveness does not depend upon strength of binding to the reactant; inclusion of an additional functional group which leads to strong chelation of the metal ion to the acetal does not lead to an increased rate enhancement in comparison with acetals where binding to the reactant is weak at metal ion concentrations greater than 0.01 M. Catalysis occurs because of chelation of the metal ion to the quinoline nitrogen and oxygen of the leaving group in the transition state as the C–O bond breaks.



This is quite analogous to the manner in which a metal ion might function in assisting breakdown of a tetrahedral intermediate in ester hydrolysis reactions. Thus, the best opportunity for demonstration of such a transition-state effect in the intramolecular

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(1) Postdoctoral fellow, University of Southern California.
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