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Importance of Work Terms in the Free Energy Relationship for Electron Transfer

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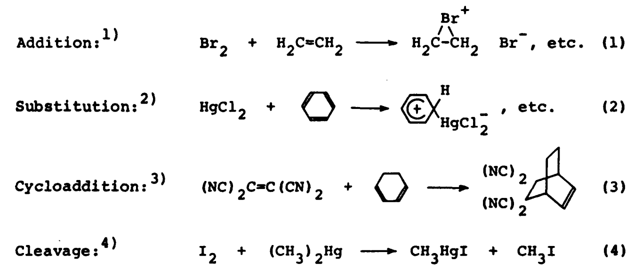
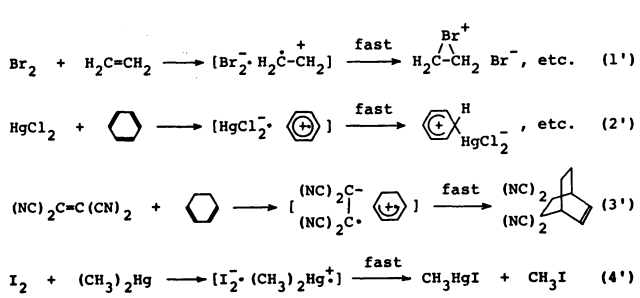
The rates of arene and alkene brominations and mercurations, Diels-Alder cycloaddition as well as alkylmetal cleavages by electrophiles, electron acceptors and free atoms can be quantitatively analyzed in terms of the driving force for electron transfer. The single, unified free energy relationship for all of these rather disparate chemical processes relates the activation free energy to the standard free energy change for electron transfer and the work term for ion-pair formation. The latter is evaluated from charge transfer spectral data of the electron donor-acceptor complexes formed as transient intermediates. The large variations in the apparent Brönsted slopes from unity to even negative values in these systems can be readily attributed to changes in the work terms arising from steric effects in ion-pair formation.

Electron transfer mechanisms are receiving increased attention in a wide variety of reactions previously formulated as more conventional ionic or concerted processes. Let us consider for example such conventional transformations as (1) the addition of halogen to alkenes, (2) aromatic substitution, (3) Diels-Alder reactions, and (4) halogenolysis of organometals. The activation process for each is commonly represented by a single step shown in the following classical examples:



[Note that the activation processes in Eqs. 1 and 2 are subsequently followed by one or more rapid steps to afford the final products.]

The same transformations can be represented by an alternative two-step mechanism in which electron transfer is rate-limiting, *i.e.*,



In this formulation, the followup steps are sufficiently rapid to render the initial electron transfer to be part of an overall irreversible transformation. Such mechanisms have been referred to as SET, or single electron transfer,[5,6] since they derive their driving force from one component (A=Br_2, $HgCl_2$, $(NC)_2C{=}C(CN)_2$, I_2) acting as an one-electron acceptor relative to the other component (D=$H_2C{=}CH_2$, C_6H_6, C_6H_8, $(CH_3)_2Hg$) which is then considered to be the electron donor.[7]

Since electron transfer mechanisms such as these are likely to be considered with increasing frequency in organic and organometallic chemistry, we wish to present in this paper the quantitative relationship between the rate of the reaction and the energetics of the electron transfer process. Such a free energy relationship (FER) would provide a better means to evaluate electron transfer mechanisms and also to facilitate their further analysis.

Mechanistic Formulation of Electron Transfer. Importance of the Work Term

The viability of the electron transfer mechanism is usually evaluated in the light of the standard potentials E^0 for each redox couple, *i.e.*, E^0_{ox} for the oxidation of the donor ($D \rightarrow D^+ + e$) and E^0_{red} for the reduction of the acceptor ($A + e \rightarrow A^-$). Thus the general reaction scheme for an irreversible process is represented by:[8]

$$D + A \overset{K_{DA}}{\rightleftharpoons} [D\ A] \xrightarrow{k_{et}} [D^+A^-] \xrightarrow{\text{fast}} \text{Products}, \quad (5)$$

in which electron transfer in the encounter complex [D A] is rate-limiting. This scheme is particularly applicable to systems which lie in the endergonic region of the driving force [*i.e.*, where the standard free energy change, $\Delta G^0 \gg 0$]. The observed second-order rate constant k_{obsd} is then given by:

$$k_{obsd} = k_{et} K_{DA}, \quad (6)$$

where K_{DA} is the formation constant of the complex and k_{et} is the intramolecular rate constant for electron transfer. The thermochemical cycle for an irreversible electron transfer in the highly endergonic region[9,10] is schematically illustrated below. In such a highly endergonic region, the activation free energy for electron transfer $\Delta G^{\ne}$ in the encounter complex is considered to be equal to the free energy change for the ion pair formation, and thus given by Eq. 10 (Scheme 1),[10]

$$\Delta G^{\ne} = \Delta G^0 + w_p - w_r, \quad (7)$$

where ΔG^0 corresponds to the standard free energy

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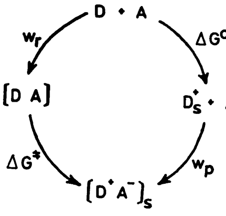


Scheme 1.

change of the redox process: $D+A \rightarrow D^+ + A^-$, and the work terms w_p and w_r represent the energy required to bring together the products and reactants, respectively, to within the mean separation r_{DA} in the ion pair $[D^+ A^-]$. The observed second-order rate constant in Eq. 6 can be expressed in terms of the activation free energy for electron transfer $\Delta G^{\neq}$ in the encounter complex and the work term w_r as:[11]

$$k_{obsd} = \frac{\kappa T}{h} \exp\left[-\frac{(\Delta G^{\neq} + w_r)}{RT}\right]. \tag{8}$$

The combination of Eqs. 7 and 8 affords the free energy relationship for electron transfer as:

$$\log k_{obsd} = -\frac{1}{2.3\,RT}(\Delta G^0 + w_p) + C_1, \tag{9}$$

where $C_1 = \log(\kappa T/h)$ is taken as 12.8 at 298 K. Since the free energy change for electron transfer ΔG^0 is obtained from the standard potentials of the acceptor and donor [*i.e.*, $\Delta G^0(\text{in V}) = E^0_{ox} - E^0_{red}$], the free energy relationship in Eq. 9 may be represented by an equivalent form in Eq. 10,

$$\log k_{obsd} = -\frac{1}{2.3\,RT}(E^0_{ox} + w_p) + \text{Constant}, \tag{10}$$

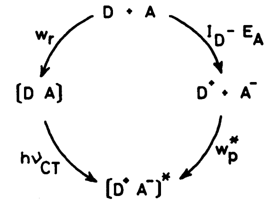
when one is dealing with a series of electron transfer reactions with a fixed acceptor.[12] Thus Eqs. 9 and 10 state that the observed rate constant ($\log k_{obsd}$) for electron transfer can be expressed as the sum of the standard free energy change (ΔG^0) and the work term of the products (w_p). Previous considerations of electron transfer have tended to focus only on the magnitude of ΔG^0, without explicitly taking account the energetics of the ion pair $[D^+ A^-]$ formation, *i.e.*, the work term w_p.[13,16] Such an oversimplication is perhaps understandable if one considers the experimental difficulty of directly evaluating the work terms of ion pairs by the usual procedures. The problem is severely compounded by exceedingly short lifetimes of the transient ion-pairs which must be involved in irreversible electron transfer. We now wish to discuss how the observation of charge-transfer spectra in these systems can be used to evaluate such ion-pairing energies.

Evaluation of the Work Term from Charge-transfer Spectral Data

The intermolecular interaction leading to the precursor complex in Scheme 1 is reminiscent of the electron donor-acceptor or EDA complexes formed between electron donors and acceptors.[18] The latter is characterized by the presence of a new absorption band in the electronic spectrum. According to the Mulliken charge-transfer (CT) theory for weak EDA complexes, the absorption maximum $h\nu_{CT}$ corresponds to the vertical (Franck-Condon) transition from the neutral ground state to the polar excited state.[19,20]

$$[D\ A] \xrightarrow{h\nu_{CT}} [D^+A^-]^* \tag{11}$$

The asterisk identifies an excited ion pair with the same mean separation r_{DA} as that in the precursor or EDA complex. The thermo-chemical cycle for such a charge-transfer transition is schematically illustrated below. The



Scheme 2.

vertical ionization potential of the electron donor is represented by I_D, and the electron affinity of the acceptor by E_A.

The charge-transfer Scheme 2 is akin to the adiabatic electron transfer cycle in Scheme 1. In this case the work term w_p^* required to bring the products D^+ and A^- together to the mean separation r_{DA} in the CT excited state is given by:

$$w_p^* = h\nu_{CT} - I_D + C_2, \tag{12}$$

where $C_2 = E_A + w_r$ and considered to be constant for a fixed acceptor.[21] In the limit of simple ion-pair interactions, the work term is largely coulombic, *i.e.*, $w_p^* \cong -e^2/r_{DA}$.

The charge-transfer spectral data listed in Table 1 relate to the various donors and acceptors pertinent to the various reactions described in Eqs. 1—4. In order to assess these systems quantitatively, we relate the work term w_p^* to that of a reference donor $w_p^{0}{}^*$, since each series in Table 1 involves a fixed acceptor. This comparative procedure allows the acceptor component in a given series to drop out by cancellation, and it follows from Eq. 12 that:[27]

$$\Delta w_p^* = w_p^* - w_p^{0}{}^* = \Delta h\nu_{CT} - \Delta I_D. \tag{13}$$

In Eq. 13, $\Delta h\nu_{CT}$ refers to the relative CT transition energy with a common acceptor, and ΔI_D is the difference in the ionization potentials of the donor and the chosen reference. Thus by selecting a reference donor, we can express all changes in the ion-pairing energies in the CT excited state (including steric, distortional and other effects in the D/A pair) by a single, composite energy term Δw_p^*.

The values of Δw_p^* for a series of EDA complexes are listed in Table 1, together with the ionization potentials of the donors. The reference donor in each series is appropriately designated.

The relative work term Δw_p^* evaluated from the data in Table 1 and Eq. 13 is plotted in Fig. 1 against the ionization potential of the donor for each series of EDA complexes in Table 1. Several features in Fig. 1 are noteworthy. First, the magnitude and the variation of

TABLE 1. CHARGE-TRANSFER TRANSITION ENERGIES AND THE VARIATION OF THE WORK TERM w_p^* OF VARIOUS ELECTRON DONOR-ACCEPTOR COMPLEXES[a]

Donor	I_D/eV	Acceptor	$h\nu_{CT}$/eV	Δw_p^*/eV
Anthracenes[b]				
1 Anthracene	7.33	TCNE	1.65	0.42
2 9-(Me)anthracene	7.17	TCNE	1.50	0.43
3 9-(Et)anthracene	7.19	TCNE	1.52	0.43
4 9-(Br)anthracene	7.38	TCNE	1.74	0.46
5 9,10-(Me_2)anthracene	7.04	TCNE	1.38	0.44
6 9,10-(Br_2)anthracene	7.44	TCNE	1.77	0.43
7 Benz(α)anthracene	7.47	TCNE	1.76	0.39
Alkylmetals[c]				
8 Me_4Pb	8.90	TCNE	3.01	0.21
9 Me_3PbEt	8.65	TCNE	2.89	0.34
10 Me_2PbEt_2	8.45	TCNE	2.73	0.38
11 $MePbEt_3$	8.26	TCNE	2.59	0.43
12 Et_4Pb	8.13	TCNE	2.52	0.49
13 Me_4Sn	9.69	TCNE	3.59	0†
14 n-Bu_4Sn	8.76	TCNE	2.98	0.32
Arenes[d]				
1 C_6H_6	9.23	Br_2	4.32	0.05
2 MeC_6H_5	8.82	Br_2	4.15	0.29
3 EtC_6H_5	8.76	Br_2	4.15	0.35
4 i-PrC_6H_5	8.69	Br_2	4.13	0.40
5 $MeOC_6H_5$	8.39	Br_2	3.73	0.30
6 o-$Me_2C_6H_4$	8.56	Br_2	4.00	0.40
7 m-$Me_2C_6H_4$	8.56	Br_2	3.97	0.37
8 p-$Me_2C_6H_4$	8.44	Br_2	4.13	0.65
9 1,3,5-$Me_3C_6H_3$	8.40	Br_2	3.79	0.35
Alkenes[e]				
10 $H_2C{=}CH_2$	10.52	Br_2	5.14	−0.42
11 $H_2C{=}CHMe$	9.74	Br_2	4.64	−0.14
12 $H_2C{=}CHEt$	9.63	Br_2	4.61	−0.06
13 $H_2C{=}CH(n\text{-}Pr)$	9.52	Br_2	4.56	0†
14 $H_2C{=}CMe_2$	9.24	Br_2	4.27	−0.01
15 $H_2C{=}CMe(Et)$	9.15	Br_2	4.21	0.02
16 (Z)-MeCH=CHMe	9.12	Br_2	4.25	0.09
17 (E)-MeCH=CHEt	9.04	Br_2	4.24	0.16
18 (E)-MeCH=CH(t-Bu)	8.91	Br_2	4.04	0.09
19 $H_2C{=}CH(t\text{-}Bu)$	9.45	Br_2	4.51	0.02
20 $Me_2C{=}CMe(Et)$	8.21	Br_2	3.57	0.32
21 $Me_2C{=}CMe_2$	8.27	Br_2	3.61	0.30
22 $Me_2C{=}CMe(n\text{-}Pr)$	8.19	Br_2	3.55	0.32
23 $Me_2C{=}CMe(n\text{-}Bu)$	8.15	Br_2	3.52	0.33
24 Cyclohexene	8.95	Br_2	4.16	0.17
Alkylmetals[f]				
25 Me_4Sn	9.69	Br_2	4.73	0†
26 Et_4Sn	8.90	Br_2	4.43	0.49
27 n-Pr_4Sn	8.82	Br_2	4.43	0.57
28 n-Bu_4Sn	8.76	Br_2	4.43	0.66
29 i-Pr_4Sn	8.46	Br_2	4.25	0.75
30 s-Bu_4Sn	8.45	Br_2	4.22	0.73
31 i-Bu_4Sn	8.68	Br_2	4.41	0.69
Alkenes[e]				
1 $H_2C{=}CH(n\text{-}Pr)$	9.52	$Hg(OAc)_2$	5.08	0†
2 $H_2C{=}CH(n\text{-}Bu)$	9.48	$Hg(OAc)_2$	5.06	0.02
3 $H_2C{=}CH(n\text{-}C_6H_{13})$	9.43	$Hg(OAc)_2$	5.04	0.05
4 Cyclohexene	8.95	$Hg(OAc)_2$	4.80	0.29
5 Cycloheptene	8.81	$Hg(OAc)_2$	4.78	0.41
6 (Z)-Cyclooctene	8.97	$Hg(OAc)_2$	4.84	0.31
7 $H_2C{=}CH(t\text{-}Bu)$	9.45	$Hg(OAc)_2$	5.08	0.07
8 (E)-MeCH=CH(t-Bu)	8.91	$Hg(OAc)_2$	4.84	0.37
9 $MeCH{=}CMe_2$	8.68	$Hg(OAc)_2$	4.68	0.44
10 $Me_2C{=}CMe_2$	8.27	$Hg(OAc)_2$	4.52	0.69
Alkylmetals[g]				
11 Me_4Sn	9.69	$HgCl_2$	5.27	0†
12 Et_4Sn	8.90	$HgCl_2$	5.08	0.60
13 n-Pr_4Sn	8.82	$HgCl_2$	5.10	0.70
14 n-Bu_4Sn	8.76	$HgCl_2$	5.12	0.78
15 i-Bu_4Sn	8.46	$HgCl_2$	5.10	0.84
16 i-Pr_4Sn	8.45	$HgCl_2$	5.14	1.10
17 s-Bu_4Sn	8.68	$HgCl_2$	5.12	1.09

a) The reference donor is designated by †. b) From Ref. 26. c) From Ref. 22. d) From Ref. 25. e) From Ref. 24. f) From Ref. 23c. g) From Ref. 23b.

the work term depends strongly on the electron donor as well as the acceptor. Thus w_p^* is rather constant for TCNE when it interacts with various substituted anthracene donors (Fig. 1a), but it decreases significantly as the ionization potential of the organometal donors increases (Fig. 1b). Furthermore, the variation in w_p^* is the largest with organometals, when considered among other donors such as arenes and alkenes. With a particular series of donors, the variation of w_p^* is the largest with the mercury(II) complexes $Hg(OAc)_2$ and $HgCl_2$, among other acceptors such as TCNE and Br_2.

We associate such variations in the work term w_p^* with changes in the mean separation r_{DA} in the EDA complexes. Qualitatively, such changes may be viewed as steric effects which hinder the close approach of the acceptor and the donor.[28] For example, the constancy of w_p^* for the substituted anthracene donors accords with the minor steric perturbation since a substituent is expected to exert on a large π-donor such as a polycyclic aromatic network. By contrast, bulky substituents on alkylmetals can effect large changes in w_p^* owing to the localized nature of the interaction in these σ-donors.[29,30]

Free Energy Relationship for Electron Transfer from the CT Work Terms

Taken all together, the relationships in Fig. 1 graphically underscore the marked variation in the work term w_p^* in the excited ion pair (Scheme 2) as a result of the structural changes in the various donor-acceptor pairs. Moreover the interrelationship between encounter and EDA complexes implies that the work term w_p in the adiabatic ion pair (Scheme 1) can be subject to similar variations arising from structural changes in the donor-acceptor pair. Indeed, we previously showed how the variation of the work terms in the adiabatic ion pairs can parallel those in the excited ion pairs.[17] In order

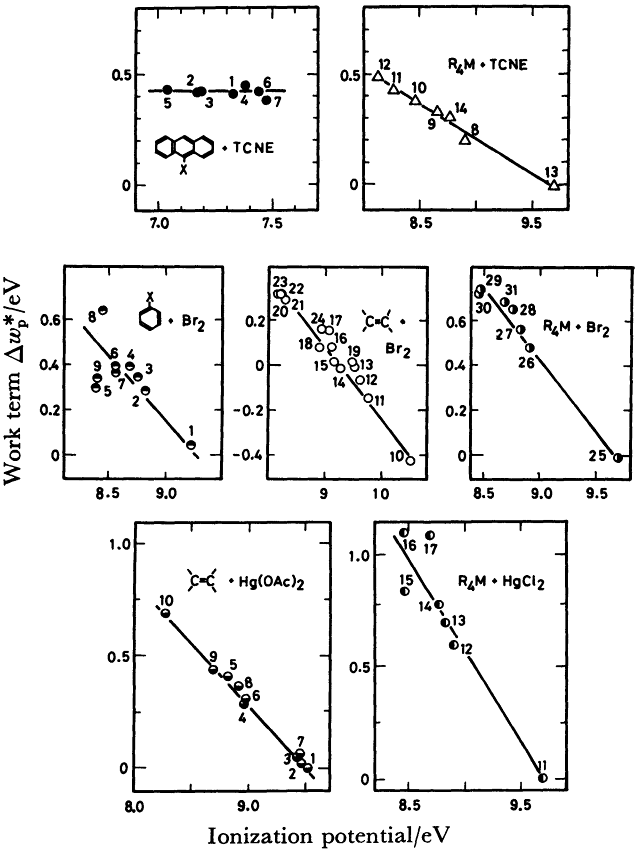


Fig. 1. Variation of the work term w_p* evaluated for the various electron donor-acceptor complexes. The numbers refer to the donors listed in Table 1.

to establish this connection, we initially examined the electron-transfer kinetics of a series of alkylmetal donors R_4M with the inorganic oxidant hexachloroiridate(IV), which is known to effect one-electron transfer, *i.e.*,[31]

$$IrCl_6^{2-} + R_4M \xrightarrow{k} [IrCl_6^{3-}\ R_4M^+]. \tag{14}$$

We next examined the electron transfer kinetics of the same series of alkylmetal donors with the organic electron acceptor tetracyanoethylene, for which the rate-limiting step had been previously established as:[21,32]

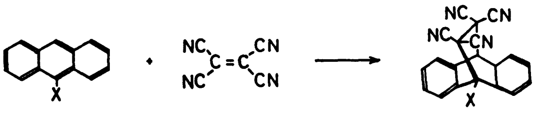
$$TCNE + R_4M \xrightarrow{k} [TCNE^-\ R_4M^+]. \tag{15}$$

In both series of electron transfer processes, the free energy relationship was found to be:

$$\log k = -\frac{1}{2.3\,RT}[E^0_{ox} + \Delta w_p^*] + \text{Constant}, \tag{16}$$

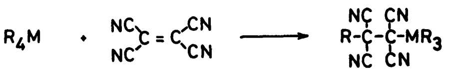
where E^0_{ox} is the standard potential for the alkylmetal donor, and the work term Δw_p^* was evaluated from the charge transfer spectral data of the EDA complex [TCNE R_4M] according to Eq. 13.[17,27,33] Thus the experimental free energy relationship in Eq. 16 is equivalent to that (Eq. 10) obtained from Scheme 1.[34]

The successful derivation of this linear free energy relationship encourages us to now apply it to the series of reactions in Eqs. 1—4 which have been variously described as either an electrophilic or a concerted process. Thus let us first consider anthracene cycloaddition with TCNE,



(17)

in the light of alkylmetal insertion,



$$R_4M + (NC)_2C{=}C(CN)_2 \longrightarrow R\text{-}C(CN)_2\text{-}C(CN)_2\text{-}MR_3 \tag{18}$$

In the following sections, we will also describe how the same treatment applies to diverse reactions of molecular bromine, mercury(II), and atomic iodine with arene, alkene, and alkylmetal donors.

Diels-Alder Cycloaddition of Anthracenes and Organometal Cleavage with Tetracyanoethylene. New, transient absorption bands are observed immediately upon mixing (1) a series of substituted anthracenes or (2) a series of tetraalkyllead and tin compounds with tetracyanoethylene in either 1,2-dichloroethane or chloroform solutions.[26] With both series of donors, the disappearance of the CT bands coincides with the product formation given in Eqs. 17 and 18. Moreover, the rates of reaction in both series follow second-order kinetics overall—first-order in TCNE and first-order in the anthracenes or the alkylmetals. For convenience, the second-order rate constants are relisted in Table 2 together with the standard potentials E^0_{ox} of the anthracenes and the alkylmetals.

In Fig. 2a, we find a direct relationship between the E^0_{ox} of anthracenes and alkylmetals and their reactivity [$\log(k_{obsd}/M^{-1}\,s^{-1})$; 1 M=1 mol dm^{-3}] toward TCNE.

TABLE 2. SECOND-ORDER RATE CONSTANTS FOR THE REACTIONS OF SUBSTITUTED ALKYLMETALS AND ANTHRACENES WITH TETRACYANOETHYLENE. THE STANDARD POTENTIALS E^0_{ox} OF THE DONORS

Donor	E^0_{ox}/V	$\log(k_{obsd}/M^{-1}\,s^{-1})$	$E^0_{ox}+\Delta w_p^*$/eV
Alkylmetals[a)]			
1 Me_4Pb	1.22	−1.49	1.43
2 Me_3PbEt	1.08	−0.28	1.42
3 Me_2PbEt_2	0.97	0.49	1.35
4 $MePbEt_3$	0.87	1.08	1.30
5 Et_4Pb	0.79	1.68	1.28
6 Me_4Sn	1.66	−4.82	1.66
7 *n*-Bu_4Sn	1.14	−2.04	1.46
Anthracenes[b)]			
8 Anthracene	0.95	0.52	1.37
9 Benz(α)anthracene	1.05	−1.51	1.44
10 9-(Me)anthracene	0.79	3.04	1.22
11 2-(Me)anthracene	0.89	0.54	1.32
12 9-(Et)anthracene	0.81	2.51[c)]	1.24
13 9-(*n*-Pr)anthracene	0.82	2.43[c)]	1.25
14 9-(*i*-Pr)anthracene	0.86	1.74[c)]	1.29
15 9-(*t*-Bu)anthracene	0.84	1.95[c)]	1.27
16 9-(Br)anthracene	0.94	−0.51	1.40
17 9,10-(Me_2)anthracene	0.65	4.60[c)]	1.09

a) In acetonitrile at 298 K from Ref. 22. b) In acetonitrile at 298 K from Ref. 26, unless noted otherwise. c) In carbon tetrachloride.

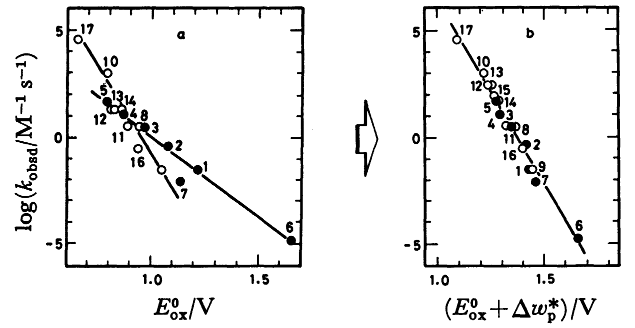


Fig. 2. (a) Free energy relationships for the Diels-Alder reaction of anthracenes (○) and the insertion reaction of alkylmetals (●) with TCNE. (b) Unified free energy relationship with the work term according to Eq. 16. Donors identified by the numbers in Table 2.

The experimental plot shows two linear, but separate correlations described by Eqs. 19 and 20.

Alkylmetal-TCNE:

$$\log k_{obsd} = -\frac{1}{2.3\,RT}(0.96\,E^0_{ox}) + 16. \tag{19}$$

Alkylmetal-TCNE:

$$\log k_{obsd} = -\frac{1}{2.3\,RT}(0.45\,E^0_{ox}) + 7.6. \tag{20}$$

It is noteworthy that the two different correlations in Fig. 2a emerge as a single correlation when the work term Δw^*_p is included. The result in Fig. 2b is a linear free energy relationship,[35]

$$\log k_{obsd} = -\frac{1}{2.3\,RT}(E^0_{ox} + \Delta w^*_p) + \text{Constant}, \tag{16}$$

which applies to both anthracene cycloaddition and alkylmetal insertion. Note the line in Fig. 2b is arbitrarily drawn with a slope of $-1/2.3RT$ to emphasize the fit of both sets of data to Eq. 16.[36] Such an unification is remarkable since these processes clearly represeninherently dissimilar reaction types. Thus the Diels-Alder reaction is usually considered to involve a concerted [$2\pi+4\pi$] cycloaddition,[3] whereas the alkylmetal insertion requires a multistep scission of a σ carbon-metal bond.[22] The applicability of Eq. 16 to such diverse processes as anthracene cycloaddition and alkylmetal insertion derives from a correspondence of the work term variation, *i.e.*, $\Delta w^*_p = \Delta w_p$.[34]

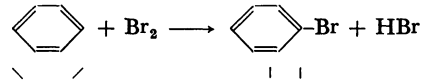
It must be emphasized that the values of w^*_p are obtained from the independent measurements of the ionization potentials and the CT transition energies in Eq. 12. As such, the constancy of Δw^*_p for the anthracenes in Fig. 1a indicates that the relative rates of cycloaddition with TCNE are solely determined by E^0_{ox}. Thus these Diels-Alder reactions can be classified as irreversible electron transfer processes in which the mean separations in the ion pairs are constant. Indeed the apparent Brönsted slope of nearly unity in Eq. 19 accords with an endergonic electron transfer process.[9,37,38]

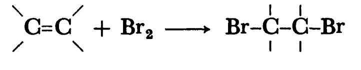
Bromination of Arenes, Alkenes, and Alkylmetals. Molecular bromine forms transient EDA complexes with a variety of π-donors (arenes and alkenes)[24,25] as well as σ-donors (alkylmetals).[23] The decay of the charge-transfer bands has been shown to coincide with the bromination of the donor molecules, as given by Eqs. 21—23.

Table 3. Second-order rate constants for the reactions of alkylmetals, alkenes, and arenes with bromine. The standard potentials E^0_{ox} of donors

Donor	E^0_{ox} / V	log (k_{obsd}/ M^{-1} s^{-1})	$E^0_{ox}+\Delta w^*_p$ / eV
Alkylmetals[a]			
1 Me_4Sn	2.36	−3.72	2.36
2 Et_4Sn	1.77	−1.60	2.26
3 n-Pr_4Sn	1.71	−1.96	2.28
4 n-Bu_4Sn	1.66	−1.89	2.32
5 i-Pr_4Sn	1.44	−0.57	2.19
6 s-Bu_4Sn	1.43	−1.19	2.16
7 i-Bu_4Sn	1.61	−2.62	2.30
Alkenes[b]			
8 $H_2C{=}CH_2$	2.66	−0.66	2.24
9 $H_2C{=}CHMe$	2.29	1.25	2.15
10 $H_2C{=}CHEt$	2.25	1.46	2.19
11 $H_2C{=}CH(n$-$Pr)$	2.19	1.22	2.19
12 $H_2C{=}CMe_2$	2.06	3.18	2.05
13 $H_2C{=}CMe(Et)$	2.02	3.52	2.04
14 (Z)-$MeCH{=}CHMe$	2.00	3.09	2.09
15 (E)-$MeCH{=}CHEt$	1.97	3.25	2.13
16 (E)-$MeCH{=}CH(t$-$Bu)$	2.02	2.48	2.11
17 $H_2C{=}CH(t$-$Bu)$	2.15	1.01	2.17
18 $Me_2C{=}CMe(Et)$	1.57	5.92	1.89
19 $Me_2C{=}CMe_2$	1.57	5.76	1.87
20 $Me_2C{=}CMe(n$-$Pr)$	1.56	5.58	1.88
21 $Me_2C{=}CMe(n$-$Bu)$	1.57	5.62	1.90
22 Cyclohexene	1.96	2.53	2.13
Arenes[c]			
23 C_6H_6	2.82	−11.63	2.87
24 MeC_6H_5	2.41	−8.85	2.70
25 EtC_6H_5	2.35	−8.97	2.70
26 i-PrC_6H_5	2.28	−9.22	2.68
27 $MeOC_6H_5$	1.98	−2.37	2.28
28 o-$Me_2C_6H_4$	2.15	−7.90	2.55
29 m-$Me_2C_6H_4$	2.15	−5.89	2.52
30 p-$Me_2C_6H_4$	2.03	−8.23	2.68
31 1,3,5-$Me_3C_6H_3$	1.99	−3.35	2.34

a) In carbon tetrachloride at 298 K from Ref. 23c. b) In acetic acid at 298 K from Refs. 40 and 41. c) In acetic acid at 298 K from Refs. 40 and 42.


(21)[39]


$$\mathrm{>C{=}C<} + Br_2 \longrightarrow \mathrm{Br{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}Br} \tag{22}$$
[24]

$$R_4M + Br_2 \longrightarrow R_3MBr + RBr \tag{23}$$
[23]

The second-order rate constants for the arene and alkene brominations have been reported[40] in acetic acid and are relisted in Table 3, together with the second-order rate constants for alkylmetal brominolysis in carbon tetrachloride.[23c] Since the standard potentials of the donors are not known, we used the general relationship in Eq. 24[43,44] to evaluate E^0_{ox} in these solvents.

$$E^0_{ox} = I_D + \Delta G^s - C \tag{24}$$

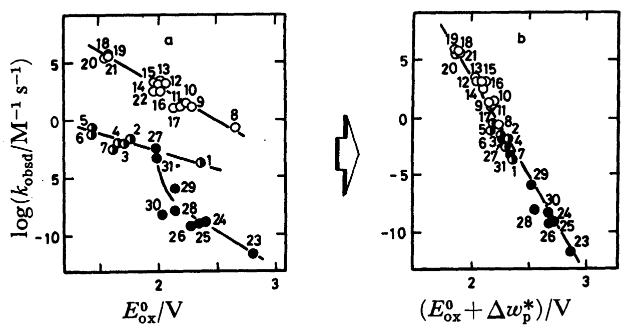
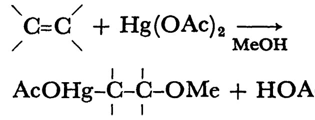


Fig. 3. Brominations. (a) Free energy relationships for arenes (●), alkenes (◑), and alkylmetals (○), as donors identified in Table 3. (b) Unified free energy relationship including the work term as described by Eq. 16.

The free energy change ΔG^s represents the solvation of the donor cation relative to the neutral donor, and are evaluated in Table 6 (see Appendix). C is a constant which includes the potential of the reference electrode on the absolute scale and the junction potential.[44] The relevant values of E^0_{ox} are included in Table 3.

The relationship between the rates of electrophilic bromination ($\log k_{obsd}$) and the standard potentials (E^0_{ox}) of the arene, alkene, and alkylmetal donors is shown in Fig. 3a.[35] Although a rough linear correlation exists for each series,[45] there is no clearcut interrelationship among any of them. However, if the variation of the work term Δw^*_p derived from the CT data in Table 1 is included, the three separate relationships in Fig. 3a become a single correlation. The result in Fig. 3b is the same linear free energy relationship previously expressed in Eq. 16.[46] Indeed the line in Fig. 3b is arbitrarily drawn with a slope of $-1/2.3RT$ to emphasize the correlation of the data with Eq. 16.

Mercuration of Alkenes and Mercurolysis of Alkylmetals. Systems with Large Steric Variations: Transient charge transfer bands are immediately observed when mercury(II) complexes such as mercuric acetate and chloride are mixed with a series of alkene, arene, and alkylmetal donors.[23b,24] The disappearance of the EDA complex of mercury(II) acetate and an alkene is accompanied by the addition reaction in Eq. 25.



$$\text{>C=C<} + Hg(OAc)_2 \xrightarrow[\text{MeOH}]{} AcOHg\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}OMe + HOAc \qquad (25)$$

The rate of this oxymercuration follows overall second-order kinetics in protic solvents such as methanol.[24]

The observed second-order rate constants ($\log k_{obsd}$) for the oxymercuration of various alkenes are collected in Table 4 together with the values of the standard potentials (E^0_{ox}) for the alkene donors in methanol.[47] It is interesting to note that the rates of oxymercuration of electron rich alkenes such as trimethyl- and tetramethylethylene are actually slower than those of normal alkenes such as 1-pentene and 1-octene. Such a trend for $\log k_{obsd}$ to generally decrease with the lowering of E^0_{ox} is in marked contrast to the results in Figs. 2a and 3a. Moreover, the plot of $\log k_{obsd}$ and E^0_{ox} affords the rather random, "buckshot" pattern shown in Fig. 4a. Nonetheless such a nondescript appearance of the data is transformed into the linear correlation shown in Fig. 4b when the work term variation Δw^*_p is included. Although the correlation in Fig. 4b has considerable scatter (owing to the experimental difficulties in the measurement of w^*_p and the limited range of rates), the fit of the data to the line which describes the general free energy relationships of Eq. 16 is unmistakable.[35]

The same relationship applies to the CT interaction of alkylmetals with mercuric chloride leading to the complete scission of a R–M bond,[48] *i.e.*,

Table 4. Second-order rate constants for the electrophilic reactions of mercury(II) complexes with alkenes and alkylmetals

	Donor	Acceptor	E^0_{ox}/V	$\log (k_{obsd}$/M^{-1} s$^{-1})$	($E^0_{ox}+\Delta w^*_p$)/eV
	Alkenes[a)]				
1	$H_2C=CH(n\text{-}Pr)$	$Hg(OAc)_2$	2.04	1.26	2.04
2	$H_2C=CH(n\text{-}Bu)$	$Hg(OAc)_2$	2.03	1.34	2.05
3	$H_2C=CH(n\text{-}C_6H_{13})$	$Hg(OAc)_2$	2.01	1.30	2.06
4	Cyclohexene	$Hg(OAc)_2$	1.86	0.26	2.15
5	Cycloheptene	$Hg(OAc)_2$	1.78	0.11	2.19
6	(*Z*)-Cyclooctene	$Hg(OAc)_2$	1.84	−2.28	2.15
7	$H_2C=CH(t\text{-}Bu)$	$Hg(OAc)_2$	2.01	−0.80	2.08
8	(*E*)-$MeCH=CH(t\text{-}Bu)$	$Hg(OAc)_2$	1.81	−3.00	2.18
9	$MeCH=CMe_2$	$Hg(OAc)_2$	1.73	0.83	2.17
10	$Me_2C=CMe_2$	$Hg(OAc)_2$	1.52	−1.96	2.21
	Alkylmetals[b)]				
1	Me_4Sn	$HgCl_2$	1.66	0.38	1.66
2	Et_4Sn	$HgCl_2$	1.22	−1.80	1.82
3	$n\text{-}Pr_4Sn$	$HgCl_2$	1.18	−2.43	1.88
4	$n\text{-}Bu_4Sn$	$HgCl_2$	1.14	−2.42	1.92
5	$i\text{-}Bu_4Sn$	$HgCl_2$	1.10	−3.25	1.94
6	$i\text{-}Pr_4Sn$	$HgCl_2$	0.98	−5.30	2.08
7	$s\text{-}Bu_4Sn$	$HgCl_2$	0.97	−6.15	2.06

a) In methanol at 298 K from Ref. 24. b) In acetonitrile at 298 K from Ref. 48.

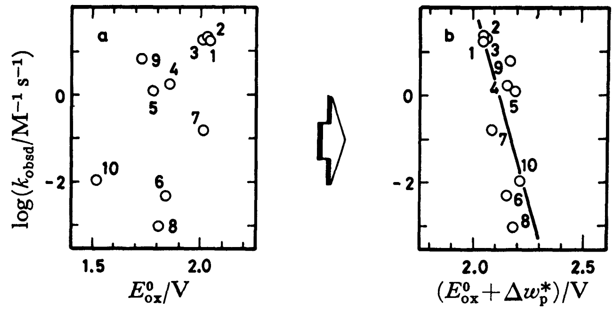


Fig. 4. Oxymercuration of Alkenes. (a) Variation of the rate constant with the standard potentials of the alkene donors identified in Table 4. (b) Unified free energy relationship by inclusion of the work term. The line is arbitrarily drawn with a slope of $-1/2.3RT$ to emphasize the correlation with Eq. 16.

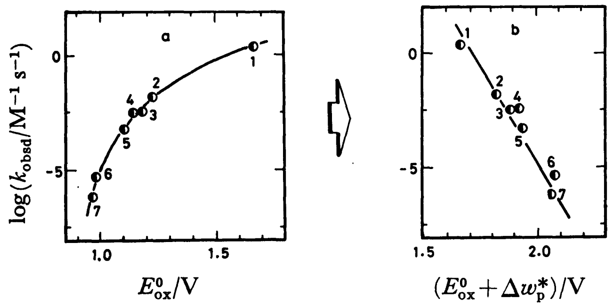


Fig. 5. Alkylmetal Cleavage with $HgCl_2$. (a) Plot of the rate (log k_{obsd}) and the oxidation potentials of the alkylmetal donors identified in Table 4. (b) Unified free energy relationship in which the line is drawn with a slope of $-1/2.3RT$ to emphasize the agreement of the data with Eq. 16.

$$R_4M + HgCl_2 \longrightarrow R_3MCl + RHgCl. \qquad (26)$$

Such a cleavage process differs fundamentally from the addition process in Eq. 25, but the rate data listed in Table 4 follows a similar inverse relationship with E^0_{ox}. Thus the apparent Brönsted slope α (which varies with E^0_{ox} in the curved relations shown in Fig. 5a) is clearly negative for these cleavage reactions. Again when the work term Δw^*_p is included with E^0_{ox}, the curved free energy relationship with negative slopes is transformed into the linear correlation in Fig. 5b.

Despite the strong dissimilarity of the addition and the cleavage processes described in Eqs. 25 and 26, they both abide by the same linear free energy relationship described by Eq. 16 when the variation of the work term Δw^*_p is specifically included as a part of the driving force. Moreover, the influence of the work term is sufficiently strong in both of these mercurations to actually invert the negative Brönsted slopes to the unified correlation in Eq. 16. Such an effect underscores the large steric variations extant in these systems. Before commenting on this point further, we wish to describe the application of the free energy relationship to a system in which the CT spectral information is unavailable.

Homolytic Substitution of Alkylmetals by Iodine Atom.

Table 5. Relative reactivity of alkylmetals in S_H2 cleavage reactions with iodine atom. The stand ardpotentials E^0_{ox} of alkylmetals in carbon tetrachloride[a)]

Alkylmetals	$\frac{E^0_{ox}}{V}$	log (k/k_0)	$\frac{E^0_{ox}+\Delta w^*_p}{eV}$
1 Me_4Sn	2.36	0	2.36
2 Et_4Sn	1.77	1.71	2.24
3 n-Pr_4Sn	1.71	1.69	2.26
4 n-Bu_4Sn	1.66	1.71	2.31
5 i-Pr_4Sn	1.44	1.58	2.28
6 s-Bu_4Sn	1.43	1.68	2.22
7 i-Bu_4Sn	1.61	1.01	2.25

a) At 298 K from Ref. 49.

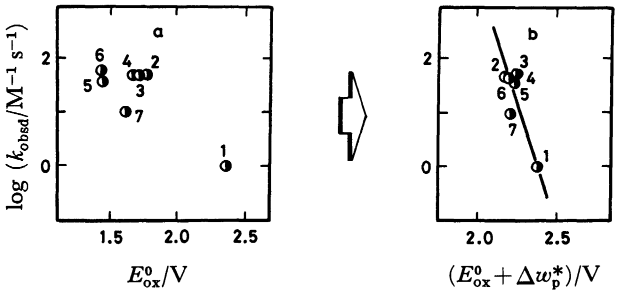


Fig. 6. Homolytic Iodinolysis of Alkylmetals. (a) Variation of the relative rates log (k/k_0) of cleavage of the alkylmetals in Table 5 by iodine atom. (b) Unified free energy relationship with the line arbitrarily drawn with a slope of $-1/2.3RT$ according to Eq. 16.

The photochemically induced iodinolysis of alkylmetals has been shown to proceed by a radical chain mechanism in which the homolytic S_H2 reaction in Eq. 27 is rate-limiting.[49] The homolytic rate constant (k) for

$$R_4M + I\cdot \xrightarrow{k} R_3MI + R\cdot, \qquad (27)$$

the iodinolysis of the various tetraalkyltin compounds in Table 5 have been evaluated relative to tetramethyltin (k_0), and the relative rates (log k/k_0) are plotted in Fig. 6a against E^0_{ox} of the alkylmetal donors.

The charge-transfer spectral data for the EDA complexes in this system are unavailable owing to the transient character of the iodine atom. Thus the values of the work term w^*_p which were previously obtained from the analogous EDA complexes of molecular iodine,[23a)] *i.e.*, [R_4M I_2], have been substituted in Table 5. Indeed the resulting free energy correlation shown in Fig. 6b provides a reasonable fit to the general relationship in Eq. 16.[35)]

The successful transferal of work terms w^*_p derived from the spectra of *molecular* iodine complexes for use with *atomic* iodine complexes indicates that these acceptors in fact share features in common, despite the substantial difference in the values of their electron affinities (*i.e.*, for I_2, E_A=1.60 eV and for I·, E_A=3.06 eV).[23a)] Indeed the steric effects of iodine donors, in both molecular and atomic forms, should be sufficiently similar to render the mean separations in the complexes [R_4M I_2] and [R_4M I·] and therefore the work terms equivalent.[50,51)]

The examples in the foregoing sections illustrate how a knowledge of the standard redox potentials and the ion-pair work terms provides a unified free energy relationship (Eq. 16) for the rates of electron transfer in quite different chemical systems. Since the apparent Brönsted slope α,[52] which measures the dependence of the reaction rate ($\log k_{\text{obsd}}$) on the standard free energy change (ΔG^0) for electron transfer, *i.e.*, $\alpha = \partial \Delta G^{\neq}/\partial \Delta G^0$, differs from system to system (see Figs. 2a, 3a, 4a, and 5a) we wish to inquire now into the origin of this variation.

Significance of the Brönsted Slope in Electron Transfer

Linear free energy relationships have been extensively studied for electron transfer and related reactions in both inorganic and organic systems.[53,54] For highly endergonic reactions, the Brönsted slope α, is close to unity.[10,55] In many cases, however, the more or less linear plots of $\Delta G^{\neq}$ (or a related quantity such as the rate constant $\log k_{\text{obsd}}$) and ΔG^0 (or some related quantity such as the polarographic $E_{1/2}$ potentials[56]) have been observed with slopes significantly less than unity (*e.g.*, typically $0.1 < \alpha < 0.5$) in systems showing irreversible electron transfer in the endergonic region.[57,58] Such contradictions have led to the explanation that electron transfer is not complete in the transition state. As such, the diminished Brönsted slope would correspond to the fraction of charge transfer in the activated complex.[59] Alternatively, the small Brönsted slopes may be ascribed to large intrinsic barriers $\Delta G_0^{\ddagger}$ for electron transfer,[60] since the limit of α will be 0.5 for a sufficiently large value of $\Delta G_0^{\ddagger}$.[8,61] For the latter, α is not related to the fractional charge transfer which is taken to be unity in all cases, but it cannot readily explain those cases with $\alpha < 0.5$.

In this light, our observations of apparent Brönsted slopes which span the limit of $\alpha = 1$ (Fig. 2a) to $\alpha \approx 0$ (Fig. 3a) cannot be easily reconciled with either explanation especially if one includes the examples (Figs. 4a and 5a) in which the apparent Brönsted slopes are actually negative. However, it clearly follows from the electron transfer cycle in Scheme 1 that the work term w_p must be explicitly included in the free energy relationship. Such a FER is expressed by Eq. 7, and the intrinsic Brönsted slope is accordingly evaluated as:[52]

$$\alpha = \frac{\partial \Delta G^{\neq}}{\partial \Delta G^0} = 1 + \frac{\partial w_p}{\partial \Delta G^0}. \qquad (28)$$

It is important to emphasize that the Brönsted slope is not a meaningful quantity without a knowledge of the variation of w_p from system to system. Indeed the systems shown in Figs. 2a and 3a, for which the apparent Brönsted slopes lie in the range $0 < \alpha < 1$, are those in which variation in the work term is $-1 < (\partial w_p/\partial \Delta G^0) < 0$. Furthermore when the variation of the work term is large enough such that $(\partial w_p/\partial \Delta G^0)$ is less than -1 in Eq. 28, the apparent Brönsted slope will become negative, as observed in Figs. 4a and 5a. In other words the variation of the work term is largely responsible for the magnitudes of the apparent Brönsted slopes in Figs. 2a, 3a, 4a, and 5a.

The right sides of Figs. 2—6 represent the unified free energy relationship in Eq. 16 and uniformly support the use of the CT work term $w_p^{\ddagger}$ in the experimental verification of the thermochemical cycle in Scheme 1 (Eq. 7). Thus the work term $w_p^{\ddagger}$ is sufficient to unify all those systems with small and even negative values of the apparent Brönsted slope into a single general relationship in Eq. 16. At this juncture, we might enquire as to why the work term evaluated from the CT interaction in Scheme 2 serves as such an adequate representation of the adiabatic work term in Scheme 1.

By employing the *variation* of the work term $\Delta w_p^{\ddagger}$ in Eq. 16, we are actually focussing in large part on the electrostatic interaction in the ion pair, since the other structural factors drop out by cancellation in the comparative procedure used in Eq. 13.[63] Thus the contribution to $\Delta w_p^{\ddagger}$ consists largely of a coulombic potential (*i.e.*, $-e^2/r_{\text{DA}}$) in which the mean separation r_{DA} in the ion pair is the determinant factor. It is then likely that steric effects which mediate the magnitude of r_{DA} in the EDA complex, and thus the CT excited ion-pair state, parallel those in the adiabatic ion pair in Schemes 2 and 1, respectively.

Summary and Conclusions

The varied reactions of the donors and acceptors in Eqs. 1—4 can be quantitatively analyzed by the free energy relationship in Eq. 10, in which the variation of the work term Δw_p in the adiabatic ion pair can be evaluated from the variation of the work term $\Delta w_p^{\ddagger}$ of the CT excited ion pair. The values of $\Delta w_p^{\ddagger}$ are readily obtained from the charge-transfer spectra of the transient electron donor-acceptor complexes extant in these systems. The activation processes are governed by the combination of two terms; the standard free energy change E^0 for electron transfer (*i.e.*, $D + A \rightarrow D^+ + A^-$) and the work term of the products w_p (*i.e.*, the interaction energy in the ion pair $[D^+ A^-]$). The importance of the work term lies in the mean separation r_{DA} of the ion pair which is mediated by the steric effects in both donor and the acceptor. The work term variation is experimentally observed in systems showing apparent Brönsted slopes[52] α of substantially less than unity.

For a series of donors reacting with a *fixed acceptor*, the variation in the work term generally increases in the order: anthracenes $\ll$ benzenes $<$ alkenes $<$ alkylmetals. Similarly, for a series of acceptors acting upon a *fixed donor*, the variation in the work term generally increases in the order: $\text{TCNE} < \text{Br}_2 < \text{HgX}_2$. Thus the interaction of anthracenes with TCNE leading to the Diels-Alder adduct is the least subject to steric effects. Accordingly, the Brönsted slope in the free energy relationship is close to unity, even without specifically taking into account the work term. At the other extreme, the interaction of alkylmetals with HgX_2 is strongly influenced by steric effects. If the work terms are neglected, the apparent Brönsted slope is actually negative. Such variations in α strongly underscore the importance of evaluating work terms in the development of free energy relationships for electron transfer, especially in those systems which proceed by an inner-sphere pathway.

Appendix

Evaluation of Solvation Energies of Donor Cations in Different Solvents. The solvation energies of arene cations are constant ($\Delta G^s = -2.01$ eV) for the solvents used in this study.[26] The difference in the solvation of $\Delta\Delta G^s$ of alkene and arene cations in acetonitrile was previously obtained from the outer-sphere electron transfer rates of a series of iron(III) oxidants with various alkenes and arenes.[40] The values of $\Delta\Delta G^s$ in other solvents were evaluated relative to those in acetonitrile, with the aid of the modified Born equation,

$$\Delta\Delta G^s = (1-1/\varepsilon)(1-1/\varepsilon_0)^{-1}\,\Delta\Delta G^s_0, \tag{29}$$

where ε and ε_0 are the dielectric constants of the solvent and acetonitrile, respectively, and $\Delta\Delta G^s_0$ is the value in acetonitrile.

The values of $\Delta\Delta G^s$ for the alkylmetal donors in acetonitrile were reported previously. Those in carbon tetrachloride are evaluated by Eq. 29. The values of $\Delta\Delta G^s$ are listed in Table 6, together with the values of E^0_{ox} evaluated from Eq. 30.

$$E^0_{\text{ox}} = I_D + \Delta\Delta G^s - 2.01 - C \tag{30}$$

Table 6. The evaluation of solvation energies of donor cations relative to arene cations. The standard potentials E^0_{ox} of donors in various solvents

Donor	$-\Delta\Delta G^s$/V		E^0_{ox}/V
Alkylmetals	CH_3CN[a)]	CCl_4[b)]	CCl_4[c)]
Me_4Sn	1.62	0.92	2.36
Et_4Sn	1.27	0.72	1.77
n-Pr_4Sn	1.23	0.70	1.71
n-Bu_4Sn	1.21	0.69	1.66
i-Pr_4Sn	1.07	0.61	1.44
s-Bu_4Sn	1.07	0.61	1.43
i-Bu_4Sn	1.17	0.66	1.61
Alkenes	CH_3CN[d)]	HOAc[b)]	HOAc[a)]
$H_2C{=}CH_2$	1.69	1.45	2.66
$H_2C{=}CHMe$	1.21	1.04	2.29
$H_2C{=}CHEt$	1.13	0.97	2.25
$H_2C{=}CH(n\text{-}Pr)$	1.07	0.92	2.19
$H_2C{=}CMe_2$	0.99	0.77	2.06
$H_2C{=}CMe(Et)$	0.84	0.72	2.02
(Z)-MeCH=CHMe	0.82	0.71	2.00
(E)-MeCH=CHEt	0.77	0.66	1.97
(E)-MeCH=CH(t-Bu)	0.73	0.48	2.02
$H_2C{=}CH(t\text{-}Bu)$	1.03	0.89	2.15
$Me_2C{=}CMe(Et)$	0.27	0.23	1.57
$Me_2C{=}CMe_2$	0.34	0.29	1.57
$Me_2C{=}CMe(n\text{-}Pr)$	0.25	0.22	1.56
$Me_2C{=}CMe(n\text{-}Bu)$	0.20	0.17	1.57
Cyclohexene	0.68	0.58	1.96
Arenes	CH_3CN[e)]	HOAc[e)]	HOAc[a)]
C_6H_6	2.01	2.01	2.82
MeC_6H_5	2.01	2.01	2.41
EtC_6H_5	2.01	2.01	2.35
i-PrC_6H_5	2.01	2.01	2.28
$MeOC_6H_5$	2.01	2.01	1.98
o-$Me_2C_6H_4$	2.01	2.01	2.15
m-$Me_2C_6H_4$	2.01	2.01	2.15
p-$Me_2C_6H_4$	2.01	2.01	2.03
1,3,5-$Me_3C_6H_3$	2.01	2.01	1.99

a) Calculated from Eq. 30. b) Calculated from Eq. 29. c) From Ref. 17. d) From Ref. 40. e) From Ref. 26.

The authors wish to thank the National Science Foundation for financial support.

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27) In previous papers (Refs. 22—26), we used the notation ΔE instead of $\Delta w_p^\ddagger$. In this paper, we use the notation $\Delta w_p^\ddagger$ to emphasize the relationship to Δw_p in Eqs. 9 and 10. Since the photoexcitation of EDA complexes is a vertical process, the CT transition energies $h\nu_{CT}$ do not include a major change in solvation during the excitation. The minor contribution of the solvent effects on $h\nu_{CT}$ which has been measured in inert solvents (Refs. 22—26) is cancelled out in the relative values of $\Delta w_p^\ddagger$ in Eq. 13.

28) Note that the sign of the work term $w_p^\ddagger$ is negative.

29) The HOMO of these alkylmetals is a sigma bonding orbital [T. P. Fehlner, J. Ulman, W. A. Nugent, and J. K. Kochi, *Inorg. Chem.*, **15**, 2544 (1976)].

30) For example, the difference between $w_p^\ddagger$ for *s*-Bu_4Sn and that for Me_4Sn in their $HgCl_2$ complexes is as large as 1.10 eV, which corresponds to 106 kJ mol^{-1}. Such a large difference in work terms corresponds to a factor of 3.6×10^{18} in the rates of reaction if $\Delta w_p^\ddagger$ is simply equated to Δw_p in Eq. 9.

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33) In Ref. 17, values of $(E^0_{ox}+w_p/F)$ were reported. The work term w_p for the electron transfer between $[FeL_3]^{3+}$ and the alkylmetals is neglected here, since the outer-sphere work term w_p with ions of the same charge is negligible (see Ref. 13).

34) Note that the constants in Eqs. 10 and 16 are different, since w_p and $\Delta w_p^\ddagger$ represent absolute and relative work terms, respectively. The equivalency implies that $\Delta w_p = w_p - w_p^0 = \Delta w_p^\ddagger$, where w_p^0 is the ***absolute*** work term of the reference system.

35) Although the error bars are not included in the figures, the correlation and trends are to be conservatively considered to 2 significant digits.

36) When E^0 is given in V (or eV), the Brönsted α corresponds to the slope of -16.9 in the plot between $\log k_{obsd}$ and E^0 at 298 K, *i.e.*, $23.04\times10^3/2.3RT=16.9$ (1 V$=$23.04 kcal mol^{-1}, $R=1.987$ cal mol^{-1} K^{-1}, $T=298$ K).

37) Since the reduction potential of TCNE is 0.22 V *vs.* SCE, the standard free energy change for electron transfer ΔG^0 is in the range of 9.9 kcal mol^{-1} for 9,10-Me_2-anthracene and $\approx$33 kcal mol^{-1} for Me_4Sn.

38) By way of contrast, note that the apparent Brönsted slope for the insertion reaction of alkylmetals with TCNE is only 0.45, despite the large positive value (Ref. 17) of ΔG^0. The explanation for the difference is discussed in the last section (*vide infra*). Furthermore, the same Brönsted slope has been reported in Ref. 31 for the more conventional electron transfer reaction of hexachloroiridate(IV) with the same series of alkylmetals (compare Eqs. 14 and 15).

39) S. Fukuzumi and J. K. Kochi, *J. Am. Chem. Soc.*, **103**, 7240 (1981).

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43) a) M. E. Peover, *Electroanal. Chem.*, **2**, 1 (1967); b) B. Case, "Reactions of Molecules at Electrodes," ed by N. S. Hush, Wiley-Interscience, New York (1971), p. 125.

44) a) R. C. Larson, R. T. Iwamoto, and R. N. Adams, *Anal. Chim. Acta*, **25**, 371 (1961); b) The value of C for the Ag/$AgClO_4$ reference in CH_3CN is 4.70 V, which is decreased by 0.30 V relative to the SCE reference electrode.

45) The apparent Brönsted slope in Fig. 3a is 0.37 for alkylmetals, 0.17 for alkenes, and 0.54 for arenes.

46) The unification of the reactions of alkylmetals with Br_2 in CCl_4 and the reactions of olefins and arenes in HOAc in Fig. 3b implies that the solvation term for Br_2^- in CCl_4 is about equal to that in HOAc.

47) See Table 6 in the Appendix.

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49) S. Fukuzumi and J. K. Kochi, *J. Org. Chem.*, **45**, 2654 (1980).

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52) We define the apparent Brönsted slope for an electron transfer process to be the dependence of the rate ($\log k_{obsd}$) on the standard free energy change ΔG^0 of the redox couple. It is to be contrasted with the intrinsic Brönsted slope, which is obtained from a consideration of all contributions to the driving force, including the work terms, as in Eq. 28.

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