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Donor–Acceptor Complexes of Organometals and Iodine. Alkyl Ligands as Probes for Steric Effects in Charge Transfer

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Charge-transfer (CT) absorptions are observed between iodine and a variety of homoleptic alkylmetals including dialkylmercury (R_2Hg) and tetraalkylmetals (R_4M) of the group 4A elements (where M = lead, tin, germanium, and silicon) in carbon tetrachloride solutions. These alkylmetal–iodine complexes are all classified as weak, the formation constants, K, being generally less than 5 M^{-1} for dialkylmercury and less than 3 M^{-1} for the methylethyllead compounds. The formation constants of tetraalkyltin, -germanium, and -silicon are too small to measure ($K < 0.1$ M^{-1}). The frequency of the charge-transfer bands ($h\nu_{CT}$) varies linearly with the vertical ionization potential (I_D) of the alkylmetal, determined independently from the photoelectron spectra. However, two separate correlations are required for these alkylmetals—one for the series of two-coordinate, linear dialkylmercury compounds and another for the series of four-coordinate, tetrahedral tetraalkylmetals corresponding to a sterically open and a quasi-spherical configuration of electron donors, respectively. Steric effects in these alkylmetal–iodine complexes may be evaluated in two ways. By the direct method, the role of steric effects in determining the charge transfer transition energy is associated with the Coulombic term (e^2/r_{DA}) in the first-order treatment of weak complexes according to the Mulliken theory. The mean separation r_{DA} in the CT complexes of R_2Hg and R_4M, calculated from the measured values of ν_{CT}, I_D, and the vertical electron affinity of iodine, shows two parallel trends, both increasing with decreasing values of the ionization potentials. This behavior is the same as that evaluated for the CT complexes of tetracyanoethylene (TCNE) with the same series of alkylmetals, in which K is larger and can be measured for $[R_2HgI_2]$ as well as $[R_4MI_2]$ complexes. By the indirect method, steric effects are evaluated relative to a reference alkylmetal (Me_2Hg for R_2Hg and Me_4Sn for R_4M). The difference ΔE, taken as the relative change in steric effects, is shown to be essentially the same in TCNE and iodine complexes. The latter bears on the general question as to whether small (indeterminant) values of K (<0.1 M^{-1}) or $-\Delta H$ (<1 kcal mol^{-1}) can be used as adequate criteria for contact charge transfer.

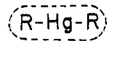
Introduction

Charge-transfer (CT) complexes of iodine are the oldest known and have been extensively studied, both by experiment and from several theoretical points of view, with a variety of organic donors.[1-3] Contact charge transfer (CCT) of iodine with weak donors such as alkyl halides and even alkanes is especially noteworthy.[4] Although there are a few examples of iodine charge transfer with metal complexes,[5,6] there are no reports heretofore of studies with organometals in which the metal is directly bonded to alkyl ligands.

Alkylmetals have many desirable properties as electron donors for the study of steric effects in charge-transfer interactions. As relatively volatile and electron-rich compounds, their photoelectron spectra are readily accessible, and the vertical ionization potentials can be accurately measured. Moreover, in alkylmetals of the main group elements, ionization occurs from the highest occupied molecular orbital (HOMO) which has σ-bonding character; that is, they are σ donors.[7] As a result, alkyl ligands exert a large dominating influence on the ionization potentials and the steric properties of alkylmetals.

In this study we have chosen two series of organometals, viz., tetraalkylmetals of the group 4A elements (Si, Ge, Sn, Pb) and dialkylmercury (R_2Hg), which are geometrically rather different, having tetrahedral (quasi-spherical) and linear (open) configurations, respectively, i.e.,

M = Si,Ge,Sn,Pb



where R represents a homologous series of alkyl ligands.

TABLE I: Steric and Polar Parameters for Alkyl Ligands[a]

α branching			β branching		
alkyl	E_s	E_p	alkyl	E_s	E_p
methyl	0	0	ethyl	−0.07	0.49
ethyl	−0.07	0.49	*n*-propyl	−0.36	0.55
isopropyl	−0.47	0.85	isobutyl	−0.93	0.58
tert-butyl	−1.54	1.02	neopentyl	−1.74	0.66

[a] In arbitrary energy units from ref 8 and 9.

Importantly, alkyl groups are highly tunable ligands for the systematic variation of the steric effects and the electron donor properties of these alkylmetals. Thus both the steric and polar properties of alkyl ligands can be made to vary merely by manipulating the extent of α- and β-methyl branching, as indicated by the magnitudes of the E_s and E_p parameters, respectively, in Table I. By the proper choice of these alkyl ligands, the stereochemistry as well as the ionization potentials of organometals can be varied to cover wide ranges of molecular properties. [Compare Table I with the PES data in Table II. Note that the effective size of alkyl groups changes dramatically with both α and β branching, but the ionization potential is strongly influenced only by α branching.] Since these alkylmetals are all substitution stable, any divergence in the behavior toward iodine can be ascribed directly to differences in their steric properties and ionization potentials.

Results

Charge-Transfer Absorption Spectra of Iodine Complexes with Alkylmetals. When a solution of dibutylmercury in carbon tetrachloride is mixed with iodine, a new absorption band with λ_{max} 332 nm is immediately observed

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TABLE II: Charge-Transfer Absorption Spectra of Alkylmetals with Iodine[a]

no.	alkylmetal	I_D,[b] eV	λ_{max}, nm	$h\nu_{CT}$, eV	ϵK, × 10^2 M^{-2} cm^{-1}
1	Me_4Sn	9.69	270	4.59	8.8
2	Et_4Sn	8.90	290	4.27	7.8
3	n-Pr_4Sn	8.82	290	4.27	9.9
4	n-Bu_4Sn	8.76	288	4.30	3.7
5	$EtSnMe_3$	9.10	276	4.49	6.9
6	n-$PrSnMe_3$	9.10	275	4.50	7.3
7	n-$BuSnMe_3$	9.10	276	4.49	7.9
8	i-$BuSnMe_3$	9.05	273	4.54	8.0
9	Et_2SnMe_2	9.01	279	4.44	7.3
10	n-Pr_2SnMe_2	8.80	285	4.35	10.6
11	n-Bu_2SnMe_2	8.80	285	4.35	5.0
12	i-Pr_2SnMe_2	8.56	290	4.27	6.8
13	t-Bu_2SnMe_2	8.22	302	4.10	6.5
14	Et_3SnMe	8.95	290	4.27	11.25
15	i-Pr_4Sn	8.46	295	4.20	5.3
16	s-Bu_4Sn	8.45	299	4.14	10.0
17	i-Bu_4Sn	8.68	294	4.22	5.8
18	i-Bu_2SnEt_2	-	301	4.00	4.8
19	Et_4Si	9.78	268	4.63	3.9
20	Et_4Ge	9.41	269	4.61	3.4
21	n-Bu_4Ge	-	286	4.33	9.4
22	Me_2Hg	9.33	297	4.17	7.5
23	$EtHgMe$	8.84	312	3.93	13.3
24	n-Pr_2Hg	8.29	332	3.73	18.7
25	n-Bu_2Hg	8.35	333	3.72	27.9
26	i-Bu_2Hg	8.30	329	3.77	25.3

[a] In carbon tetrachloride solutions at 25 °C, except for dialkylmercury at 3 °C. [b] Taken from ref 11–13.

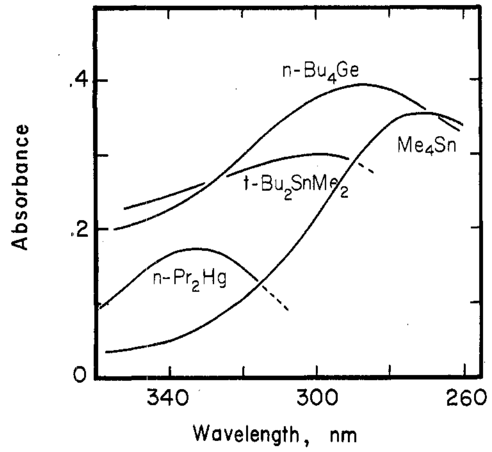


Figure 1. Charge-transfer spectra of alkylmetals with 8.0 × 10^{-3} M iodine in carbon tetrachloride solution at 25 °C: Me_4Sn = 4.9 × 10^{-2} M, t-Bu_2SnMe_2 = 6.3 × 10^{-2} M, n-Bu_4Ge = 5.2 × 10^{-2} M, n-Pr_2Hg = 1.2 × 10^{-2} M (at 3 °C).

in the ultraviolet spectrum. The broad absorption band shown in Figure 1 is characteristic for intermolecular charge transfer complexes,[10] e.g.,

$$n\text{-Pr}_2\text{Hg} + \text{I}_2 \overset{K}{\rightleftharpoons} [n\text{-Pr}_2\text{Hg}\,\text{I}_2] \qquad (1)$$

Homologous dialkylmercury compounds show the same behavior, but the absorption maximum varies with the nature of the alkyl ligands. Indeed the energy of the charge-transfer transition, $h\nu_{CT}$, increases with the ionization potential of the dialkylmercury compounds listed in Table II.

The series of group 4A metal alkyls listed in Table II also exhibit new spectral bands due to charge transfer interaction with iodine, i.e.,

$$\text{R}_4\text{M} + \text{I}_2 \overset{K}{\rightleftharpoons} [\text{R}_4\text{M}\,\text{I}_2] \qquad (2)$$

where M = Si, Ge, and Sn. Compared to dialkylmercury compounds, the absorption maxima of these tetraalkylmetals are generally shifted further into the ultraviolet and are sometimes partially obscured by the tail absorption of the tetraalkylmetal, particularly with the tin derivatives. However, the difference spectra obtained under calibrated conditions allowed values of λ_{max} in Table II to be clearly identified, as described in the Experimental Section. (This technique was also facilitated by λ_{max} of the charge-transfer band increasing in parallel with the tail of the alkylmetal absorption.) The energy $h\nu_{CT}$ for the iodine complexes of tetraalkylmetals also varies in the manner described above for dialkylmercury. Although there is a general trend for $h\nu_{CT}$ to parallel I_D, there is considerable scatter of points, the deviation from any linear correlation generally being the greatest with sterically hindered alkylmetals.

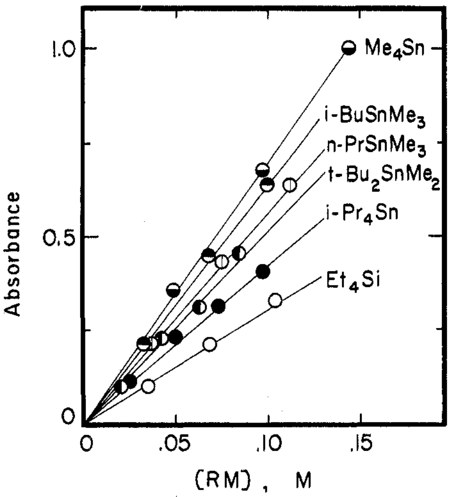


Figure 2. Changes in the charge-transfer absorptions with the variation in the concentrations of various alkylmetals and 8.0 × 10^{-3} M iodine in carbon tetrachloride solution at 25 °C: (◒) Me_4Sn, (◓) i-$BuSnMe_3$, (◑) n-$PrSnMe_3$, (◐) t-Bu_2SnMe_2, (●) i-Pr_4Sn, (○) Et_4Si.

Formation Constants of Alkylmetal–Iodine Complexes. The absorbance change of the CT band was measured at various concentrations of alkylmetal and iodine to evaluate the formation constants K in eq 1 and 2. The CT absorbance is represented in terms of the initial concentrations of the alkylmetal donors D_0 and the iodine acceptor A_0 by the Benesi–Hildebrand equation,[14] reexpressed by Person as[15]

$$A = \frac{\epsilon K D_0 A_0}{1 + K D_0} \qquad (3)$$

where the cell pathlength is taken as 1.00 cm, ϵ is the extinction coefficient, and K is the formation constant of the CT complex. However, the plot of the absorbance against either D_0 or A_0 as shown in Figure 2 was linear and not curved as expected. From eq 3, linearity would be obtained if $KD_0 \ll 1$, i.e.

$$A \simeq \epsilon K D_0 A_0 \qquad (4)$$

as it would be for weak complexes at low donor concentrations. Indeed the change in absorbance followed eq 4 for all the alkylmetals in Table II. The linear dependence of the absorption at λ_{max} 288 nm for n-Bu_4Sn with changes in the iodine concentration shown in Figure 3 indicates the formation of a 1:1 complex, as in eq 2. The values of ϵK for various alkylmetals, obtained from the linear correlations according to eq 4, are included in Table II. We estimate that K is less than 0.1 M^{-1} for the tetraalkyltin, -germanium, and -silicon compounds.[16]

Although the values of ϵK for the dialkylmercury compounds are larger than those of the other alkylmetals in

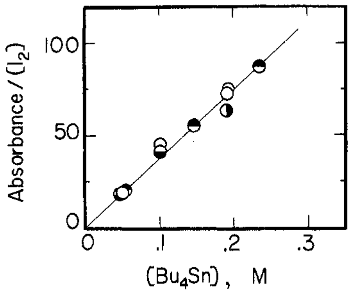


Figure 3. The linear dependence on iodine concentration of the charge-transfer absorption of the n-Bu$_4$Sn complex in carbon tetrachloride solution at 25 °C: $[I_2]$ = (◑) 1.0 × 10^{-3} M, (◒) 2.0 × 10^{-3} M, (◓) 4.0 × 10^{-3} M, (○) 8.0 × 10^{-3} M.

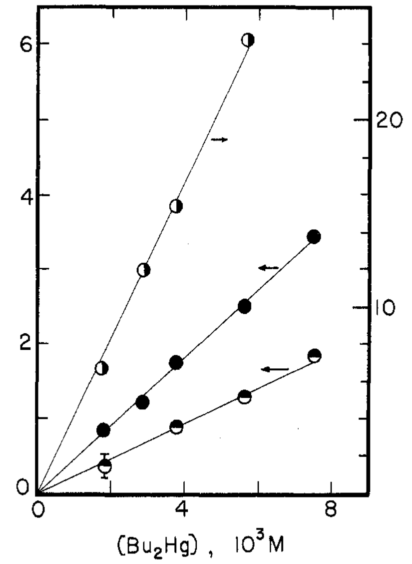


Figure 4. Formation of the charge-transfer complex of di-n-butylmercury with various concentrations of iodine: (◑) 8.6 × 10^{-3} M, (●) 1.0 × 10^{-3} M, (◓) 5.2 × 10^{-4} M, in carbon tetrachloride solution at 25 °C.

Table II, K could not be determined by the Benesi–Hildebrand method.[17] However, the iodine absorption at 520 nm (ϵ 900 M^{-1} cm^{-1}) in carbon tetrachloride diminished in intensity immediately upon the addition of dibutylmercury.[18] From eq 1, the change in the intensity of this band is given by

$$\frac{A}{A_0} = \frac{[I_2]_0 - [R_2HgI_2]}{[I_2]_0} \tag{5}$$

where A_0 and A are the absorbance before and after the addition of dibutylmercury, $[I_2]_0$ is the initial concentration of iodine, and $[R_2HgI_2]$ is the concentration of the charge-transfer complex. Rearranging eq 5 yields eq 6 and 7. When $K[R_2Hg]_0 \ll 1$, eq 7 reduces to eq 8. The linear

$$[R_2HgI_2] = [I_2]_0 \left\{1 - \frac{A}{A_0}\right\} \tag{6}$$

$$[R_2HgI_2] = [I_2]_0 \frac{K[R_2Hg]_0}{1 + K[R_2Hg]_0} \tag{7}$$

$$[R_2HgI_2] = K[R_2Hg]_0[I_2]_0 \tag{8}$$

dependence at various iodine and dibutylmercury concentrations is shown in Figure 4, from which $K = 4.7$ M^{-1} is obtained. The extinction coefficient $\epsilon = 5.9 \times 10^2$ is derived from $\epsilon K = 2.79 \times 10^3$ M^{-2} cm^{-1} in Table II. The formation constants of iodine CT complexes with the other dialkylmercury compounds are included in Table III. A series of methylethyllead compounds $Me_nEt_{4-n}Pb$, where n = 0, 1, 2, 3, also behaves in a manner similar to that shown by dialkylmercury, and the formation constants of the CT complexes are also listed in Table III. It is noteworthy that there is no perceptible change in the visible absorption band of iodine due to complex formation with the alkyltin, -germanium, and -silicon compounds in Table II, providing an additional indication of the weakness of these CT complexes in carbon tetrachloride solutions. The opposing trend of K and ϵ with changing alkylmetal structures in Table III is similar to that previously observed in the related tetracyanoethylene CT complexes.[11]

TABLE III: Formation Constants of Iodine Charge-Transfer Complexes with Dialkylmercury and Methylethyllead Compounds in Carbon Tetrachloride Solutions

no.	alkylmetal	K, M^{-1}	ϵ, M^{-1} cm^{-1}[a]
22	Me_2Hg	0.07	1.1×10^4
23	MeHgEt	0.63	2.1×10^3
24	n-Pr_2Hg	1.5	1.3×10^3
25	n-Bu_2Hg	4.7	5.9×10^2
26	i-Bu_2Hg	4.5	5.6×10^2
27	$EtPbMe_3$	0.83	b
28	Et_2PbMe_2	1.6	b
29	Et_3PbMe	2.9	b
30	Et_4Pb	3.1	b

[a] Calculated for ϵK values in Table II. [b] Not determined.

TABLE IV: Solvent Effects on Alkylmetal-Iodine CT Spectra

alkylmetal	CCl_4, nm	n-hexane, nm	cyclohexane, nm
Me_2Hg	297 ± 1	297 ± 1	296 ± 1
EtHgMe	312 ± 2	312 ± 2	313 ± 2
Me_4Sn	270 ± 1	269 ± 1	270 ± 1
t-Bu_2SnEt_2	301 ± 2	303 ± 2	303 ± 2

Solvent Effects. The absorption spectra of alkylmetals with iodine were essentially unchanged in hydrocarbon solvents such as n-hexane and cyclohexane, as indicated by the constancy of λ_{max} in Table IV. Unfortunately, in the more polar solvents such as methylene chloride, chloroform, and chlorobenzene, the chemical reaction leading to triiodide could not be prevented, and the intense absorption of I_3^- [ϵ_{295}(aq) = 4.5×10^4][20] obliterated the CT bands.

Discussion

The alkylmetal–iodine system is noteworthy since it represents a rather unique opportunity to examine steric effects in charge-transfer complexes.[21] In the following discussion we wish (1) to evaluate the steric effects quantitatively, (2) to compare steric effects in $[R_4SnI_2]$ complexes with $K < 0.1$ M^{-1} and those in $[R_4Sn\,TCNE]$ complexes with $K > 1$ M^{-1}, and (3) to employ steric effects as a guide to charge transfer in those systems with $K < 0.1$ M^{-1} in which the distinction from contact charge transfer is not clearly delineated.

1. Steric Effects in Alkylmetal–Iodine Complexes. In order to examine steric effects in alkylmetal–iodine complexes, we focus on the relationship between the charge-transfer transition $h\nu_{CT}$ and the ionization potentials of a series of dialkylmercury and tetraalkyltin compounds in Figure 5. Such an experimental correlation may be expressed as

$$h\nu_{CT} = mI_D + \text{constant} \tag{9}$$

where the slopes are m = 0.40 for tetraalkyltin and 0.43 for dialkylmercury.

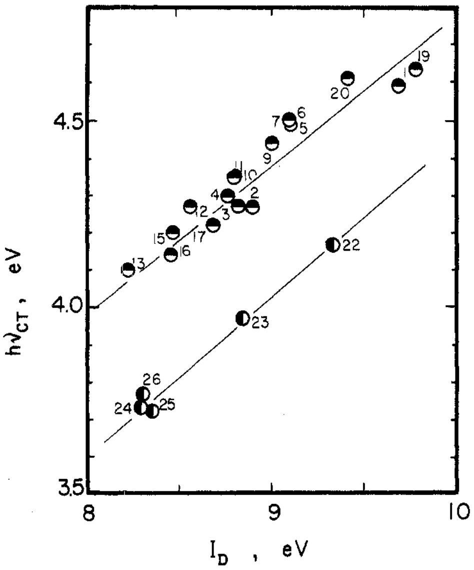


Figure 5. The correlation of the charge-transfer energy ($h\nu_{CT}$) with the ionization potentials (I_D) of alkylmetals. (◐) Dialkylmercury and (⊖) tetraalkyltin, -germanium, and -silicon. Numbers refer to alkylmetals identified in Table II.

For *weak complexes* of the type described here,[22] the charge-transfer transition, according to a first-order treatment of Mulliken's theory, is given by[1,2,23]

$$h\nu_{CT} = I_D - E_A - \frac{e^2}{r_{DA}} \tag{10}$$

where E_A is the vertical electron affinity of iodine and r_{DA} in the Coulombic term represents the mean separation of iodine and the alkylmetal in the complex. If r_{DA} is a constant for a series of related donors, as is commonly assumed,[2] the plots in Figure 5 should have unit slopes. Since m in eq 9 is ~0.4 and clearly not 1.0, the assumption that r_{DA} is invariant must be abandoned. Before doing so, however, let us consider two alternative explanations for reduced slopes which have been presented in the extant CT literature, viz., the solvent effect[2,24] and contributions from charge separation[1,2,19a,25] in the ground state of the complex. The solvent effect can be immediately dismissed for alkylmetal–iodine complexes, since the results in Table IV show that $h\nu_{CT}$ remains unchanged in such nonpolar solvents as cyclohexane, *n*-hexane, and carbon tetrachloride. (Measurements in the more polar solvents are complicated by the enhanced rates of iodinolysis.[26])

Reduced slopes arising from charge separation in the ground state of CT complexes are included in the second-order perturbation treatment of Mulliken's theory, viz.,[2]

$$h\nu_{CT} = I_D - E_A - \frac{e^2}{r_{DA}} + \frac{\beta_0^2 + \beta_1^2}{I_D - E_A - e^2/r_{DA}} \tag{11}$$

The last term in eq 11 represents the resonance interaction between $\Psi_0(DA)$ and $\Psi_1(D^+A^-)$, i.e., β_0 and β_1 are the matrix elements ($H_{01} - S_{01}H_{00}$) and ($H_{01} - S_{01}H_{11}$), respectively, in which S_{01} is the overlap integral.[2] Importantly, eq 11 will produce an approximate linear correlation with I_D,[27] with the slope m evaluated by the differential $d(h\nu_{CT})/dI_D$, i.e.,

$$m = 1 - \frac{\beta_0^2 + \beta_1^2}{(I_D - E_A - e^2/r_{DA})^2} \tag{12}$$[28]

Since the resonance terms in this equation are related to the heat of formation of the CT complex, i.e., $-\Delta H_{CT} \sim \beta_0^2/h\nu_{CT} \sim \beta_1^2/h\nu_{CT}$,[29] the slope can be reexpressed as

$$m \simeq 1 + \frac{2\Delta H_{CT}}{h\nu_{CT}} \tag{13}$$

Such a relationship correctly accounts for the decreased slopes generally associated with rather strong CT complexes. Indeed a value of $-\Delta H_{CT} \sim 30$ kcal mol^{-1} is required to alter the slope of unity to the observed value of ~0.4 for R_4Sn and R_2Hg in Figure 5.[30] However, such magnitudes for ΔH_{CT} are clearly in serious conflict with the experimental values.[32]

We now return to the alternative possibility that r_{DA} in eq 10 is variable and its magnitude is determined by the steric properties of the alkylmetal. Indeed with this formulation, the first anomaly in Figure 5 is immediately resolved—the displacement of ν_{CT} to lower energies in the series of R_2Hg relative to R_4Sn follows from their smaller values of r_{DA} as a result of diminished steric hindrance in these linear, open molecules (vide supra). Furthermore, the linearity of the plots in Figure 5 indicates that the mean separation r_{DA} is related to I_D for a series of related alkylmetals. The relationship is illustrated in Figure 6, where the mean separation is calculated from eq 10 by using the data in Table II for ν_{CT} and I_D. (A value of 1.6 eV is used for the vertical ionization potential of iodine, as elaborated in the Experimental Section.) The calculated values of r_{DA} in Table V are in the range 4–6 Å.[33] They are larger by about an angstrom for the tetrahedral tin

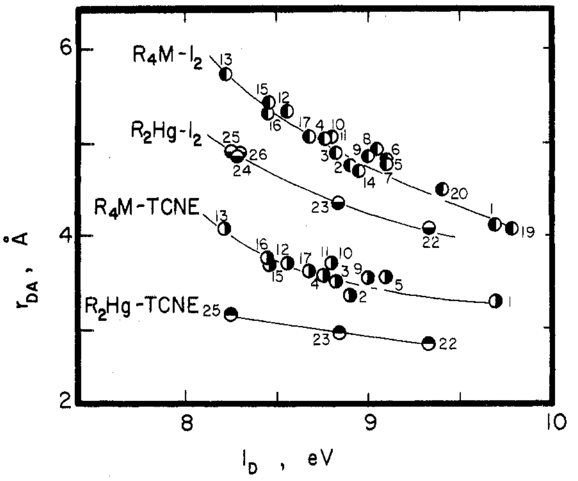


Figure 6. The relationship between steric effects in charge-transfer complexes with the ionization potentials of alkylmetals: (◐) [$R_4M\ I_2$], (◒) [$R_2Hg\ I_2$], (◑) [R_4M TCNE], (⊖) [R_2Hg TCNE]. Numbers identify alkylmetals in Table II.

TABLE V: Mean Separations in the CT Complexes of Alkylmetals and Iodine

alkylmetal	e^2/r_{DA}, eV	r_{DA}, Å	alkylmetal	e^2/r_{DA}, eV	r_{DA}, Å
Me_4Sn	3.50	4.11	Et_3SnMe	3.08	4.68
Et_4Sn	3.03	4.75	*i*-Pr_4Sn	2.66	5.41
n-Pr_4Sn	2.95	4.88	*s*-Bu_4Sn	2.71	5.31
n-Bu_4Sn	2.86	5.03	*i*-Bu_4Sn	2.86	5.03
$EtSnMe_3$	3.01	4.78	*i*-Bu_2SnEt_2		
n-$PrSnMe_3$	3.00	4.80	Et_4Si	3.55	4.06
n-$BuSnMe_3$	3.01	4.78	Et_4Ge	3.20	4.50
i-$BuSnMe_3$	2.91	4.95	*n*-Bu_4Ge		
Et_2SnMe_2	2.97	4.85	Me_2Hg	3.56	4.04
n-Pr_2SnMe_2	2.85	5.05	$EtHgMe$	3.31	4.35
n-Bu_2SnMe_2	2.85	5.05	*n*-Pr_2Hg	2.96	4.86
i-Pr_2SnMe_2	2.69	5.35	*n*-Bu_2Hg	3.03	4.75
t-Bu_2SnMe_2	2.52	5.71	*i*-Bu_2Hg	2.93	4.91

alkyls compared to the corresponding dialkylmercurial of the same ionization potential, as expected from the difference in steric configurations of these two series of organometals. According to this formulation of the charge-transfer transitions in weak alkylmetal–iodine complexes, the slopes of the plot in Figure 5 are directly related to steric effects (as the parameter r_{DA}) via the Coulombic term in eq 10.[34] Thus the differentiation of eq 10 leads to a slope in the form

$$\frac{d(h\nu_{CT})}{d(I_D)} = 1 + \frac{e^2}{(r_{DA})^2}\frac{d(r_{DA})}{d(I_D)} \tag{14}$$

in which $d(r_{DA})/d(I_D)$ relates the steric effect to the ionization potential. Indeed the negative trends for $d(r_{DA})/d(I_D)$ shown in Figure 6 will cause the slope to be less than unity, in accord with the correlations in Figure 5.

This formulation also accords well with the recent studies of CT interactions between a series of alkyl halides with iodine atom,[35]

$$RX + I\cdot \rightleftharpoons [RX\,I\cdot]$$

where X = Br and I. Two absorption bands were observed for each alkyl halide and attributed to coupled spin–orbit splitting of the first ionization potential of the alkyl halide donor. The slopes of the correlation similar to those of Figure 5 for various alkyl halides are appreciably less than 1, being 0.44 (first I_D) and 0.43 (second I_D) for alkyl bromides and 0.36 (first I_D) and 0.37 (second I_D) for alkyl iodides.[36] However, for a *particular* alkyl halide, the slope of $h\nu_{CT}$ between the first I_D and the second I_D is close to 1, being 0.92 ± 0.04 for a series of ten CT complexes of RX and I· in the gas phase and 0.99 ± 0.11 for five CT complexes of RI and I· in hexane solution.[36] The latter accord with eq 14, since the steric effects are obviously the same for the first I_D and second I_D, i.e., $d(r_{DA})/d(I_D) = 0$.

2. *Comparison with Steric Effects in Alkylmetal–TCNE Complexes.* Tetracyanoethylene (TCNE) is a well-known organic π acceptor which also forms discrete charge-transfer complexes with the same alkylmetals examined in this study, i.e.,[37]

$$RM + TCNE \overset{K}{\rightleftharpoons} [RM\,CNE] \tag{15}$$

The formation constants of these 1:1 complexes are small, but measurable in chloroform solution either by the Benesi–Hildebrand method or by direct techniques.[11,38] For convenience, they are retabulated in Table VI. Since the heats of formation, determined from the temperature dependence of K,[39] are generally less than 1 kcal mol^{-1}, the second-order perturbation term is negligible for these complexes, and eq 10 is applicable (vide supra). The mean separations r_{DA} in the [alkylmetal–TCNE] complexes, calculated by the same procedure employed for the [alkylmetal–iodine] complexes, are included in Table VI.

The direct comparison of the charge-transfer complexes of [alkylmetal–TCNE] with [alkylmetal–iodine] is desirable for two reasons. First, [alkylmetal–TCNE] complexes are weak, but their formation constants can be measured by standard spectroscopic methods, whereas the absorption bands from some alkylmetals interacting with iodine could result from contact charge transfer. The common behavior of these systems to steric perturbations would relate electronic transitions from weak charge-transfer complexes with those involving contact charge transfer. Second, this interrelationship allows a clearer focus on the nebulous delineation of contact charge transfer in solution.[40] The parallel trends in r_{DA} for [alkylmetal–TCNE] and [alkylmetal–iodine] are clearly shown in Figure 6. In both systems, separate correlations are required for tetraalkyltin and for dialkylmercury. Furthermore the correlations for TCNE lie below those of iodine, indicating that the mean separation for alkylmetal–TCNE is less than that for alkylmetal–iodine, as expected from the difference in van der Waals distance for carbon and iodine centers.[41]

TABLE VI: Mean Separation in the CT Complexes of Alkylmetals and TCNE[a]

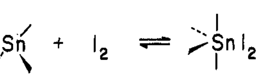
no.	alkylmetal	$h\nu_{CT}$,[b] eV	K[b], M^{-1}	ϵ, M^{-1} cm^{-1}	e^2/r_{DA}, eV	r_{DA}, Å
1	Me_4Sn	3.59	0.17	500	4.40	3.27
2	Et_4Sn	2.95	0.53	167	4.30	3.34
3	n-Pr_4Sn	2.99	2.2	29	4.13	3.48
4	n-Bu_4Sn	2.98	7.7	16	4.08	3.53
5	$EtSnMe_3$	3.32	0.24	222	4.08	3.53
9	Et_2SnMe_2	3.25	0.80	143	4.06	3.55
10	n-Pr_2SnMe_2	3.20	1.5	77	3.90	3.69
11	n-Bu_2SnMe_2	3.21	1.1	50	3.89	3.70
12	i-Pr_2SnMe_2	2.95	0.95	118	3.91	3.68
13	t-Bu_2SnMe_2	2.95	0.65	77	3.57	4.03
15	i-Pr_4Sn	2.83	1.0	95	3.92	3.67
16	sec-Bu_4Sn	2.89	2.5	71	3.86	3.73
17	i-Bu_4Sn	2.99	0.30	125	3.99	3.61
22	Me_2Hg	3.14	-	-	5.10	2.82
23	EtHgMe	2.79	-	-	4.89	2.94
25	n-Bu_2Hg	2.44	-	-	4.58	3.14

[a] In chloroform solution for R_4Sn and 1,2-dichloropropane for R_2Hg. [b] From ref 39. [c] Calculated using E_A(TCNE) = 1.7 eV.

In order to assess quantitatively the steric effects of alkylmetals, we relate all of them to a reference RM_0. Thus for a series of related alkylmetals, it follows from either eq 10 or 11 that the difference in the electrostatic terms ΔE between a particular alkylmetal RM relative to a chosen reference RM_0 is expressed as:

$$\Delta E = -\Delta I_D + \Delta h\nu_{CT} \tag{16}$$

where ΔI_D is the difference in the ionization potentials between RM and RM_0, and $\Delta h\nu_{CT}$ is the difference in their charge-transfer energies with a common acceptor. We arbitrarily choose the reference RM_0 = Me_4Sn for the tetraalkyltin series and RM_0 = Me_2Hg for the dialkylmercury series. Although ΔE is obtained directly from the experimental data by a purely operational approach in eq 16, it can be considered as a direct contribution from steric effects arising from the interaction of the acceptor with the alkylmetal. For example, the steric effect could result from the distortion of a tetrahedral tetraalkyltin to a trigonal-bipyramidal configuration in the complex, e.g.,[11]



(17)

If ΔE for $[RM\,I_2]$ is plotted against that for [RM TCNE], the points in Figure 7 appear to lie roughly along two linear correlations, shown by the pair of lines which are drawn parallel to the dashed line representing $\Delta E(I_2) = \Delta E$(TCNE). Correlation on line a includes all the symmetrical R_4Sn, but of course excluding Me_4Sn. Line b includes the series of di- and trimethyltin compounds Me_2SnR_2 and Me_3SnR, as well as the two dialkylmercury compounds MeHgEt and n-Bu_2Hg. (Diisopropyldimethyltin is an exception.) Alkylmetals included on line a are sterically the most hindered (compare E_s values in Table I), according with a displacement of 0.3 eV above the dashed line. By comparison, line b containing alkyltin compounds with the least hindered methyl ligands is displaced only 0.1 eV from the dashed line. The separation of alkylmetals onto either line a or b according to steric differences

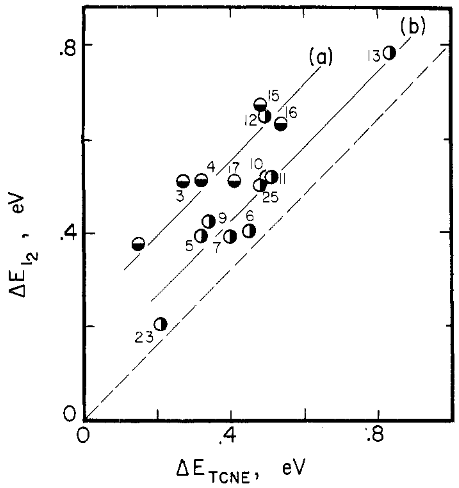
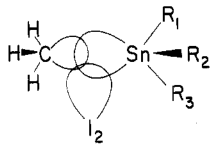


Figure 7. Relationship between the steric effects in [alkylmetal-I_2] complexes with those in [alkylmetal-TCNE] complexes. The dashed line is arbitrarily drawn with slope of 1, and it corresponds to $\Delta E(I_2) = \Delta E(\text{TCNE})$. The alkylmetals are identified by numbers in Table II.

suggests that the charge-transfer interaction with iodine is rather localized at the alkyl to metal σ-bond—that with the least hindered methyl ligand being the most favored. A schematic representation is given below:



Such a selective interaction is generally recognized as the steric effect of alkyl groups.[8]

3. Comments on the Classification of Alkylmetal-Iodine Charge Transfer in Solution. Numerous attempts have been made to characterize contact charge transfer (CCT) bands for weak charge-transfer complexes.[40] Indeed, the small values of the formation constant ($K < 0.1$) which can be estimated for alkylmetals and iodine in eq 2 suggest the possibility of CCT for this system. In other words, the observed absorption bands may be induced only by collisions, and attractive forces between the iodine acceptor and the alkylmetals may be absent. This notion may derive from the plot in Figure 8 of the ϵK values in Table II against the I_D of the alkylmetals, in which the insensitivity of ϵK to I_D might be recognized as a characteristic of CCT.[43]

In order to estimate the limiting values of K for CCT, we employ the collisional model of Tamres and Grundnes in which Z_{AD}, the collision frequency, and t, the time in which D and A remain in contact, are given by eq 18 and 19,[44] respectively, where N_D and N_A are the donor and

$$Z_{DA} = \pi N_D N_A (r_{DA})^2 \bar{c} \qquad (18)$$

$$t = 2\overline{\Delta r}/\bar{c} \qquad (19)$$

acceptor concentrations (in units of molecules per cm^3), $\bar{c}$ is the average velocity, and $\overline{\Delta r}$, is the range (distance) over which CT transition can occur. The product $Z_{AD}t$ (i.e., the number of collisions per unit volume) is equal to KN_DN_A. Combining this with eq 18 and 19 yields

$$K = 3.8 \times 10^{-3} (r_{DA})^2 \overline{\Delta r} \text{ Å}^{-3} \qquad (20)$$

If $\overline{\Delta r}$ is assumed to be 1 Å,[43,45] the calculated value of K for Me_4Sn with $r_{DA} = 4.11$ Å is 0.08 M^{-1}, and $\epsilon = 1.1 \times 10^4$ from ϵK in Table II. This calculated value of K is comparable to the limiting experimental value (<0.1), and the calculated ϵ is reasonable in comparison with those of other weak iodine CT complexes.[4c]

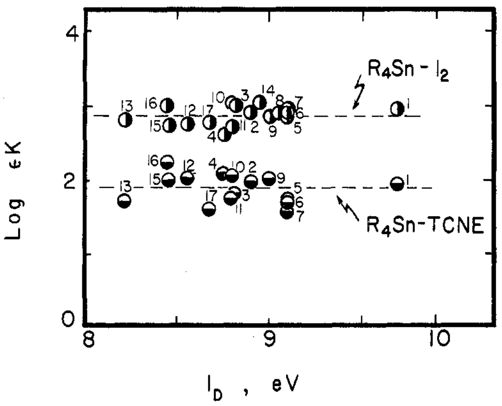


Figure 8. Comparison of ϵK values of [R_4SnI_2] complexes with $K < 0.1$ M^{-1} in carbon tetrachloride solutions and [R_4SnTCNE] complexes with $K \geq 0.2$ M^{-1} in chloroform solutions. Alkylmetals are identified by numbers in Tables II and III.

Such an agreement for K, however, does not necessarily indicate CCT, since eq 18 and 19 are applicable only in the gas phase. In solution, the encounter probability in the range of $\overline{\Delta r}$ will diminish considerably since solvation will inhibit encounter closer than $r_{DA} + \overline{\Delta r}$ in the absence of attractive forces between the alkylmetal and iodine. For example, a method to estimate K for CCT in solution has been proposed by Prue[45] as

$$K = 4\pi (r_{DA})^2 \overline{\Delta r} N \qquad (21)$$

where N is Avogadro's number and the other terms are the same as those in eq 18. When this equation and the same values for r_{DA} and $\overline{\Delta r}$ above are used, $K = 0.14$ M^{-1}, which is even larger than the gas-phase estimate of 0.08 M^{-1}. Clearly, using the same value of $\overline{\Delta r}$ in eq 20 and 21 is incorrect. Furthermore, smaller values of $\overline{\Delta r}$ in solution lack physical significance.[46] Indeed, the mere notion of such a parameter as $\overline{\Delta r}$ in solution includes an implicit assumption of the presence of a complex,[47] however weak the attractive force. Stated alternatively, the concept of CCT absorption in solution is nebulous when it is based on the magnitude of K. Instead, we suggest that the steric perturbation as described here for alkylmetal-iodine complexes is a more appropriate criterion for distinguishing CCT from weak CT complexes.

In another light, the concept of CCT is similar to the nonadiabatic, outer-sphere mechanism for electron transfer.[48] In both, the encounter collision complex involves no (or very small with a minor degree of adiabaticity) interaction between the donor (reductant) and acceptor (oxidant). Recently we showed that the outer-sphere mechanism for electron transfer from the same alkylmetals to iron(III) oxidants involves no steric effect.[49] Even the highly encumbered di-*tert*-butyldimethyltin and tetraneopentyltin are included with a variety of other alkylmetals in the Marcus relationship in eq 22[48] for an outer-sphere mechanism. Similarly, CCT is also expected

$$\Delta G^\ddagger = \tfrac{1}{2}\Delta G^0 + \alpha \qquad (22)$$

to be rather free of steric effects. Thus the strong steric perturbations which we have observed in charge-transfer transition support [R_4SnI_2] complexes as discrete intermediates[50] and not contact charge transfer.

Summary

Charge-transfer absorption bands can be observed with iodine and the alkylmetals of mercury(II), tin(IV), and lead(IV) in carbon tetrachloride solutions. The complexes are classified as weak, in accord with expectations of poor orbital overlap between an alkylmetal σ-donor interacting with a common iodine acceptor. Nonetheless the formation constants can be measured by standard methods for a series of dialkylmercury and methylethyllead compounds. The formation constants for the tetraalkyltin–iodine system are not measurable because of the small values of K (<0.1 M) and large ϵ. In the latter, the distinction between absorptions arising from very weak charge-transfer complexes or contact charge transfer is difficult to delineate by criteria based on either K or ΔH. Thus, the constancy of the ϵK values with variations in the ionization potential of the alkylmetal in Figure 8 is not an adequate measure of CCT, since the same alkylmetals behave similarly with TCNE in which measurements of K show the presence of CT complexes. The constancy in ϵK for alkylmetal–iodine complexes can be attributed to compensating trends in both ϵ and K, as previously discussed for alkylmetal–TCNE complexes.[11] The quantitative evaluation of steric effects indicated by Figure 7 represents the best measure of complex formation, as shown by the parallel behavior of ΔE from eq 16 in a series of alkyltin compounds with iodine and TCNE as acceptors.

Experimental Section

Materials. Symmetrical dialkylmercury was prepared from mercuric bromide by treatment with excess Grignard reagent. The general procedure of Singh and Reddy[51] was followed for the preparation of the unsymmetrical mercurials. The alkylmercury bromide of the *more* reactive alkyl group was treated with a 1.5 equiv excess of the Grignard reagent of the less reactive alkyl group. Most of the alkylmercury bromides used in these preparations were prepared in the usual manner[52] involving treatment of excess mercuric bromide with the corresponding Grignard reagent. The dialkylmercurials were examined by NMR, mass spectroscopy, and elemental analysis as described earlier.[53]

The series of symmetrical tetraalkyltin compounds used in this study was prepared according to standard procedures.[54] In a typical example 70 g (0.27 mol) of stannic chloride was added dropwise to 1.5 mol of EtMgBr in ether under a nitrogen atmosphere. After the addition was completed, the reaction mixture was refluxed for 4 h and hydrolyzed with dilute (0.1 N) aqueous HCl. After repeated extractions with ether, the combined ethereal layer was finally washed with saturated $NaHCO_3$ and dried over $CaCl_2$. Distillation following the removal of solvent afforded Et_4Sn, bp 84 °C (11 mm).[54] Other products, R_4Sn (bp): Me_4Sn (78 °C (758 mm)),[54] *n*-Pr_4Sn (79 °C (2 mm)),[54] *i*-Pr_4Sn (102 °C (30 mm)),[54] *n*-Bu_4Sn (92 °C (1 mm)),[54] *i*-Bu_4Sn (101 °C (1.5 mm)),[54] *sec*-Bu_4Sn (108 °C (0.8 mm)),[55] and *neo*-$Pent_4Sn$ (mp 124 °C after three recrystallizations from *n*-hexane).[56] The unsymmetrical tetraalkyltin compounds, $RSnMe_3$ and R_2SnMe_2, were prepared by a similar procedure starting with Me_3SnCl and Me_2SnCl_2, respectively. Trimethyltin chloride was prepared either from Me_4Sn by HCl cleavage or by syn proportionation with a stoichiometric amount of $SnCl_4$. Dimethyltin dichloride was prepared from Me_4Sn and $SnCl_4$ at 130 °C for 4 h. Triethyltin chloride was prepared from Et_4Sn and acetyl chloride in the presence of aluminum chloride. $RSnMe_3$ (bp): $EtSnMe_3$ (105 °C (760 mm)),[54] *n*-$PrSnMe_3$ (131 °C (760 mm)),[57] *i*-$PrSnMe_3$ (123 °C (120 mm)),[58] *n*-$BuSnMe_3$ (150 °C (750 mm)),[54] *t*-$BuSnMe_3$ (56 °C (36 mm)).[59] R_2SnMe_2 (bp): Et_2SnMe_2 (65 °C (50 mm)),[57] *n*-Pr_2SnMe_2 (74 °C (30 mm)),[57] *i*-Pr_2SnMe_2 (66 °C (30 mm)),[54] *n*-Bu_2SnMe_2 (70 °C (4 mm)),[54] *t*-Bu_2SnMe_2 (75 °C (30 mm)).[54,60] *i*-Bu_2SnEt_2[54] was prepared from *i*-BuMgCl and Et_2SnCl_2 (from Et_4Sn and $SnCl_4$) (bp 124 °C (13 mm)).

The synthesis of the series of methylethyllead compounds was described earlier.[61]

Iodine (Mallinckrodt, sublimed reagent grade containing less than 0.003% chlorine and bromine) was resublimed. Carbon tetrachloride (Fisher Scientific Co., Spectranalyzed grade) was repurified by successive washings with concentrated sulfuric acid, 5% aqueous sodium bicarbonate, and distilled water. It was dried over calcium sulfate and redistilled from calcium hydride.

Spectral Measurements. The spectra were recorded on a Cary 14 spectrophotometer with the compartment thermostated at 25 and 3 °C. The pair of 10-mm quartz cuvettes could be fitted with rubber septum caps. The maximum concentration of alkylmetal and iodine was limited to below that which would cause the slit width of the spectrometer to open to its maximum (3.0 mm). In the region of interest, we were aware that several species could have appreciable absorbances beside the alkylmetal–iodine complex, viz., the alkylmetal itself, the I_2–I_2 interaction (or I_4 complex),[62] and possible I_2–solvent contacts. All transfers were effected with glass pipets to obviate contamination by trace metals. Exposure to light was minimized to avoid any possible photochemical reactions.[63]

The difference spectrum of a CT complex was obtained by first measuring the spectrum of the solution of the alkylmetal and iodine against a reference containing an iodine solution at the same concentration. Next, the solution of alkylmetal in carbon tetrachloride was run against a pure carbon tetrachloride reference. The second spectrum was subtracted from that obtained in the first run to afford the spectrum of the CT complex.

The procedure was more involved with dialkylmercury since the thermal reaction leading to cleavage was appreciable even at 3 °C. The products, alkyl iodides and alkylmercuric iodide in combination with iodine, also led to absorptions in the spectral region of interest.[4c] In order to exclude the absorption due to $[RI\,I_2]$ contacts, the following procedure was employed. First, the rate of cleavage of dialkylmercury by iodine in CCl_4 was measured at 3 °C.[64] Next, the spectrum of a solution of alkyl iodide and iodine of known concentrations was measured in the region of interest (generally 300 ± 40 nm) against the reference containing an iodine solution at the same concentration. The iodine concentration which was chosen corresponded to that to be used for the measurement of the $[R_2Hg\,I_2]$ CT spectrum. From the rate constant obtained by the kinetic study, the time dependence of the absorption due to $[RI\,I_2]$ contacts and RI was determined. The corrected CT spectrum of $[R_2Hg\,I_2]$ was obtained by subtracting (point by point) the spectra of $[RI\,I_2]$ contacts and RI, in the amounts determined by the time elapsed for the recording of the spectrum. With this procedure the contribution from $[RI\,I_2]$ contacts and RI could be limited to 10–30% of the $[R_2Hg\,I_2]$ spectrum. Determinations of λ_{max} for the most reactive *n*-Pr_2Hg at various time intervals (between 20 and 60 s) were reproducible to ±2 nm by this method.

The methylethyllead compounds were too reactive to iodinolysis and rapidly led to products which were strongly absorbing in the region of interest. The values of λ_{max} for the CT complex are correspondingly less reliable.

The measurements of the formation constants for dialkylmercury and methylethyllead compounds with iodine using the iodine absorption are described in the following paper.[65]

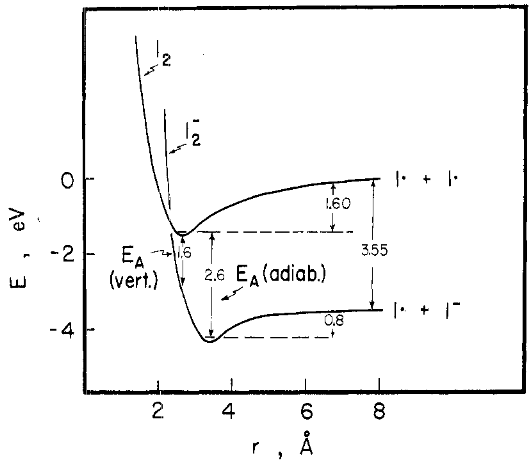


Figure 9. The potential energy diagram for I_2 and I_2^-.

Electron Affinity of Iodine and Tetracyanoethylene. In order to apply eq 9 or 10, the vertical electron affinity of the acceptor is required, which is difficult to measure experimentally in most cases.[66] For example, the vertical electron affinity of iodine was only estimated by Person[67] as 1.7 ± 0.5 eV by applying the Morse function and making use of the interatomic equilibrium distance, dissociation energy, and fundamental vibrational frequencies of I_2 and I_2^-. However, there is a more accurate experimental approach to the vertical electron affinity based on the measured difference in the CT transition energy of I_2 and I· with a common series of alkyl iodides,[35b] where $h\nu_{CT}(I_2) - h\nu_{CT}(I\cdot) = 1.46 \pm 0.05$ eV $= E_A(I\cdot) - E_A(I_2)$.[68] Since the electron affinity of the iodine atom I· is accurately known to be 3.063 eV,[69] the vertical electron affinity of I_2 is 1.60 ± 0.05 eV, in reasonable agreement with Person's estimate. This value compares with the adiabatic electron affinity of 2.58 ± 0.1 eV, determined experimentally by Chupka and Berkowitz[70] from endoergic electron transfer in reactions of the type $I^- + I_2 \rightarrow I\cdot + I_2^-$. The relationships between the vertical and adiabatic electron affinities of iodine are depicted in Figure 9.[71]

For TCNE, the adiabatic electron affinity of 2.3 ± 0.3 eV has been determined from the threshold energy for photodetachment of electrons for the negative ion.[72] The vertical electron affinity of TCNE has not been determined experimentally, but we have arbitrarily chosen the value of 1.7 eV, estimated by Briegleb[73] from CT data of π–π complexes.

Acknowledgment. We thank Dr. M. Tamres for kindly giving us a preprint of the Tamres and Strong review[40] and the National Science Foundation for financial support.

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(17) Absorptions by the cleavage products of these alkylmetals by iodine overlap with the CT bands. The cleavage rates are the fastest with R_2Hg and R_4Pb, but too slow with R_4Sn, Ge, and Si to interfere.
(18) The iodine absorption at λ_{max} 520 nm in carbon tetrachloride is known to be blue shifted by charge-transfer complexation, particularly with strong n donors such as amines and sulfides.[1,19] However, it is clear that the sudden change in the iodine spectrum with R_2Hg is not due to a blue shift in the spectrum accompanied by *enhanced* intensities as observed in those cases cited in ref 1 and 19. For the *decreased* intensities of the blue-shifted iodine band, see the accompanying paper.[26]
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(22) It is important to note that these alkylmetals are σ-donors, since the HOMO is a *bonding* orbital (see ref 7 and Wong, C. L.; Mochida, K.; Gin, A.; Weiner, M. A.; Kochi, J. K. *J. Org. Chem.* **1979**, *44*, 3979). As such, the orbital overlap with iodine is expected to be poor and the CT complexes to be weak.
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(27) In order to fit eq 11 to the experimental data, Mulliken[1] assumed r_{DA} to be constant for a series of compounds and employed three parameters, viz., $C_1 = E_A + e^2/r_{DA}$, $\beta_1 = \beta_0 - S_{01}(I_D - C_1)$, to correlate the data for a variety of π donors. The best fit for $m = 0.9$ was formed with $C_1 = 6.2$ eV, $\beta_0 = -1.4$ eV and $S_{01} < 0.1$ eV. Mulliken also considered that r_{DA} may be inversely related to I_D (see ref 1, p 146).
(28) (a) To effect a decrease in the slope, the second perturbation term in eq 11 must increase as a result of an increase in β_0. (b) Recently, Poh[25a] has suggested on the basis of Hammett ρ values that the slope has a physical significance, viz., $m = 1 - 2b^2$, where b^2 represents the contribution from the charge-separated structure in the CT wave function, i.e., $\Psi_N = a\Psi_0(DA) + b\Psi_1(D^+A^-)$. This analysis, with r_{DA} a constant, is equivalent to eq 12, since $b = -\beta/(I_D - E_A - e^2/r_{DA})$.
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(30) (a) For $m = 0.4$ in eq 13, $\Delta H_{CT} = (0.6/2)h\nu_{CT}$. Taking an average value of $h\nu_{CT}$ for R_4Sn as 4.3 eV, $-\Delta H_{CT} \sim 30$ kcal mol^{-1}. (b) For these complexes, $K \simeq 0.1$ M^{-1} corresponds to $-\Delta H \simeq 1$ kcal mol^{-1}[31] which probably also represents the limiting value of $[R_4SnI_2]$ complexes.
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(32) (a) There is no change in absorbance of the $[Bu_4SnI_2]$ complex between measurements at 25 °C and 3 °C in CCl_4. Within an experimental uncertainty for determining A to be less than 10%, the limiting value of $-\Delta H$ is 0.7 kcal mol^{-1}. (b) With this minimum value of $-\Delta H$, the contribution from the second perturbation term is $(\beta_0^2 + \beta_1^2)/(I_D - E_A - e^2/r_{DA})(h\nu_{CT}) \simeq 2\beta_0^2/(h\nu_{CT})^2$ or about 0.1%, which can be neglected.
(33) The parameter r_{DA} is to be considered as merely an operational device, and its physical significance is not clearly defined, especially for molecules.
(34) Solvation complicates the strict application of eq 10 to CT in solution. We consider the red shift usually encountered in going from the gas phase to solution as mainly due to compressional changes, i.e., cage effects [compare: Prochorow, J.; Tramer, A. *J. Chem. Phys.* **1966**, *44*, 4545. Trotter, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 5721; Ham, J. *Ibid.* **1954**, *76*, 3881. Kwan, O. C.; Lentz, H. *Z. Phys. Chem. (Frankfurt am Main)* **1975**, *96*, 177. Sawamura, S.; Taniguchi, Y.; Suzuki, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 281, 284]. The dielectric effects on these weak complexes are probably negligible [compare: Kroll, M. *J. Am. Chem. Soc.* **1968**, *90*, 1097. Voigt, E. M. *J. Phys. Chem.* **1966**, *70*, 598]. In any case, neither of these factors will affect our principal conclusions about the *relative* magnitudes of steric effects as described later in eq 16, since they will cancel out.

(35) (a) Strong, R. L.; Kaye, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5460. (b) Strong, R. L.; Venditti, F., Jr. *Chem. Phys. Lett.* **1977**, *46*, 546.

(36) Calculated from the data in ref 35.

(37) Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 2460.

(38) The more polar chloroform solvent can be employed for measurements of [alkylmetal–TCNE] complexes, since they are less thermally labile than the corresponding [alkylmetal–iodine] complexes. The CT spectra for RM–TCNE in CCl_4 could not be obtained because of the low solubility of TCNE in CCl_4.

(39) Fukuzumi, S.; Wong, C. L.; Kochi, J. K., *J. Am. Chem. Soc.*, in press.

(40) For an excellent review of contact charge transfer see: Tamres, M.; Strong, R. L. In "Molecular Association"; Foster, R., Ed.; Academic Press: New York, in press; Vol. II.

(41) (a) The antibonding exchange repulsion between the acceptor for excited states with the same donor is also expected to be greater for iodine than for TCNE by virtue of the difference between 5p iodine and 2p carbon atomic orbitals. Actually the r_{DA} for [alkylmetal–iodine] complexes are comparable to the van der Waals distance of 4.15 Å predicted by Mulliken.[42] (b) Part of the difference may also be attributed to the lower solvent polarity of carbon tetrachloride relative to chloroform[2] [e.g., the E_T values of CCl_4 and $CHCl_3$ are 32.5 and 38.3 kcal mol^{-1}, respectively.]

(42) (a) Taking van der Waals distance 2.0 Å for a methyl group and 2.15 Å for an iodine atom (Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260) to give van der Waals distance between CH_3 and I as 4.15 Å. (b) Mulliken, R. S. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 845.

(43) For example, the collisional models of CCT make no significant structural distinctions in various donors and acceptors (see eq 20 and 21).[44,45]

(44) Tamres, M.; Grundnes, J. *J. Am. Chem. Soc.* **1971**, *93*, 801.

(45) Prue, J. E. *J. Chem. Soc.* **1965**, 7534.

(46) Because of solvation it is unreasonable to expect $\overline{\Delta r}$ to be smaller in solution than in the gas phase.

(47) Since the kinetic theories of gases do not apply quantitatively to solution.

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(49) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593.

(50) One may still argue that such a small K and corresponding small ($-\Delta H$) will not provide any evidence of an attractive force between donor and acceptor beyond a van der Waals interaction. In solution, however, Kroll has pointed out changes in solvation during complex formation are likely to cancel out van der Waals forces (Kroll, M. *J. Am. Chem. Soc.* **1968**, *90*, 1097).

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(64) The rate follows a second-order kinetics: $-d[I_2]/dt = k[HgR_2][I_2]$. The details of the reaction of alkylmetals and iodine will be reported elsewhere. [Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.*, in press.] Alkyltin, -germanium, and -silicon compounds do not react with I_2 in CCl_4 during the CT measurements.

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