

Electron Transfer Reactions in Organic Chemistry. V.*

Examination of Postulated Electron Transfer Processes Involving Anionic and Carbanionic Nucleophiles with the Aid of the Marcus Theory

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Many reactions between nucleophiles and electrophiles which previously were believed to follow polar mechanisms have recently been proposed to proceed *via* initial $1e^-$ transfer and subsequent radicaloid steps. Nucleophiles which have been implicated in such behaviour are, among others, carbanions, Grignard reagents and alkoxide, thiolate, tetrahydroaluminate, amide and trialkylstannate ions. It is the aim of this article to provide a consistent theoretical treatment of the electron transfer steps possible for such nucleophiles on the basis of the Marcus theory.

With due reservations regarding the preliminary and/or uncertain nature of some of the necessary thermodynamic data, it appears possible to rationalize the electron transfer reactions of these nucleophiles in a consistent manner. The most important conclusion is that postulated electron transfer reactions with alkoxide ions acting as $1e^-$ reductants toward polycyclic aromatics, halides, nitroaromatic compounds, ketones, and aldehydes do not appear feasible, as is also concluded for some thiolate ion reactions.

It has been in vogue for some time to reinterpret previously postulated polar organic reaction mechanisms in favour of mechanisms involving electron transfer and radical steps. Often new experimental evidence is quoted, such as the identification of radical species by ESR, the

observation of radical rearrangements in specifically designed experiments with so-called "radical clocks", and/or detection of by-products of distinct redox process origin. Examples include reactions of carbanionic species^{1–3} (Ref. 1 being a pioneering and influential study in this area), Grignard^{4–6} and organolithium^{7–10} reagents, trialkylstannyl alkalis,^{11–15} dialkylamides,^{16–18} alkoxides^{17,18–22} and thiolates,^{23,24} Wittig reagents,²⁵ complex metal hydride anions,^{26–32} nitronium^{33–35} and nitrosonium ions,³⁶ arenediazonium ions,³⁷ carbocations like trityl³⁸ and tropylium ion,³⁹ and diacyl peroxides.⁴⁰ Several reviews on the role of electron transfer in organic reaction mechanisms are available.^{41–43}

To focus on the crucial problem of a possible entry into a radical mechanism in the reaction between two even-electron species, two types of elementary steps are in principle feasible in the encounter between an acceptor (A) and donor (D) molecule (eqns. 1 and 2). Eqn. (1) shows an associative process and symbolizes the typical

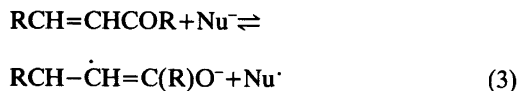


polar, two-electron reaction, so familiar and well-entrenched in physical organic chemistry. Eqn. 2 shows on the other hand a much less known reaction type, namely *non-bonded electron transfer* in which an electron is transferred

*Part IV, see Ref. 63.

from D to A to give two open-shell species (*i.e.*, neutral or charged radicals; note that the charge type of A and D can be of any kind but is given here as neutral for convenience). The term "non-bonded" for organic electron transfer processes corresponds to the expression "outer-sphere" for inorganic ones⁴⁴ and refers to the requirement that the electronic interaction between A and D in the transition state be small, say, less than 1 kcal mol⁻¹. Now the important question is: Is there any simple theoretical method to predict what will happen in an encounter between any given pair of [A,D]'s? Or, put in a less demanding way: Is it possible to find a simple theoretical tool by which one can sort out electron transfer steps which are feasible and not feasible, respectively? Rephrased, the latter question asks for a theoretical treatment of "forbidding" certain electron transfer steps and "allowing" others; of course an "allowed" electron transfer step must be examined critically by proper experiments to certify that electron transfer indeed is involved. If we have reasonable faith in our theory, the "forbidden" steps can however be left aside, perhaps with our belief in their polar nature reinforced, and in addition a number of borderline cases will be left to quarrel about!

Previous treatments of this problem have been very simple indeed, but have nevertheless had some degree of predictive power. As a typical example, House² discussed possible electron transfer between carbanionic nucleophiles, such as lithium organocuprates and trityl anion, and unsaturated carbonyl compounds [eqn. (3)] in terms of the difference in standard electrode potential (or, as the normally applied approximation, experimental electrode potential) for reduction of the enone, E_{red}° , and oxidation of Nu⁻, E_{ox}° , respectively. This difference is equivalent to



the standard free energy change of the process, and can be converted to kcal units by the expression $\Delta G^{\circ} = -23.06(E_{\text{red}}^{\circ} - E_{\text{ox}}^{\circ})$. For the systems treated by House, it was concluded that with $E_{\text{red}}^{\circ} - E_{\text{ox}}^{\circ}$ more positive than -0.4 V (corresponding to $\Delta G^{\circ} < +9.2$ kcal mol⁻¹) electron transfer would be feasible for eqn. (3), since

only then would sufficiently high concentrations ($>10^{-3}$ M) of the radical intermediates be obtained. This rule was used to rationalize the chemical behaviour of a number of carbanion/enone reactions. Similar reasoning was used by Buncel and Menon³ to elucidate the detailed reaction scheme for base/4-nitrotoluene interactions.

While free energy considerations of this type certainly can be used with advantage for quick rule-of-thumb judgements, it is of interest to see if more elaborate treatments can be used to increase the predictive capabilities of the organic chemist in the electron transfer field. The Marcus-Hush theory,^{45,46} to be described below, and its congeners, the Rehm-Weller⁴⁷ and Balzani-Scandola⁴⁸ treatments, have been widely used to interpret experimental studies of mainly inorganic,⁴⁹ but sometimes also organic electron transfer mechanisms (*e.g.*, quenching of excited states).⁴⁷ It was found that all essential features of the inorganic version of the Marcus theory can be retained in the treatment of organic electron transfer steps, and that it can then be used as a powerful guide for further experimentation.⁵⁰ The mathematical form of this theory is in fact very familiar to the organic chemist. It is a free-energy ($\log k - \Delta G^{\circ}$) relationship, although not of the common linear type (an LFER), but a quadratic one (a QFER), and has as an additional parameter λ , the *reorganization free energy*. This will be discussed in some detail below, since it seems to represent a new and alien concept to organic chemists. However, in contrast to ρ values of LFER:s λ has a precise physical meaning in the Marcus model of the electron transfer process and can be experimentally measured or calculated theoretically.

This author has previously explored the application of the Marcus treatment to a broad range of possible organic electron transfer steps,⁵⁰ as well as to more specific problems, such as the nature of the reaction between alkyl halides and radical anions and supernucleophiles,⁵¹ the possible role of electron transfer in aromatic nitration and nitrosation,³⁵ and the possible electron transfer nature of the reaction between diacyl peroxides and polycyclic aromatic hydrocarbons⁵² (strongly chemiluminescent systems). This paper aims at a quantitative study of such "nucleophilic" processes which until recently have been considered to follow polar mechan-

isms, but now are under active discussion as candidates for electron transfer/radical mechanisms. The treatment will be limited to ground-state species (nucleophiles and electrophiles) with an even number of electrons (*i.e.*, radicals and radical ions are left out), and it lies in the nature of things that most, if not all nucleophiles considered are negatively charged.

RESULTS AND DISCUSSION

The Marcus theory in its simplest version treats A and D of eqn. (2) as two spheres of radii r_A and r_D , embedded in a continuous medium of dielectric constant D_E , which diffuse together to form a collision (precursor) complex with a distance of $r=r_A+r_D$ between the centres of the spheres (this picture can be made considerably more complex by assuming various types of non-spherical shapes⁵⁰ and allowing for a specified range of r 's,⁵³ this does not change the description of physical model, but adds mathematical complexity, and will not be considered in this context). If A and D are charged (Z_A and Z_D) a Coulombic free energy term, W , must be included to account for the gain or loss of free energy in bringing the reactants from infinite distance from each other to that of the collision complex, r [eqn. (4), where e is the electronic charge].

$$W = \frac{Z_A Z_D e^2}{D_E r} \quad (4)$$

Again considerable mathematical complexity can be added by introducing the effect of the ionic strength of the medium and the ionic atmosphere around the reacting ion(s),⁵³ and again we will neglect such a complication in the description of the theory. In most cases to be treated here, Z_A is anyway 0 and hence $W=0$.

The activation process to reach the transition state is a consequence of the Franck-Condon principle: Transfer of an electron occurs on a much faster time-scale than nuclear movements (10^{-16} vs. 10^{-14} s). This means that *bond and solvent reorganization* must occur in the reactants (held together in the collision complex) in order to reach the structure and energy of the transition state. In this the energy levels between which the electron is to be transferred must be made exactly matching in energy by the reorganization pro-

cess. Bond reorganization involves lengthening or shortening of bonds and changes in bond and/or torsional angles and is associated with the bond reorganization energy (λ_i ; *i* for inner). Solvent reorganization implies reorientation of solvent molecules around the transition state to accommodate, among other things, the change of charge situation upon transfer of the electron in the transition state, and is associated with the solvent reorganization energy (λ_o ; *o* for outer). The sum of λ_i and λ_o is λ , the reorganization energy, a parameter that we have already touched upon in the introduction.

A particularly simple type of electron transfer reaction is the so-called *self-exchange (homomolecular or identity) reaction*, in which an electron is transferred between a species and one of its $\pm 1e^-$ redox forms. For the general electron transfer process of eqn. (2) the two pertinent self-exchange reactions are given in eqns. (5) and (6).



The rate of self-exchange can be measured (by the ESR technique, for example) and hence the free energy of activation $\Delta G^\ddagger(0)$ (sometimes called the intrinsic barrier; the zero refers to the fact that the standard free energy change of a self-exchange process is zero) can be calculated *via* the Eyring equation. It is a consequence of the Marcus theory that the reorganization energy $\lambda(0)$ of a self-exchange reaction is equal to $4\Delta G^\ddagger(0)$.

In order to get acquainted with the possible range of variation of $\lambda(0)$, it is instructive to consider two examples of organic self-exchange reactions, one with a very low $\lambda(0)$ and one with a relatively high one. The first is electron exchange between 9,10-diphenylanthracene and its radical cation (DPA/DPA $^{\cdot+}$, $\lambda(0)$ in $\text{CH}_2\text{Cl}_2=7.0$ kcal mol $^{-1}$)⁵⁵ and the second between cyclooctatetraene and its radical anion (COT/COT $^{\cdot-}$, $\lambda(0)$ in THF ≥ 38 kcal mol $^{-1}$).⁵⁶

We have as yet no direct experimental information about the structural change in going from DPA to DPA $^{\cdot+}$, but we know from electrochemical and ESR studies that practically only the anthracene nucleus is involved, the phenyl groups merely serving to block the reac-



tive 9,10-positions of $\text{DPA}^{\cdot+}$ from reacting with nucleophiles and hence stabilizing $\text{DPA}^{\cdot+}$ kinetically.⁵⁷ An approximation to the structural change in the anthracene nucleus can be inferred from the naphthalene system, where X-ray crystallographic studies⁵⁸ show that at most 0.035 Å changes in bond lengths and practically no changes in angles are involved in going from naphthalene to naphthalene.^{•+} Thus the bond reorganization energy for the $\text{DPA}/\text{DPA}^{\cdot+}$ system must be small; in addition, the solvent reorganization energy in a weakly interacting solvent like CH_2Cl_2 is expected to be small. Thus we can understand why we observe the low $\lambda(0)$ value of 7.0 kcal mol⁻¹ for $\text{DPA}/\text{DPA}^{\cdot+}$.

The $\text{COT}/\text{COT}^{\cdot-}$ is very much different in this respect, in that COT and $\text{COT}^{\cdot-}$ must change considerably in conformational energy as they adjust themselves to the requirements of the transition state (eqn. (7)); note that one always gives both the reactants' and products' transition states in electron transfer reactions). Thus the high $\lambda(0)$ value of >38 kcal mol⁻¹ for $\text{COT}/\text{COT}^{\cdot-}$ is expected; as a corollary we note that $\lambda(0)$ for $\text{COT}^{\cdot-}/\text{COT}^{2-}$ is low (~11 kcal mol⁻¹ in THF) since the conformational adjustment in the transition state is now negligible: Both species are planar.

Table 1 shows a list of typical $\lambda(0)$ values for organic and organometallic self-exchange reac-

Table 1. Typical values of $\lambda(0)$ for self-exchange reactions at ambient temperature (taken from Refs. 50–52, unless otherwise noted).

Self-exchange reaction	Solvent	$\lambda/\text{kcal mol}^{-1}$
9,10-Diphenylanthracene/ $\text{CR}^{\cdot+}$	CH_2Cl_2	7.0
Phenothiazine/ $\text{CR}^{\cdot+}$	CH_3CN	8.8
$\text{FcH}/\text{FcH}^{\cdot+}$ ^b	$\text{ROH}/\text{H}_2\text{O}$	23
$\text{Cr}(\text{Ph})_2/\text{Cr}(\text{I})(\text{Ph})_2^{\cdot+}$	Me_2SO	20
Naphthalene/ $\text{AR}^{\cdot-}$ ^c (free)	DME^d	8
Naphthalene/ $\text{AR}^{\cdot-}$ ^c (ion pair)	DME^d	16
Naphthalene/ $\text{AR}^{\cdot-}$ ^c	DMF	12
$\text{PhNO}_2/\text{AR}^{\cdot-}$ ^c	DMF	19
$\text{PhNO}_2/\text{AR}^{\cdot-}$ ^c	$\text{DMF}/\text{H}_2\text{O}$	30
$\text{COT}/\text{COT}^{\cdot-}$ ^e	THF	>38
$\text{COT}^{\cdot-}/\text{COT}^{2-}$ ^e	THF	11
$\text{Me}_4\text{Sn}/\text{Me}_4\text{Sn}^{\cdot+}$	CH_3CN	34
$(\text{RCOO})_2/\text{RCOO}^{\cdot} + \text{RCOO}^{\cdot-}$ ^f	CH_3CN	80–90
$\text{RCI}/\text{R}^{\cdot} + \text{Cl}^{\cdot-}$ ^f		80 ^g
$\text{RBr}/\text{R}^{\cdot} + \text{Br}^{\cdot-}$ ^f		74 ^g
$\text{RI}/\text{R}^{\cdot} + \text{I}^{\cdot-}$ ^f		56 ^g
$\text{PhCl}/\text{PhCl}^{\cdot-}$	DMF	46 ^h
$\text{PhBr}/\text{PhBr}^{\cdot-}$	DMF	40 ^h
$\text{ClO}_2^{\cdot}/\text{ClO}_2^{\cdot-}$	H_2O	55 ⁱ
$\text{NO}_2^{\cdot}/\text{NO}_2^{\cdot-}$	H_2O	71 ⁱ
$\text{Co}(\text{III})/\text{Co}(\text{II})$	H_2O	57
$\text{Fe}(\text{CN})_6^{3-/2-}$	H_2O	44
$\text{Fe}(\text{phenanthroline})_3^{3+/4+}$	H_2O	≤19
$\text{IrCl}_6^{2-/3-}$	H_2O	31

^a CR =cation radical. ^b FcH =ferrocene. ^c AR =anion radical. ^d DME =1,2-dimethoxyethane. ^e COT =cyclo-octatetraene. ^f This reaction was treated as a case of dissociative electron transfer. ^g Averaged value from several solvents, assuming an average value of 20 kcal mol⁻¹ for $\lambda_{\text{A/A}^{\cdot-}}$. ^h Assuming that $\lambda_{\text{A/A}^{\cdot-}}$ (aromatic radical anions) is 10 kcal mol⁻¹. ⁱ Ref. 54.

tions (for an extended list and discussion of $\lambda(0)$, see Ref. 50). The following generalizations are presently possible:^{50,59}

A low $\lambda(0)$ is associated with
Delocalized bond system
Weakly solvating medium
Free ions
Little or no conformational change

A high $\lambda(0)$ is associated with
Localized bond system
Strongly solvating medium, especially water
Ion pairing
Conformational change

It is especially important to note that quite high $\lambda(0)$ values do exist and are indeed expected in many situations. As a typical example, very high $\lambda(0)$ values (40–70 kcal mol⁻¹) were experimentally determined for alkylmetals (R₄Sn, R₄Pb, R₂Hg) a few years ago.⁶⁰ Now this has been experimentally corroborated by ESR studies^{61,62} of Me₄Sn^{•+}, Me₄Pb^{•+} and *t*-BuMe₃Sn^{•+} which indicate gross distortion of bond lengths and angles from tetrahedral symmetry. It is perhaps a bit unfortunate that the classical study of electron transfer quenching of excited states by Rehm and Weller⁴⁷ used aromatic quenchers with low $\lambda(0)$'s only; from this study originates a belief that reorganization energies of organic electron transfer reactions necessarily must be low. The technique most used so far for the measurement of $\lambda(0)$ (ESR line broadening) for organic systems, has also favoured the accumulation of low λ values; if the rate constant for self-exchange is $\leq 10^7$ M⁻¹s⁻¹ (corresponds to $\lambda(0) \leq 22$ kcal mol⁻¹) this technique cannot be used and there is no good alternative technique for measuring self-exchange rates below this rate constant limit, unless they are very small.

Concluding, $\lambda(0)$ is a parameter that for organic electron transfer reactions can vary over a wide range of values, depending on the particular system studied. It should be emphasized that high values of $\lambda(0)$ by no means are unusual or physically unrealistic; one needs only to look at typical inorganic systems (for a few examples, see lower part of Table 1) to find an abundance of large $\lambda(0)$ values.

Returning to the hetero-exchange reaction of eqn. (2), the Marcus expression for the free

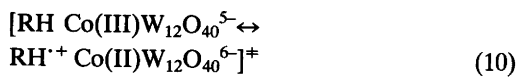
energy of activation [W , see eqn. (4)] is given by eqn. (8), where $\Delta G^{\circ'}$ is composed of the standard

$$\Delta G^{\ddagger} = \frac{\lambda}{4} \left(1 + \frac{\Delta G^{\circ'}}{\lambda} \right)^2 + W \quad (8)$$

free energy change (ΔG°) under the prevailing reaction conditions and a Coulombic free energy term, originating from the gain or loss of electrostatic free energy upon transfer of the electron in the transition state [eqn. (9)].

$$\Delta G^{\circ'} = \Delta G^{\circ} + (Z_1 - Z_2 - 1) \frac{e^2}{r D_E} \quad (9)$$

The effect of including an electrostatic term in the appropriate case is obvious from the example given in eqn. (10), the transition state for oxidation of a neutral organic molecule by Co(III)W₁₂O₄₀.⁵⁻⁶³ Here the gain of electrostatic free energy upon



transfer of the electron in the transition state is quite large. In most cases to be discussed in this paper, the electrostatic free energy term is zero, since we will be dealing with Z_1, Z_2 combinations of the (0, -1) type.

We now have to find a method for obtaining λ for the hetero-exchange reaction [eqn. (2)], before its ΔG^{\ddagger} can be estimated according to eqn. (8). This is an easy task, since the Marcus treatment derives λ as the average of the $\lambda(0)$'s of the two corresponding self-exchange reactions [eqns. (5) and (6)], as shown in eqn. (11). Thus we have completed the list of what is needed to

$$\lambda = [\lambda(0)_{A/A-} + \lambda(0)_{D^+/D}]/2 \quad (11)$$

estimate the free energy of activation of an electron transfer reaction: Its standard free energy change, the $\lambda(0)$ values of the two corresponding self-exchange reactions and estimates of the electrostatic free energy term(s), when necessary.

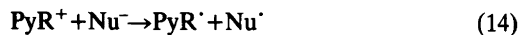
Finally, since we are mostly interested in rate constants, it is common to give the rate constant,

k_{obs} in terms of eqn. (8), the Eyring equation, and the assumption of the simple kinetic scheme of eqn. (12). Here the two reactants diffuse together with the rate constant k_d to form an encounter complex which then undergoes an electron transfer step with rate constant k_{el} . Applying the steady state approximation to $[A \cdots D]$ gives k_{obs} as shown in eqn. (13) where A normally has the value 0.2.⁵⁰



$$k_{\text{obs}} = \frac{k_d}{1 + A \exp[(W + \lambda(1 + \Delta G^\circ/\lambda)^2/4)/RT]} \quad (13)$$

To take an example, let us try to calculate the rate constant for a recently proposed electron transfer process, namely the initial rate-determining step in the *C*-alkylation of nitroalkanide ions (Nu^-) and 1-benzyl-2,4,6-triphenylpyridinium ion (PyR^+) in Me_2SO [eqn. (14)].⁶⁴



The standard free energy change is obtained from the half-wave potentials for the two redox couples, $E^\circ_{\text{PyR}^+/\text{PyR}^\cdot} = -0.55$ V and $E^\circ_{\text{Nu}^-/\text{Nu}^\cdot} = -0.83$ V; * ΔG° is then -23.06 ($-0.55 - 0.83$) = 31.8 kcal mol⁻¹. The corresponding $\lambda(0)$ values are not known but by analogy with similar systems, $\lambda(0)_{\text{PyR}^+/\text{PyR}^\cdot}$ should be low, ≤ 10 kcal mol⁻¹. For the nitromethanide ion \rightarrow nitromethyl radical reaction it is more difficult to find known analogies, but for reasons to be outlined in detail later there are grounds for assuming that $\lambda(0)$ is rather large for $\text{R}^\cdot/\text{R}^-$ couples. An estimate of 50 kcal mol⁻¹ gives λ of eqn. (14) = $(10 + 50)/2 = 30$ kcal mol⁻¹. Finally, to be accurate one should include electrostatic terms in the treatment [eqns. (8) and (9)], but due to the rather high dielectric constant this correction is rather small (< 2 kcal mol⁻¹) in the first place and secondly for all practical purposes it cancels in the final calculation.

* All potentials in this paper are given relative to the normal hydrogen electrode.

tion due to the opposing effects of the electrostatic terms in a reaction of this charge type.

From eqn. (8) we now can calculate $\Delta G^\ddagger = 30/4(1 + 32.8/30)^2 = 31.8$ kcal mol⁻¹ which translates into a second-order rate constant of *ca.* 10^{-13} M⁻¹s⁻¹, many orders of magnitude smaller than the observed rate constant, 3.3 M⁻¹s⁻¹. Thus we can conclude that either the electron transfer step of eqn. (11) is not feasible or something is wrong with the input data. The suspected culprit would then be the redox potential of $\text{Nu}^\cdot/\text{Nu}^-$ which might be too high due to an appreciable overpotential, common in the electrochemistry of anions. If the overpotential is assumed to be 0.5 V, ΔG^\ddagger would become 22 kcal mol⁻¹ corresponding to $k_{\text{el}} \approx 14 \times 10^{-6}$ M⁻¹s⁻¹, still far from the experimental one⁶⁵ (see also discussion of entries 7 and 8 of Table 5).

Standard free energy data. The discussion above clearly shows the importance of having access to good standard free energy data for the redox couples involved in an electron transfer process. Such are normally obtained from electrochemical measurements which nowadays can give accurate reversible potentials even for electrode reactions that are complicated by slow heterogeneous electron transfer and/or fast chemical follow-up reactions, and more seldom from thermochemical data. The possibilities of and difficulties involved in arriving at good reversible potentials in cases where experimental data are scarce or lacking, have been discussed.⁵⁰

Table 2 lists standard potentials or best possible estimates thereof for a number of $\text{Nu}^\cdot/\text{Nu}^-$ redox couples (or, sometimes, their organometallic equivalents). It must be remembered that the quality of the data set is not uniform, and that future work might bring about re-evaluations of these values.

Table 2 clearly shows that many carbanions are strong reducing agents in the electron transfer sense, and the same applies to Grignard reagents. The weakest reductants of the set are those carbanions in which the anionic centers are stabilized by resonance with *-E*-substituents; note that all these yet are better $1e^-$ reducing agents than iodide ion (Table 3). Federlin^{71,72,75,76} has found that E_{ox} of many carbanions is linearly correlated with the *pK* (DMSO) of the parent compounds over a *pK* range of *ca.* 20 [eqn. (15)].

$$E_{\text{ox}} = 0.93(\text{NHE}) - 0.067 \text{ pK}(\text{DMSO}) \quad (15)$$

Table 2. Best available experimental values of reversible potentials (E°) for Nu^-/Nu^- redox couples where Nu corresponds to a carbanion or carbanion equivalent.

Nu ⁻	Medium	E°/V vs. NHE ^a	Ref.
CH ₃ ⁻	THF/HMPA ^b	(-0.48) ^c	66
C ₄ H ₉ ⁻	THF/HMPA ^b	(<-1.17) ^c	66
<i>t</i> -C ₄ H ₉ ⁻	CH ₃ CN	-2.32	67
<i>t</i> -C ₄ H ₉ ⁻	DME	-2.00	67
PhCH ₂ ⁻	THF/HMPA ^b	-1.11	66
Ph ₂ CH ⁻	THF/HMPA ^b ; DME	-0.88; -0.86	66; 2
Ph ₃ C ⁻	THF/HMPA ^b	-0.88	66
Ph ₃ C ⁻	CH ₃ CN	-0.73	67
Ph ₃ C ⁻	DMSO	-0.81; 0.91	68; 69
Ph ₃ C ⁻	DME	-0.96; -1.06	70; 2
Allyl ⁻	THF/HMPA ^b	-1.33	66
Ph ⁻	THF/HMPA ^b	(<-0.10) ^c	66
CH ₂ =CH ⁻	THF/HMPA ^b	(<-0.33) ^c	66
Cyclopentadienide	THF/HMPA ^b	-0.10	66
Cyclopentadienide	DMSO	-0.28	69
Indenide	DMSO	-0.49	69
Fluorenyl	DMSO	-0.63	69
(CH ₃ CO) ₂ CH ⁻	DMSO	1.04	71
CH ₃ CO(COOEt)CH ⁻	DMSO	0.93	71
(EtOCO) ₂ CH ⁻	DMSO; DMF	0.94; 0.64	71; 2
(EtOCO) ₂ (CH ₃)C ⁻	DMSO	0.58	71
(CN) ₂ CH ⁻	DMSO	0.59	71
(CN) ₂ (CH ₃)C ⁻	DMSO	0.28	72
(CH ₃) ₂ (NO ₂)C ⁻	MeOH/PhH (1:1); DMSO	0.94; 0.83	73; 64
Ph(CH ₃ CO)CH ⁻	DMSO; DMF	-0.19; 0.04	72; 2
PhCO(Ar)CH ⁻	DMSO	0.18	72
CH ₃ MgBr	Et ₂ O	-0.25	6
C ₂ H ₅ MgBr	Et ₂ O	-0.66	6
<i>i</i> -C ₃ H ₇ MgBr	Et ₂ O	-0.95	6
C ₄ H ₉ MgBr	Et ₂ O	-0.53	6
<i>i</i> -C ₄ H ₉ MgBr	Et ₂ O	-0.63	6
<i>s</i> -C ₄ H ₉ MgBr	Et ₂ O	-0.87	6
<i>t</i> -C ₄ H ₉ MgBr	Et ₂ O	-1.07	6
CH ₂ =CHCH ₂ MgBr	Et ₂ O	-1.16	6
PhCH ₂ MgBr	Et ₂ O	-0.73	6
Cyclo-C ₃ H ₉ MgBr	Et ₂ O	-0.88	6
PhMgBr	Et ₂ O	-0.0 ^d	74

^a NHE=normal hydrogen electrode. ^b 30 % HMPA (v/v). ^c Values within parentheses are uncertain due to experimental complications. ^d Extrapolated value; see text.

$$E_{\text{ox}} = 0.23(\text{NHE}) - 0.033 \text{ pK} \quad (16)$$

Exceptions were the $-E$ substituent stabilized carbanions which have much too high E_{ox} values with respect to the correlation line. Using the extended set of *hydrocarbon* derived carbanion data of Table 2 (covering *ca.* 55 pK units), a correlation line (eqn. (16), $r=0.98$, see Fig. 1) with approximately half the slope of that given by

Federlin is obtained (pK data were taken from the compilation in Ref. 77). Again, points corresponding to $-E$ substituent stabilized carbanions fall well above the line.

E_{ox} of Grignard reagents have been obtained from Holm's work,⁶ but earlier determinations of "decomposition potentials" are also known.⁷⁴ From the correlation between these values and those of Holm, E_{ox} of PhMgBr was estimated by

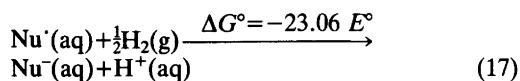
Table 3. Standard potentials for a number of Nu'/Nu⁻ redox couples, as estimated from thermochemical data or the Marcus treatment. ΔG^o_{tr}(Nu⁻) were obtained from Ref. 89.

Nu ⁻ in Nu'/Nu ⁻	H ₂ O	E ^o /V vs. NHE CH ₃ CN ^a	THF ^b	Ref. to value of E ^o (H ₂ O)
F ^{-c}	3.6	2.4	3.0	78
Cl ⁻	2.55	1.6	2.0	78
Br ⁻	2.0	1.2	1.5	78
I ⁻	1.4; 1.33	0.7	1.1	78
SCN ⁻	1.66	1.0	1.4	79
N ₃ ^{-d}	1.87	1.0	1.6	80
NO ₂ ^{-d}	1.0	0.4		78
NO ₃ ^{-e}	2.3	1.6		78
CN ^{-e}	1.9	1.1	1.4	78
HO ^{-c}	1.9	0.8	1.1	78
MeO ^{-c}	1.4	0.3	0.6	This work
<i>t</i> -BuO ^{-c}	1.4	0.3	0.6	This work
CH ₃ COO ⁻	2.41	1.3	1.6	81
C ₂ H ₅ COO ^{-c}	2.2	1.2	1.4	81
CF ₃ COO ^{-c,f}	2.2	1.1	1.4	82
PhCOO ^{-c}	1.7	0.6	0.9	81
EtS ^{-g}	0.9	0.3	0.6	This work
PhS ^{-g}	0.4	-0.2	0.1	This work
AlH ₄ ^{-g}			-(0.1-0.3) ^h	
H ⁻	-0.14 ⁱ		-0.5	
Ph ₃ Ge ⁻			-0.8 ^j	86
Ph ₃ Sn ⁻			-0.55 ^j	86
Me ₃ Sn ⁻			-1.0	See text
S ^{-c,k}	≥1.35	≥0.3		84
<i>i</i> -Pr ₂ N ⁻			-(1.1-1.3)	See text

^a ΔG^o_{tr}(H⁺) from water was set equal to 11.1 kcal mol⁻¹. ^b ΔG^o_{tr}(H⁺) from water was set equal to 2.5 kcal mol⁻¹ (same as for methanol). ^c ΔG^o_{tr}(Nu⁻) was set equal to ΔG^o_{tr}(CH₃COO⁻). ^d ΔG^o_{tr}(NO₂⁻) was set equal to ΔG^o_{tr}(SCN⁻). ^e ΔG^o_{tr}(Nu⁻) was set equal to ΔG^o_{tr}(Br⁻). ^f E^o(H₂O) has been adjusted slightly upwards in view of new experimental data on the O-O bond energy of perfluoroacyl peroxides. ^g ΔG^o_{tr}(Nu⁻) was set equal to ΔG^o_{tr}(SCN⁻). ^h Calculated *via* eqn. (13); see text. ⁱ Obtained from E^o(H₂/H)⁸³ and D₂(H-H). ^j Measured value. ^k S⁻=succinimide anion.

extrapolation (see Fig. 2).

Table 3 shows redox potentials for Nu'/Nu⁻ couples, but now of different origin. The majority of these values, except those of AlH₄⁻, Ph₃Ge⁻, Ph₃Sn⁻, Me₃Sn⁻ and *i*-Pr₂N⁻ have been calculated from thermodynamic data, simply because it has not been possible to determine these values by direct electrochemical measurements (the chemical follow-up reactions of Nu' are too fast, and in most cases heterogeneous electron transfer is slow or very slow). This means that at best satisfactory E^o data for *aqueous solution* can be obtained; if we want to transfer the processes to other solvents, this must be done by applying ΔG^o_{tr}(water→solvent) values to each of the species of the pertinent redox equilibrium [eqn. (17)].^{82,87,88} This creates



difficulties of two kinds: In some cases ΔG^o_{tr} is not known but has to be estimated by comparison with data for similar ions, and, perhaps more troublesome, ΔG^o_{tr}(H⁺) is not always known with the necessary degree of accuracy. The acetonitrile case illustrates the latter problem, in that several values of ΔG^o_{tr}(H⁺) from water to acetonitrile have been given earlier (*e.g.*, 3.3, 6.9, and 11 kcal mol⁻¹, corresponding to 0.18, 0.3 and 0.48 eV).⁸⁹ Earlier estimates of E^o (Nu'/Nu⁻) in acetonitrile^{82,87,88} were based on ΔG^o_{tr}(H⁺)=0, whereas here (Table 3, column 3) the high value, 11.1 kcal⁻¹, has been used, mainly

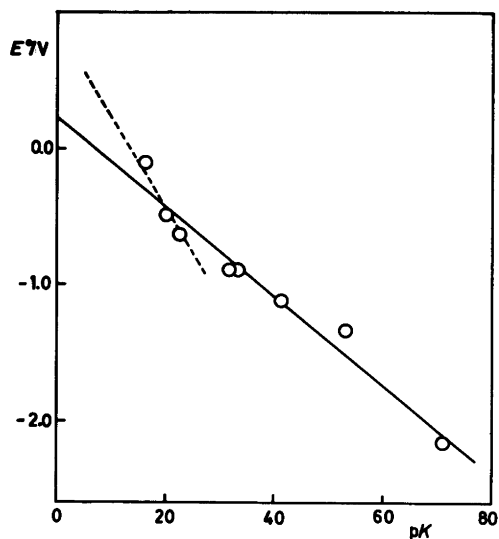


Fig. 1. Plot of hydrocarbon derived carbanion oxidation potentials vs. pK [eqn. (16)]. The points refer to the following hydrocarbons (pK; E°): cyclopentadiene (16; -0.10), indene (19.9; -0.49), fluorene (22.6; -0.63), triphenylmethane (31.5; -0.88), diphenylmethane (33.1; -0.88), toluene (41.2; -1.11), propene (53; -1.33) and isobutane (71; -2.16). The broken line corresponds to eqn. (15).

because this now is the one recommended by IUPAC*.⁸⁹

For THF, a very common solvent for reactions of the type considered here, few ΔG°_{tr} data are known, and therefore the same procedure was adapted as before;⁵¹ $\Delta G^\circ_{tr}(H^+)$ was taken as that for transfer between water and methanol, and $\Delta G^\circ_{tr}(Nu^-)$ were approximated as those for transfer between water and DMF. For the neutral species of eqn. (17), ΔG°_{tr} was set equal to 0 in all cases.^{82,87,88}

The E_{ox} value for $AlH_4^-/AlH_4^{\cdot-}$ was estimated in yet another way. It is known that the "electron reservoir" system $CpFe^+C_6H_6$ is reduced by $LiAlH_4$ in an electron transfer step in THF at $-60^\circ C$ [eqn. (18)].^{90a} From the data given an approximate rate constant could



* Thus the E° values given for CH_3CN in Table 8 of Ref. 50 should be subtracted by 0.48 V; fortunately, conclusions regarding the feasibility of pertinent electron transfer steps of Tables 15–17 are not affected.

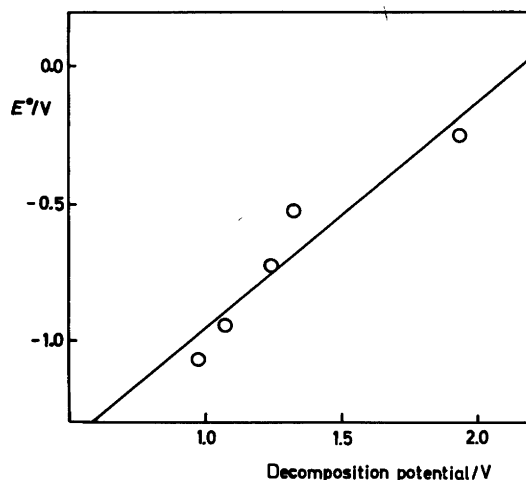


Fig. 2. Plot of Holm's E° values⁶ for oxidation of $RMgBr$ vs. decomposition potentials.⁷⁴ The equation of the regression line is $y = -1.78 + 0.82x$ ($r = 0.95$).

be estimated to be in the range of $0.5-0.02 M^{-1}s^{-1}$ and with some reasonable assumption about λ (put equal to 30 kcal mol^{-1} ; for the related system, $(C_6H_6)_2Cr(I)/(0)$ in DMSO, $\lambda(0)$ is ca 20 kcal mol^{-1} ^{90b}) and W (15 kcal mol^{-1}), $\Delta G^\circ = 24-28 \text{ kcal mol}^{-1}$ was obtained from eqn. (13). With E° of $CpFe^+C_6H_6/CpFeC_6H_6$ being -1.35 V ,⁹⁰ one arrives at an E_{ox} of $AlH_4^-/AlH_4^{\cdot-}$ of $-(0.1-0.3) \text{ V}$. Similarly, an analysis of kinetic data for the reaction between Me_3Sn^- and alkyl halides⁹¹ gave an estimate of $E^\circ(Me_3Sn^-/Me_3Sn^{\cdot-})$ at -1.0 V (see below) and of data for the reaction between $i-Pr_2N^-$ and aromatic hydrocarbons¹⁷ a value of $-(1.1-1.3) \text{ V}$ for $E^\circ(i-Pr_2N^-/i-Pr_2N^{\cdot-})$.

In order to proceed with our analysis of electrophile/nucleophile interactions by the Marcus theory, we need estimates of a few more λ values for donor systems of critical importance, such as $R^-/R^{\cdot-}$, $RMgX^+/RMgX$, and $RO^-/RO^{\cdot-}$. For this purpose we can use kinetic data for non-bonded electron transfer reactions involving these species, from which the Marcus eqn. (13) can be used to extract a set of reasonably accurate λ values. Table 4 lists reactions of this type, together with their λ values obtained by fitting the experimental data to eqn. (13) by a non-linear regression analysis method.* The last

*Due to Marquardt (HP system 35 NonLinear Regression Program).

Table 4. Values of λ for typical anionoid reactions.

Entry No.	Reaction	No. of data pairs	$\lambda/\text{kcal mol}^{-1 a}$	$\lambda_{D/D-}/\text{kcal mol}^{-1}$
1	Carbanions of the cyclopentadienide type + nitrobenzene, 1,3-dinitrobenzene and azobenzene in alcoholic solvents ¹	8 ^b	48(6)	66
2a	RMgBr + benzophenone in diethyl ether ⁶	10	44(5)	70
2b	RMgBr + azobenzene in diethyl ether ⁶	9	70(5)	120
2c	RMgBr + di- <i>tert</i> -butyl peroxide in diethyl ether ⁹²	4	110	130
3	Me ₃ SnNa + alkyl chlorides and bromides in THF or tetraglym ⁹¹	22	49(3) ^c	21
		22	59(2) ^d	41
		22	70(2) ^e	63
4	Ph ₂ CH ⁻ or Ph ₃ C ⁻ + PhCH ₂ Cl in THF ⁹³	1	63	46
5	Me ₃ CCOCH ₂ ⁻ + ethyl 4-nitrobenzoate in THF ⁹⁴	1	36	57
6	HO ⁻ + excited ArH in 20–50 % ethanol-water ⁸⁰	4	7(6)	-1 (!)
		4	25(6)	35

^a Number within parentheses gives the confidence interval at the 95 % level. ^b Approximate rate constants were obtained from information given in the reference. ^c For $E^\circ = -0.8$ V; no primary halides included. ^d For $E^\circ = -1.02$ V; no primary halides included. ^e For $E^\circ = -1.23$ V; no primary halides included.

column gives the desired $\lambda_{D/D-}$, obtained from the appropriate data in Tables 1 and 4 and Ref. 50.

Some comments are necessary to appreciate the problems involved in arriving at these λ values, and the type of approximations that has to be applied. For entry no 1, only semiquantitative rate data were available in the form of percentage radical anion formation after a specified period of time, so the conversion of these numbers to second-order rate constants is marred by considerable uncertainty. A judicious choice of systems was necessitated by the fact that complete conversion of substrate to carbanion is a prerequisite for the rate constants to be related to electron transfer and not proton abstraction by the base used; thus only carbanions of the cyclopentadienide type (cyclopentadienide, indenide, fluorenyl and 9-phenylfluorenyl) were included in the data set. Fig. 3 shows the $\log k/\Delta G^\ddagger$ plot and the best Marcus curve through the points. The λ value is large, 48 kcal mol⁻¹, as expected in view of the fact that we are dealing with a strongly solvating protic solvent.

Entry 2a, the reaction between RMgBr and benzophenone, has been discussed by Holm⁶ and it only needs to be stressed here once more that

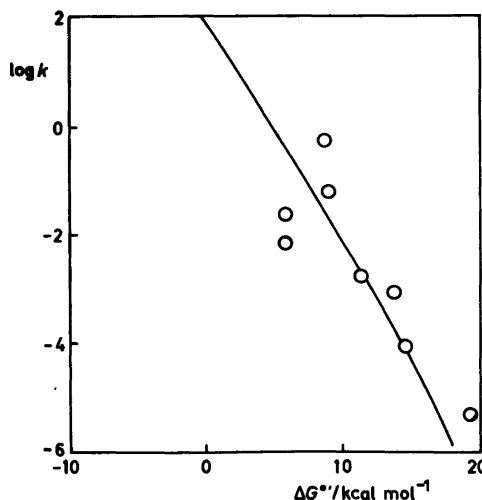


Fig. 3. Marcus plot of $\log k$ (estimated from information given in Ref. 1) vs. ΔG^\ddagger . The points refer to the following reactions (reaction, $\log k$, ΔG^\ddagger): cyclopentadiene (CPD)/*p*-dinitrobenzene, -0.27 , 8.7 ; CPD/azobenzene (AB), -5.33 , 19.3 ; CPD/nitrobenzene (NB), -3.04 , 13.8 ; indenide/AB, -4.06 , 14.5 ; indenide/NB, -1.21 , 9.0 ; fluorenyl/AB, -2.77 , 11.3 ; fluorenyl/NB, -1.64 , 5.8 ; 9-Ph-fluorenyl/NB, -2.16 , 5.8 .

an appreciable electrostatic free energy term (15 kcal mol⁻¹) must be subtracted from the $\Delta G^{\circ'}$ value in order to give a good fit to the Marcus equation. This is in line with the proper application of the Marcus theory, and it is only the difficulty of estimating the electrostatic free energy term in a low dielectric constant medium (diethyl ether) that dictates some care in judging the validity of the data obtained.

Entry 2b, reaction between azobenzene and RMgBr, illustrates that the previously found $\lambda(0)$ value of the RMgX⁺/RMgX self-exchange reaction (entry 2a, 70 kcal mol⁻¹) cannot be more than a strong indication that this particular $\lambda(0)$ must be very high. Here the same set of RMgBr reagents with a different acceptor molecule gives $\lambda(0)=120$ kcal mol⁻¹ for the RMgBr⁺/RMgBr self-exchange reaction, unless we assume that the azobenzene/azobenzene⁻ self-exchange reaction has an extremely high $\lambda(0)$. From a consideration of $\lambda(0)$ for similar systems, *e.g.* stilbene,⁵⁰ there does not seem to be any reason for doing so. Thus, we must presently accept that $\lambda(\text{RMgX}^+/\text{RMgX})$ is only known in a semiquantitative manner: It is very high, in the range between 70 and 120 kcal mol⁻¹.

Entry 2c, an established electron transfer reaction between RMgBr and di-*tert*-butyl peroxide, represents the highest λ value found in this study. As with entry 2a, an electrostatic free energy term of -15 kcal mol⁻¹ was employed to correct $\Delta G^{\circ'}$ for the change of charge type upon transfer of the electron in the transition state. Another source of uncertainty resides in the E° of the dialkyl peroxide redox couple. This was calculated on the basis of the same assumption as previously applied to diacyl peroxides, namely that the O-O bond is cleaved in the transition state. Thus $E^{\circ}(t\text{-Bu}_2\text{O}_2/t\text{-BuO}^- + t\text{-BuO}^{\cdot})$ in water came out at 0.04 V in water, and accordingly at -0.5 V in an ethereal solvent. The very high λ value found, 110 kcal mol⁻¹, should then be taken as an indication that the value predicted from the self-exchange reaction $\lambda(0)$'s of 70 (entry 2a, Table 4) and 80-90 (Table 1, assuming that dialkyl peroxides behave as diacyl peroxides in this respect)=75-80 kcal mol⁻¹ is indeed of the appropriate magnitude. If we use the higher $\lambda(0)$ of 120 kcal mol⁻¹ (entry 2b, Table 4), the agreement is of course better, but again it must be stressed that this would be to stretch the data beyond their actual range of validity.

Entry 3 is a rather straightforward one, except for the fact that we do not have any experimental value of E° for the Me₃Sn⁺/Me₃Sn⁻ couple. The approach here was to find an E°/λ pair that gave the best possible fit to the Marcus equation. This turned out to be $E^{\circ}=-1.2$ V and $\lambda=70$ kcal mol⁻¹; the rather low E° presumably includes an electrostatic free energy term (Me₃Sn⁻ is not likely to exist as the free ion in THF) and thus the E° value should be somewhat more positive. A preliminary suggestion of -1.0 V is listed in Table 3. Only data for secondary and tertiary alkyl halides + allyl and benzyl halides were included in the calculations of entry 3, since these are the ones for which experimental evidence for electron transfer is available. If data for primary halides are included as well (an additional 10 data pairs) the λ value comes out the same, but the

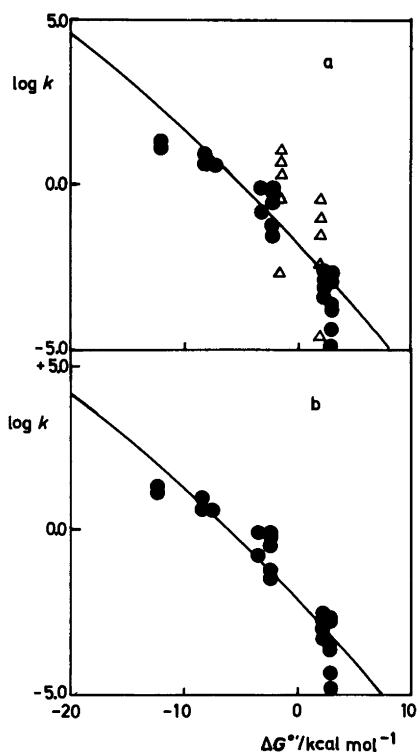


Fig. 4. Marcus plot of $\log k$ vs. $\Delta G^{\circ'}$ for the reaction between alkyl halides⁵¹ and Me₃Sn⁻ in THF and tetraglym.⁹¹ (a) Primary, secondary, and tertiary halides. (b) Same as (a), except that primary halides have been left out; triangles, primary halides.

Table 5. Marcus analysis of possible electron transfer steps in reactions between anionic nucleophiles and organic electrophiles.

Entry	Reaction	ΔG° , kcal mol ^{-1a}	$k_{\text{obs}}/M^{-1}s^{-1}$ ^c	$k_{\text{calc}}/M^{-1}s^{-1d}$	Remark (Ref.)
1	(a) Bu ⁻ + EtI in benzene-Et ₂ O (b) Bu ⁻ + BuBr in benzene (c) Bu ⁻ + <i>i</i> -PrI in benzene-TMEDA	< -0.9 < -0.2 < -2.5	53 62 53	Fast $\approx 10^{-2}$ $\approx 10^{-2}$	>20 >0.25 >70 Feasible (7) Feasible (8) Feasible (9)
2	(a) Bu ⁻ + fluorenone in hexane-Et ₂ O (b) Bu ⁻ + [Fe ₄ S ₄ (SPh) ₄] ²⁻ in hexane-Et ₂ O (c) [Fe ₄ S ₄ (SPh) ₄] ²⁻ + fluorenone in hexane-Et ₂ O	4.2 -3.0 7.2	32.2 37.5 ^e 19.7	1.4 × 10 ³ 7.6 × 10 ⁴ 1 × 10 ⁴	} See text (97)
3	CH ₃ ⁻ + 3-phenylimido-2-phenyl-3H-indole in benzene-THF	4.4	30	3 × 10 ³	Feasible (10a)
4	Me ₃ CCOCH ₂ ⁻ + Ph ₂ CO in THF	29.7 ^f	37.5 ^f	4 × 10 ⁻¹²	Not feasible (99)
5	(a) Me ₃ CCOCH ₂ ⁻ + PhI in DMSO (b) Me ₃ CCOCH ₂ ⁻ + PhBr in DMSO	27.9 ^g 37.8 ^g	48.5 ^g 48.5 ^g	7 × 10 ⁻⁷ 1.1 × 10 ⁻⁷	} See text (100)
6	(a) 4-NO ₂ C ₆ H ₄ CH ₂ ⁻ + 4-NO ₂ C ₆ H ₄ CH ₃ in DMSO- <i>t</i> -BuOH (80:20) (b) 4-NO ₂ C ₆ H ₄ CH ₂ ⁻ + 4-NO ₂ C ₆ H ₄ CH ₃ in DME ⁱ (c) Same as b by (d) H ⁻ + 4-NO ₂ C ₆ H ₄ CH ₃ (e) Ph ₃ C ⁻ + 4-NO ₂ C ₆ H ₄ CH ₃	10.8 ^g 10.8 ^g 10.8 ^g 10.6 0.0	35 ^h 35 ^h 35 ^h 35 35	Fast $\approx 2.5 \times 10^{-2}$ ≈ 1.2 0.6 2 × 10 ⁴	} Feasible (101) Feasible (3) (3) (3)
7	NO ₂ Me ₂ C ⁻ + 1,4-C ₆ H ₄ (NO ₂) ₂ in DMSO	26.5	31	1.4 × 10 ⁻⁹	See text (102)
8	(a) NO ₂ Me ₂ C ⁻ + 4-NO ₂ C ₆ H ₄ CH ₂ Cl in DMF at 0°C (b) NO ₂ Me ₂ C ⁻ + 4-NO ₂ C ₆ H ₄ CH ₂ Br in DMF	21.9 ^k 17.5 ^k	65 62	0.021 0.068	See text (103) See text (103)
9	1-Acetonyl-2,4,6-trinitrocyclohexadienide ion + tropylium ion in water	23.3	20	$\approx 10^{-2}$	Borderline (50, 104)
10	CH ₂ =CH(CH ₂) ₄ MgBr + 3-phenylimido-2-phenyl-3H-indole in THF	-5.8	40	Fast	Feasible (105)
11	CH ₂ =CH(CH ₂) ₄ MgBr + 2-methoxy-1-nitronaphthalene in THF	-2.8	40	Fast	Feasible (106)
12	EtMgBr + pyrazine in ethers	18.2 ^l	48.5	Fast	Not feasible (107)
13	PhMgBr + ClCH ₂ C≡CCH ₂ Cl in Et ₂ O	12.7 ^m 4.6 ⁿ	75 ^m 75	>10 ⁻²	} See text (108)
14	<i>t</i> -BuO ⁻ + polycyclic ArH in THF	47 ^o	30	Very slow	Not feasible (17)
15	<i>t</i> -BuO ⁻ + Ph ₃ CCl in THF	34.8 ^p 13.8 ^q	65 65	Rapid	} Not feasible (19)
16	<i>t</i> -BuO ⁻ + 4-NO ₂ C ₆ H ₄ CH ₃ in <i>t</i> -BuOH	44.7 ^r	35	Rel. fast	Not feasible (3, 109)
17	<i>t</i> -BuO ⁻ + 4-NO ₂ C ₆ H ₄ CH ₂ Cl in <i>t</i> -BuOH	28.8 ^r	65	Rel. fast	Not feasible (110)

18	$t\text{-BuO}^- + \text{Ph}_2\text{CO}$ in THF	47	34	$>10^6$	2×10^{-25}	Not feasible (20)
19	(a) $\text{PhCH}(\text{OH})\text{O}^- + \text{PhCHO}$ in dioxane-water (1:1)	68. ^{5s} 29.2 ^u 50	32. ^{5f} 32. ^{5f} 32.5		2×10^{-47} 2×10^{-11} 2×10^{-28}	See text (21, 22)
20	(b) Same as 19 (a) but in THF-HMPA(9:1)	47.5	34	5.2	8×10^{-26}	Not feasible (111)
21	$\text{HO}^- + p\text{-benzoquinone}$ in water	26.5	62	$>10^{-4}$	4×10^{-13}	See text (112)
22	(a) $\text{MeO}^- + 4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}$ in methanol	26.5	62		3×10^{-13}	
23	(b) $\text{CN}^- + 4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br}$ in acetonitrile	43.8	31	5	4×10^{-23}	Not feasible (113)
	(a) $\text{PhS}^- + \text{CF}_2\text{ClBr}^+$ in DMF	15.7-22.6	62	Rel. fast	7×10^{-8}	
24	(b) $\text{PhS}^- + 4\text{-NO}_2\text{C}_6\text{H}_4\text{Cl}$ in DMF	26.7	65	Rel. fast	3×10^{-11}	See text (114)
25	PhS^- + butyl or 1-norbornyl nosylate in EtOH-water	23.0 35.5 ^x 21.7 ^y	35 34 34	10^{-2} - 10^{-3} $>10^{-4}$	1×10^{-7} 5×10^{-16} 10^{-6}	See text (23)
26	$\text{BuS}^- + \text{Ph}_2\text{CO}$ in THF	21.7 ^y 35.5 ^x 21.7 ^y	30 30 30	$>10^{-4}$ $>10^{-4}$ $>10^{-4}$	3×10^{-16} 2×10^{-6}	Not feasible (24)
27	BuS^- + perylene in THF	-4.4	65	$>10^{-6}$	2	Not feasible (24)
28	$i\text{-Pr}_2\text{N}^- + \text{Ph}_3\text{CCl}$ in THF	7.8	34	$>10^{-4}$	20	Feasible (17)
29	$i\text{-Pr}_2\text{N}^- + \text{Ph}_2\text{CO}$ in THF at 0 °C	29.5	39	$>10^{-4}$	4×10^{-12}	Feasible (16)
30	$i\text{-Pr}_2\text{N}^-$ + pyridine in HMPA at 0 °C	21.4 ^z	53	$>10^{-4}$	4×10^{-9}	Not feasible (18)
31	$\text{AlH}_4^- + \text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{I}$ in THF	9.9 ^{aa} 41.5 ^z 30 ^{aa}	53 39 39	Rel. fast	1×10^{-3} 2×10^{-20} 2×10^{-12}	Not feasible (29)
32	$\text{AlH}_4^- + 2,2'$ -bipyridine in THF	14.8 ^{bb}	62	$>10^{-4}$	2×10^{-7}	Feasible (13)
33	$\text{Me}_3\text{Sn}^- + 2\text{-octyl bromide}$ in THF	3.0 ^{bb}	66.5	$>10^{-4}$	2×10^{-3}	Feasible (13)

^a From data in Refs. 50 and 51, Tables 2 and/or 3, and/or Ref(s) given in column 7, unless otherwise stated. ^b From data in Refs. 50 and 51, Tables 1 and/or 4, and/or Ref(s) given in column 7, unless otherwise stated. ^c Rate constant either given in the Ref(s) of column 7 or estimated from data given therein; estimated values are preceded by the symbol \approx . ^d From eqn. (13), using the appropriate value of k_q (taken from Ref. 96 or calculated by methods given therein). ^e A $\lambda(0)$ of 25 kcal mol⁻¹ was calculated from the self-exchange rate constant of $2.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for $[\text{Fe}_2(\text{SPh})_2]^{1-2-}$ (Ref. 98). ^f Assuming that the redox properties of pinacolone enolate ion is the same as that of phenylacetone enolate ion. ^g E° of $4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2/4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^-$ was estimated from its pK (20.5³) and eqn. (15). ^h $\lambda(0)$ of $4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2/4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^-$ was taken to be 20 kcal mol⁻¹ (cf. nitrobenzene in Table 7 of Ref. 50). ⁱ KH/18-crown-6 was used as a base to generate $4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^-$. ^j Ph₃CK was used as a base to generate $4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2^-$. ^k E° for reduction of $4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{X}$ was assumed to be 0.4 V less cathodic than that of $\text{C}_6\text{H}_5\text{CH}_2\text{X}$; see discussion in text. ^l ΔG° was corrected by an electrostatic free energy term of -9.0 kcal mol⁻¹. ^m The redox properties of $\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Cl}$ were taken to be the same as those of allyl chloride. ⁿ Calculations were made for perylene. ^o Calculations were made for perylene. ^p Assuming that E° for reduction of Ph_3CCl is 0.0 V. ^q E° of $t\text{-BuO}^-/t\text{-BuO}^-$ was taken to be 1.0 V. ^r E° for the same as that of PhCH_2Cl . ^s Assuming that E° for reduction of $\text{PhCH}(\text{OH})\text{O}^-/\text{PhCH}(\text{OH})\text{O}^-$ was taken to be 1.7 V. ^t $\lambda(0)$ for $\text{PhCH}(\text{OH})\text{O}^-/\text{PhCH}(\text{OH})\text{O}^-$ was taken to be 0.0 V. ^u Assumed to have the same redox properties as CCl_4 . ^v E° for $\text{BuS}^-/\text{BuS}^-$ was taken to be equal to that of $\text{EtS}^-/\text{EtS}^-$. ^w E° of BuS^- was taken to be 0.6 V more cathodic than that of EtS^- . ^x E° of $\text{AlH}_4^-/\text{AlH}_4^-$ taken to be -0.2 V. ^{aa} E° of $\text{AlH}_4^-/\text{AlH}_4^-$ taken to be -0.7 V. ^{bb} The redox properties of 2-octyl bromide were taken to be the same as those of isopropyl bromide.⁵¹

spread around the Marcus curve is much more pronounced (see Fig. 4).

Entry 4 again rests on some uncertainty as to the actual value of the rate constant to be used. From the information given in the paper it was deduced that the reaction half-life under the conditions used must be 10–30 s, corresponding to second-order rate constants in the region of $0.1\text{--}0.3\text{ M}^{-1}\text{s}^{-1}$. It is also important to recognize that the model for $1e^-$ reduction of benzyl chloride was assumed to be of the dissociative type.⁵¹

Entry 5 is complicated by some uncertainty with regard to the E° value of $\text{Me}_3\text{CCOCH}_2^-$ which was taken to be the same as that of phenylacetone enolate ion, -0.19 V , but may actually be somewhat more negative. Finally, entry 6 shows an attempt to evaluate λ for a postulated electron transfer oxidation of hydroxide ion by excited states of aromatic compounds. With the accepted value of $E^\circ(\text{HO}^\cdot/\text{HO}^-)$ (1.9 V , see Table 3) the λ values comes out as being physically unrealistic; $\lambda_{\text{D}^\cdot/\text{D}^-}$ is negative if we assume that $\lambda_{\text{A}^\cdot+/\text{A}}$ is 15 kcal mol^{-1} in the protic medium used, and only with a lower E° , in the $1.4\text{--}1.6\text{ V}$ range, is a reasonable λ value obtained. Some lowering of $E^\circ(\text{HO}^\cdot/\text{HO}^-)$ upon transfer from water to 30–50 % ethanol is to be expected, but certainly not as much as indicated here. The reason for this behaviour is probably to be found in the fact that quenching of excited states by inorganic anions (such as HO^- , halide and pseudohalide ions) takes place *via* energy transfer instead of electron transfer, as shown earlier by several groups.^{88,95} In fact, the slowness of electron transfer quenching by inorganic anions, in spite of high exergonicity of the reactions, was explained in terms of very high $\lambda(0)$ values for oxidation of inorganic anions in aqueous medium.

These problems notwithstanding, a safe conclusion is that self-exchange reactions of the $\text{R}^\cdot/\text{R}^-$ or $\text{R-metal}^\cdot+/\text{R-metal}$ type have very high $\lambda(0)$ values. This might reflect several of the factors contributing to high $\lambda(0)$ values, in particular the effect of ion pairing, extensive changes in going from a tetrahedral carbanion to a planar radical, large changes in bond lengths, *etc.* Although we cannot presently obtain $\lambda(0)$'s for other carbanionic or anionic systems of interest in this context due to the lack of suitable data, it will be assumed that the same generaliza-

tion holds in these cases. Thus $\lambda(0)$ for $\text{R}^\cdot/\text{R}^-$, $\text{R}_2\text{N}^\cdot/\text{R}_2\text{N}^-$, $\text{RO}^\cdot/\text{RO}^-$, $\text{RS}^\cdot/\text{RS}^-$ and $\text{AlH}_4^\cdot/\text{AlH}_4^-$ will all be taken to be 50 kcal mol^{-1} in the analysis of the feasibility of postulated electron transfer steps to follow. For the time being this seems to be the only useful simple strategy for the theoretical study of these reactions.

Table 5 summarizes results of the Marcus treatment of a number of possible electron transfer steps, involving R^- , RMgX , RO^- , RS^- , R_2N^- , AlH_4^- and R_3Sn^- as donor species, many of which have recently been postulated to take place instead of conventional polar steps. Many additional interesting examples could have been included, but space limitations dictate that only the most typical and best documented cases can be discussed.

Entry 1 covers a few cases of alkyl-lithium/alkyl halide reactions, now well established as proceeding *via* an electron transfer mechanism with the indicated crucial step. Although E° for $\text{Bu}^\cdot/\text{Bu}^-$ has been given as an upper limit only, the feasibility of this type of electron transfer step is clearly demonstrated by the Marcus treatment.

Entry 2 is related to a very interesting case of mediated electron transfer. It was found that addition of the iron-sulfur cluster $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ to the reaction between butyl-lithium and fluorenone changes the product composition from 98 % 9-butylfluorenone in its absence to 63 % fluorenone, 6 % 1,2-bisfluorenylidene-1,2-ethanediol and 10 % 9-butylfluorenone. The interpretation of this phenomenon was that electrons from butyl-lithium were transferred to the iron-sulfur cluster which then reduced fluorenone *via* an electron transfer mechanism, thus suppressing the expected addition process (this may be either of polar or electron transfer type). The calculated rate constants are entirely in agreement with this suggestion: Transfer of an electron from butyl-lithium to the cluster is the fastest step possible in the system, and from cluster to fluorenone the next fastest. Electron transfer directly from butyl-lithium to fluorenone is the slowest step of the possible ones, and thus the iron-sulfur cluster can exert its mediating role.

Entries 3 and 10 are related, insofar as the first reaction was inferred to follow an electron transfer mechanism from a study of its product distribution which, however, could not be conclusively demonstrated by other experiments. The second reaction utilized the 5-hexenyl Grignard

reagent to show that the addition products were partly rearranged (5-hexenyl→cyclopentylmethyl) during the reaction. This constitutes strong evidence for the intermediacy of the 5-hexenyl radical which rearranges to cyclopentylmethyl radical with a rate constant of 10^5 s^{-1} . In both cases the calculated rate constants are fully compatible with the suggested electron transfer mechanism.

Entry 4 is the first step of an aldol condensation for which ESR evidence for the slow formation of benzophenone radical anion was adduced. Here the calculated rate constant is smaller than the experimental one by a factor of $<10^{-7}$ which would seem to militate against this particular electron transfer process. It must however be kept in mind that E° for oxidation of $\text{Me}_3\text{CCOCH}_2^-$ was assumed to be equal to that of phenylacetone enolate ion which most probably represents an upper limit. If E° of $\text{Me}_3\text{CCOCH}_2^-/\text{Me}_3\text{CCOCH}_2$ is assumed to be 0.5 V lower, the calculated electron transfer rate constant comes out at $\approx 3 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$; whether this E° difference between these two enolate ions is a realistic one remains to be experimentally tested.

The same reservation holds for entry 5, showing the postulated initiation steps of the $\text{S}_{\text{RN}}1$ reaction between pinacol enolate ion and iodo- and bromobenzene. Among its type, this reaction is unusual in that it occurs spontaneously and does not require the normal stimulation by light, alkali metal or electrons from the cathode. Consequently, the electron transfer steps of entry 5 were suggested as initiation steps. As seen from Table 5, the calculated rate constants are very small, especially for bromobenzene, but again the uncertainty in the value of $E^\circ(\text{Me}_3\text{CCOCH}_2^-/\text{Me}_3\text{CCOCH}_2)$ makes these values estimates of the lower limits of electron transfer rate constants in the system. Moreover, the possibility that unusually long chains might be found in these reactions should be experimentally tested.

Entries 6 and 16 exemplify a much studied problem of wide interest, namely the redox reactions that can take place when a compound, suitably activated by one or several $-I, -E$ substituents, is treated by a strong donor (a nucleophile/base/reductant). In such a case either the donor can act as a $1e^-$ transfer reductant toward the substrate, or, since the latter is likely to be a reasonably strong C-H acid, act as a base and abstract a proton from it. The carbanion

formed is normally an easily oxidizable species, thus opening an electron transfer pathway to the parent molecule.

Two limiting cases of donor/4-nitrotoluene reactions are illustrated in entries 6 and 16. Using *t*-butoxide as the donor species, an electron transfer process to 4-nitrotoluene is not feasible with any reasonable assumption about E° of $t\text{-BuO}^-/t\text{-BuO}$. Consequently, the pathway to formation of $(4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3)^-$ goes *via* proton abstraction to form the more effective $1e^-$ reductant, 4-nitrobenzyl anion, which rapidly reduces nitrotoluene (entry 6a). The other limiting case appears when Ph_3C^- is used as the base. Now the reducing properties of the donor are such as to allow for fast electron transfer to 4-nitrotoluene (entry 6e), but since Ph_3C^- is also a very strong base proton transfer, essentially irreversible in this case, prevails and again the net result is that the reaction is shunted *via* the carbanion/substrate step (entry 6e). The agreement between the experimental and calculated rate constants is excellent, as is also the qualitative behaviour of the system.

Entry 7 is an attempt to find out whether the synthetically useful displacement of the nitro group in suitably substituted aromatics might be due to a $\text{S}_{\text{RN}}1$ mechanism. Using the E° for oxidation of $\text{Me}_2(\text{NO}_2)\text{C}^-$ given in Table 2, the calculated electron transfer rate constant comes out at far too low a value and thus this possibility would seem to be precluded. However, as entry 8 shows, $\text{Me}_2(\text{NO}_2)\text{C}^-$ is a case where the reported E° value must be viewed with some scepticism. The reactions treated in entry 8 are well established cases of $\text{S}_{\text{RN}}1$ behaviour with exactly those steps shows as initiation steps. It thus appears necessary to assume that $E^\circ(\text{Me}_2(\text{NO}_2)\text{C}^-/\text{Me}_2(\text{NO}_2)\text{C})$ should be considerably lower than the one given in Table 2.

Another rationale for arriving at this value is to use eqn. (16). With $\text{p}K$ (DMSO) of the Me_2CHNO_2 equal to 17, a value of E° of -0.33 V is obtained which *via* eqn. (13) gives electron transfer rate constants of 10^4 , 0.03, and $1.6 \text{ M}^{-1}\text{s}^{-1}$ for entries 7, 8a and 8b, respectively. Qualitatively, this can be summarized by the conclusion that the $\text{S}_{\text{RN}}1$ initiation steps of entry 8 will come out as theoretically feasible with $E^\circ(\text{Me}_2(\text{NO}_2)\text{C}^-/\text{Me}_2(\text{NO}_2)\text{C}) \leq 0.0 \text{ V}$; from this starting point also the reactions of entry 7 and eqn. (14) should be feasible.

Grignard reagents have by now been convincingly implicated as electron transfer reductants toward many types of compounds,⁴ *e.g.* ketones, quinones, azo compounds, diazonium salts, nitro compounds and organic halides, and the most important problem in this context is presently to define the region of borderline behaviour between polar and electron transfer mechanisms. As already pointed out, the E° values of RMgBr listed in Table 2 must still be considered preliminary ones, as also applies to their $\lambda(0)$ values. However, conclusions regarding entries 10 and 11 are presumably on the safe side since even with an E° more positive by 0.4 V these reactions would still come out with calculated rate constants ($\approx 10^1$) compatible with experiments. For entry 12 the calculated rate constant would seem to be far too low to be consistent with the ready formation of radical anion-organometallic cation complexes in these systems, and a mechanism similar to that given for *t*-BuO⁻/nitrobenzene might therefore be more likely. *Cf.* also the apparent electron transfer reaction between *t*-BuO⁻ and nitrobenzene.¹⁰⁹

Entry 13 was included more for its principal interest (ArMgBr is oxidized by a propargyl type halide to give an excellent yield of the biaryl, Ar-Ar) than for the actual possibility of making any reasonable estimate of the rate constant. The two calculations performed only serve to illustrate the need for more work aiming at obtaining E° values for the two redox couples involved (and related ones).

Entries 14-19 deal with alkoxide species and their possible electron transfer oxidation by various organic compounds. Generally, the $E^\circ(\text{RO}^\cdot/\text{RO}^-)$ values are known with an accuracy good enough to make estimates of ΔG° of the type needed here decisive and thus it can be concluded that direct electron transfer between RO⁻ and organic species are not feasible. Even with extreme, and unrealistic, assumptions (second case of entries 15 and 19) about E° values the calculated rate constants remain far too low to be compatible with experiments. The formation of radicals and/or radical anions under the conditions of these experiments must therefore be ascribed to other, and presumably more complex mechanisms (see for example the discussion above about the *t*-BuO⁻/4-nitrotoluene reaction and also Ref. 109). The same conclusion should be valid for the hydroxide ion reactions

listed (entries 20 and 22).

Entry 21 deserves to be commented upon in more detail. Reaction 21a leads to the formation of a 97 % yield of the methyl ether in a normal S_N2 process, whereas 21b gives a 96 % yield of 1,2-bis-(4-nitrophenyl)ethane, a reaction that was assumed to be initiated by the 1e⁻ transfer between 4-nitrobenzyl bromide and cyanide ion and then proceeding according to the S_{RN}1 mechanism. The theoretical rate constant is a rather small one, but perhaps not entirely impossible for the suggested mechanism, taking into account errors in E° values and the possibility of a long chain reaction.

Thiolate ions are expected to be borderline nucleophiles/1e reductants in view of the relatively low E° values for oxidation, 0.4 V for PhS⁻/PhS⁻ and 0.9 V for EtS⁻/EtS⁻. Even so, three of the five cases given in Table 5 (entries 23b, 25, 26) do not seem to be consistent with direct 1e transfer from RS⁻ to substrate, whereas entries 23a and 24 are still open for discussion. In case 24 one has designed an easily reducible substrate by incorporating a nitro group into the leaving group, and indeed evidence for electron transfer (*e.g.* formation of products of C-O cleavage in the 1-norbornyl system) was obtained. Theoretically, the reaction is a feasible one.

Entry 23a is an additional suspected case of electron transfer oxidation of polyhalides, among which carbon tetrachloride previously is the most studied one. This possibility has certain implications for the possible mode of action of polyhalides in biological systems. In fact, there is agreement that the irreversible toxic properties of carbon tetrachloride are due to the intermediacy of trichloromethyl radical, formed *via* 1e⁻ reduction of carbon tetrachloride.^{116,117}

The remaining cases of Table 5, dealing with possible electron transfer reactions of i-Pr₂N⁻, AlH₄⁻, and R₃Sn⁻, are relatively straightforward in their interpretation. These anions are moderately strong or strong 1e⁻ reductants, and it is to be expected that they should undergo 1e⁻ oxidation with great ease by suitable organic substrates (though not by pyridine or 2,2'-bipyridine, two difficultly reducible compounds; *cf.* also entry 12). The same should apply to R₃Si⁻, known to reduce aromatic hydrocarbons (even naphthalene) to radical anions in HMPA.¹¹⁸

Table 6. Errors in log k for given error limits of $\Delta G^{\circ'}$ and λ at different $\Delta G^{\circ'}$ and λ .

$\Delta G^{\circ'}/\text{kcal mol}^{-1}$	5			10			15		
$\lambda/\text{kcal mol}^{-1}$	10	30	50	10	30	50	10	30	50
$\Delta\Delta G^{\circ'} = \pm 2.3^a \text{ kcal mol}^{-1}$	± 1.3	± 1.0	± 0.9	± 1.7	± 1.1	± 1.0	± 2.1	± 1.3	± 1.1
$\Delta\lambda = \pm 2.3^a \text{ kcal mol}^{-1}$	± 0.3	± 0.4	± 0.4	± 0.1	± 0.4	± 0.4	± 0.6	± 0.3	± 0.4

^a Corresponding to ± 0.1 eV.

Possible errors. A few words of caution must be injected with respect to the discussion of the reactions of Table 5. Among the different classes of donors, carbanions and other soft or borderline nucleophiles are bound to present the most difficult mechanistic problems by virtue of their rather intractable electrochemistry. It should therefore again be emphasized that the E° values of Tables 2 and 3 may be subjected to errors to a varying degree, and that future studies might bring about changes in these values. The application of the Marcus theory to these systems should presently be regarded more as an attempt to provide a tool for guidance of experimentation around crucial problems of organic electron transfer chemistry, and less as a definitive answer to such problems.

The sensitivity of the rate constant estimates to errors in E° and λ are shown for different combinations of $\Delta G^{\circ'}$ and λ in Table 6. Thus the

reader can judge for himself how any assumptions about errors in these variables will affect log k . Generally, the error in log k increases with decreasing λ and increasing ΔG° .

Comparison with the simple thermodynamic treatment. Fig. 5 shows a family of truncated Marcus parabolas with $\lambda = 10, 20, 30, 40, 50$ and 60 kcal mol^{-1} (eqn. (8), $W=0$) in relation to a straight line of slope 1 through the origin. This line represents the simple model of equating ΔG^{\ddagger} of electron transfer with $\Delta G^{\circ'}$, a treatment that has been used many times for discussing the feasibility of electron transfer steps and was exemplified in the introduction. For calibration, the broken lines were included to delineate the region between moderately fast ($k=10^{-2} \text{ M}^{-1}\text{s}^{-1}$, corresponding to a half-life of ca. 0.25 h at 0.1 M initial concentrations of reactants) rates and very slow ones ($k=10^{-6} \text{ M}^{-1}\text{s}^{-1}$; half-life ca. 2500 h under the same conditions). Somewhere in this

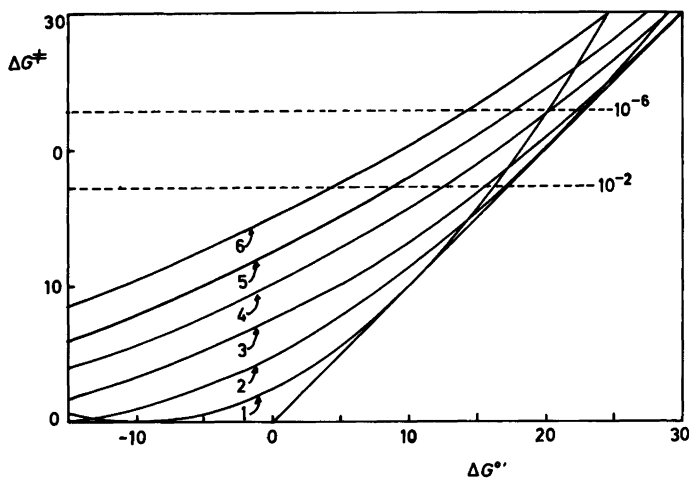


Fig. 5. Marcus parabolas (ΔG^{\ddagger} vs. $\Delta G^{\circ'}/\text{kcal mol}^{-1}$) for $\lambda = (1) 10, (2) 20, (3) 30, (4) 40, (5) 50$ and $(6) 60 \text{ kcal mol}^{-1}$. The broken lines correspond to rate constants 10^{-2} and $10^{-6} \text{ M}^{-1}\text{s}^{-1}$.

region the lower limit for a practically feasible electron transfer step is reached.

The solid line is a tangent to each parabola in the point λ/λ , *i.e.* for small λ 's (up to 20 kcal mol⁻¹) the differences in rate constant as predicted from the Marcus or thermodynamic treatment are hardly of any practical consequence for the range $5 < \Delta G^\circ < 20$ kcal mol⁻¹ and only for higher λ 's do the differences become significant. It is also evident that for $\Delta G^\circ > 23$ kcal mol⁻¹ (> 1 eV) k_{el} is $< 10^{-6}$ M⁻¹s⁻¹, irrespective of the value of λ .

Calculations of standard potentials. Data for the calculations of standard potentials of MeO⁻/MeO⁻, *t*-BuO⁻/*t*-BuO⁻, EtS⁻/EtS⁻ and PhS⁻/PhS⁻ were obtained from Refs. 119–127.

REFERENCES

- Russell, G. A., Janzen, E. G. and Strom, T. *J. Am. Chem. Soc.* 86 (1964) 1807.
- House, H. O. *Acc. Chem. Res.* 9 (1976) 59.
- Buncel, E. and Menon, B. G. *J. Am. Chem. Soc.* 102 (1980) 3499.
- Dagonneau, M. *Bull. Soc. Chim. Fr.* (1982) II-269.
- a. Ashby, E. C. and Wiesemann, T. L. *J. Am. Chem. Soc.* 100 (1978) 189; b. Ashby, E. C. and Bowers, J. R. *Ibid.* 103 (1981) 2242.
- Holm, T. *Acta Chem. Scand. B* 37 (1983) 567.
- Russell, G. A. and Lamson, D. W. *J. Am. Chem. Soc.* 91 (1969) 3967.
- Ward, H. R., Lawler, R. G. and Cooper, R. A. *J. Am. Chem. Soc.* 91 (1969) 746.
- Lepley, A. R. and Landau, R. L. *J. Am. Chem. Soc.* 91 (1969) 749.
- a. Berti, C., Greci, L. and Marchetti, L. *J. Chem. Soc. Perkin Trans. 2* (1977) 1032; b. Liotta, D., Saindane, M. and Waykole, L. *J. Am. Chem. Soc.* 105 (1983) 2922.
- Blake, D., Coates, G. E. and Tate, J. M. *J. Chem. Soc.* (1961) 618.
- Smith, G. F., Kuivila, H. G., Simon, R. and Sulta, L. *J. Am. Chem. Soc.* 103 (1981) 833.
- San Filippo, J., Jr. and Silbermann, R. *J. Am. Chem. Soc.* 104 (1982) 2831.
- Kitching, W., Olszowy, H. A. and Harvey, K. *J. Org. Chem.* 47 (1982) 1893.
- Ashby, E. C. and DePriest, R. *J. Am. Chem. Soc.* 104 (1982) 6144.
- Scott, L. T., Carlin, K. J. and Schultz, T. H. *Tetrahedron Lett.* (1978) 4637; Ashby, E. C., Goel, A. B. and DePriest, R. *Ibid.* 22 (1981) 4355.
- Ashby, E. C., Goel, A. B. and DePriest, R. *J. Org. Chem.* 46 (1981) 2431.
- Newkome, G. R. and Hager, D. C. *J. Org. Chem.* 47 (1982) 601.
- Bilevich, K. A., Bubnov, N. N. and Okhlobystin, O. Yu. *Tetrahedron Lett.* (1968) 3465; Huszthy, P., Lempert, K., Simig, G. and Ve'key, K. *J. Chem. Soc. Perkin Trans. 1* (1982) 3021.
- Ashby, E. C., Goel, A. B. and Argyropoulos, J. N. *Tetrahedron Lett.* 22 (1982) 2273.
- Chung, S. K. *J. Chem. Soc. Chem. Commun.* (1982) 480.
- Ashby, E. C., Coleman, D. T. and Gama-sa, M. P. *Tetrahedron Lett.* 24 (1983) 851.
- Bank, S. and Noyd, D. A. *J. Am. Chem. Soc.* 95 (1973) 8203; Noyd, D. A., *Diss.*, State Univ. New York, Albany 1972.
- Ashby, E. C., Goel, A. B. and Park, W. S. *Tetrahedron Lett.* 22 (1981) 4209.
- Olah, G. A. and Krishnamurthy, V. V. *J. Am. Chem. Soc.* 104 (1982) 3987.
- Ashby, E. C., DePriest, R. N. and Goel, A. B. *Tetrahedron Lett.* 22 (1981) 1763.
- Ashby, E. C., Goel, A. B. and DePriest, R. N. *Tetrahedron Lett.* 22 (1981) 3729.
- Singh, P. R., Khurana, J. M. and Nigam, A. *Tetrahedron Lett.* 22 (1981) 2901.
- Ashby, E. C. and Goel, A. B. *Tetrahedron Lett.* 22 (1981) 4783.
- Kaim, W. Z. *Naturforsch. Teil B* 37 (1982) 783.
- a. Chung, S. K. and Filmore, K. L. *J. Chem. Soc. Chem. Commun.* (1983) 358; b. Wagner, W. R. and Rasletter, W. H. *J. Org. Chem.* 48 (1983) 294.
- Singh, P. R. and Khanna, R. K. *Tetrahedron Lett.* 24 (1983) 1411.
- Perrin, C. L. *J. Am. Chem. Soc.* 99 (1977) 5516.
- Ebersson, L., Jönsson, L. and Radner, F. *Acta Chem. Scand. B* 32 (1978) 749; Ebersson, L. and Radner, F. *Ibid. B* 34 (1980) 739.
- Ebersson, L., Ericson, S. and Radner, F. *Abstract Int. Symposium on Nitration*, SRI International, Menlo Park, Calif., July 27–29, 1983; *Acta Chem. Scand. B. In press.*
- Clemens, A. H., Ridd, J. H. and Sandall, J. P. B. *J. Chem. Soc. Chem. Commun.*

- (1983) 343; Al-Omrau, F., Fujiwara, K., Griffrey, J. C., Ridd, J. H. and Robinson, S. R. *J. Chem. Soc. Perkin Trans. 2* (1981) 518.
37. Galli, C. *J. Chem. Soc. Perkin Trans. 2* (1981) 1459.
 38. Dauben, H. J. and Wilson, J. D. *J. Chem. Soc. Chem. Commun.* (1968) 1629.
 39. Ledwith, A. and Sambhi, M. *J. Chem. Soc. Chem. Commun.* (1965) 64.
 40. Schuster, G. B. *Adv. Phys. Org. Chem.* 18 (1982) 187; *Acc. Chem. Res.* 12 (1979) 366.
 41. Bilevich, K. A. and Okhlobystin, O. Yu. *Russ. Chem. Rev.* 37 (1968) 1.
 42. Todres, Z. V. *Russ. Chem. Rev.* 43 (1974) 1099; 47 (1978) 148.
 43. For an up-to-date list of further examples, see Shibo, E. B. and Bruce, T. C. *J. Am. Chem. Soc.* 105 (1983) 3316, Ref. 25.
 44. Littler, J. S. *Essays on Free-Radical Chemistry*, Spec. Publ. No. 24, Chem. Soc., London 1970, p 383.
 45. Marcus, R. A. *Ann. Rev. Phys. Chem.* 15 (1964) 155.
 46. Cannon, R. D. *Electron Transfer Reactions*, Butterworth, London 1980.
 47. Rehm, D. and Weller, A. *Isr. J. Chem.* 8 (1970) 259.
 48. Scandola, F. and Balzani, V. *J. Am. Chem. Soc.* 101 (1979) 6140.
 49. Pennington, D. E. In Martell, E. D., Ed., *Coordination Chemistry*, Am. Chem. Soc. Washington, D.C. 1978, Vol. 2.
 50. Ebersson, L. *Adv. Phys. Org. Chem.* 18 (1982) 79.
 51. Ebersson, L. *Acta Chem. Scand. B* 36 (1982) 533.
 52. Ebersson, L. *Chem. Scr.* 20 (1982) 29.
 53. Sutin, N. *Acc. Chem. Res.* 15 (1982) 275.
 54. Lednicky, L. A. and Stanbury, D. M. *J. Am. Chem. Soc.* 105 (1983) 3098.
 55. Ref. 50, Table 7.
 56. Katz, T. J. *J. Am. Chem. Soc.* 82 (1960) 3785; Strauss, H. L., Katz, T. J. and Fraenkel, G. K. *Ibid.* 85 (1983) 2360.
 57. Hammerich, O. and Parker, V. D. *J. Am. Chem. Soc.* 96 (1974) 4289 and references therein.
 58. Fritz, H. R., Gebauer, H., Friedrich, P., Ecker, P., Artes, R. and Schubert, U. Z. *Naturforsch. Teil B* 33 (1978) 498.
 59. Moore, G. A. and Williams, R. J. P. *Coord. Chem. Rev.* 18 (1976) 125.
 60. Fukuzumi, S., Wong, C. L. and Kochi, J. K. *J. Am. Chem. Soc.* 102 (1980) 2928; Wong, C. L. and Kochi, J. K. *Ibid.* 101 (1979) 5593.
 61. Symons, M. C. R. *J. Chem. Soc. Chem. Commun.* (1982) 869.
 62. Walther, B. W., Williams, F., Lau, W. and Kochi, J. K. *Organometallics* 2 (1983) 688.
 63. Ebersson, L. *J. Am. Chem. Soc.* 105 (1983) 3192.
 64. Katritzky, A. R., Kashmiri, M. A., de Ville, G. Z. and Patel, R. C. *J. Am. Chem. Soc.* 105 (1983) 90.
 65. Grimshaw, J., Moore, S., Thompson, N. and Trocha-Grimshaw, T. *J. Chem. Soc. Chem. Commun.* (1983) 783.
 66. Jaun, B., Schwarz, J. and Breslow, R. *J. Am. Chem. Soc.* 102 (1980) 5741.
 67. Breslow, R. and Grant, J. L. *J. Am. Chem. Soc.* 99 (1977) 7745.
 68. Breslow, R. and Chu, W. *J. Am. Chem. Soc.* 95 (1973) 411.
 69. Lochert, P. and Federlin, P. *Tetrahedron Lett.* (1973) 1109.
 70. Bank, S., Ehrlich, C. L. and Zubieta, J. A. *J. Org. Chem.* 44 (1979) 1454.
 71. Kern, J. M. and Federlin, P. *Tetrahedron Lett.* (1977) 837.
 72. Kern, J. M. and Federlin, P. *Tetrahedron* 34 (1978) 661.
 73. Schäfer, H. *Chem.-Ing.-Tech.* 41 (1969) 179.
 74. Evans, W. V., Lee, F. H. and Lee, C. H. *J. Am. Chem. Soc.* 57 (1935) 489.
 75. Kern, J. M. and Federlin, P. *J. Electroanal. Chem.* 96 (1979) 209.
 76. Kern, J. M., Sauser, J. D. and Federlin, P. *Tetrahedron* 38 (1982) 3023.
 77. Lowry, T. H. and Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd Ed., Harper & Row, New York 1981.
 78. Berdnikov, V. M. and Bazhin, N. M. *Russ. J. Phys. Chem.* 44 (1970) 395; Malone, S. D. and Endicott, J. F. *J. Phys. Chem.* 76 (1972) 2223.
 79. Stanbury, D. M., Wilmarth, W. K., Khalaf, S., Po, H. N. and Byrd, J. E. *Inorg. Chem.* 19 (1980) 2715.
 80. Shizuka, H., Saito, T. and Morita, T. *Chem. Phys. Lett.* 56 (1978) 519.
 81. Ebersson, L. *Acta Chem. Scand.* 17 (1963) 2004.
 82. Ebersson, L., Jönsson, L. and Wistrand, L.-G. *Acta Chem. Scand. B* 32 (1978) 520.
 83. Latimer, W. M. *The Oxidation States of the Elements and their Potentials in Aqueous Solution*, Prentice-Hall, New York 1952.
 84. Barry, J. E., Finkelstein, M., Moore, W. M., Ross, S. D., Ebersson, L. and Jönsson, L. *J. Org. Chem.* 47 (1982) 1292.

85. Chengzue, Z., Renmo, Z., Heqi, P., Xiangshan, J., Yangling, Q., Chengjiu, W. and Xikui, J. *J. Org. Chem.* 47 (1982) 2009.
86. Dessy, R. E., Pohl, R. L. and King, R. B. *J. Am. Chem. Soc.* 88 (1966) 5112.
87. Ebersson, L. and Nyberg, K. *Acta Chem. Scand. B* 32 (1978) 235.
88. Watkins, A. R. *J. Phys. Chem.* 7 (1974) 2555.
89. Marcus, Y. *Pure Appl. Chem.* 55 (1983) 977.
90. a. Michaud, P., Astruc, D. and Ammeter, J. H. *J. Am. Chem. Soc.* 104 (1982) 3755; Moinet, C., Roman, E. and Astruc, D. *J. Electroanal. Chem.* 121 (1981) 241; Astruc, D. and Dabard, R. *Bull. Soc. Chim. Fr.* (1976) 228; b. Li, T. T. T., Weaver, M. J. and Brubaker, C. H. *J. Am. Chem. Soc.* 104 (1982) 2381.
91. Kuivila, H. G. and Reeves, W. G. *Bull. Soc. Chim. Belg.* 89 (1980) 801.
92. Nugent, W. A., Bertini, F. and Kochi, J. K. *J. Am. Chem. Soc.* 96 (1974) 4945.
93. Zieger, H. E., Angres, I. and Mathisen, D. *J. Am. Chem. Soc.* 98 (1976) 2580.
94. Ashby, E. C. and Park, W.-S. *Tetrahedron Lett.* 24 (1983) 1667.
95. Treinin, A. and Hayon, E. *J. Am. Chem. Soc.* 98 (1976) 3884; Watkins, A. R. *J. Phys. Chem.* 78 (1974) 1885; 77 (1973) 1207.
96. Ridd, J. H. *Adv. Phys. Org. Chem.* 16 (1978) 1.
97. Inone, H., Fujimoto, N. and Imoto, E. *J. Chem. Soc. Chem. Commun.* (1977) 412.
98. Reynolds, J. G., Coyle, C. L. and Holm, R. H. *J. Am. Chem. Soc.* 102 (1980) 4350.
99. Ashby, E. C., Argyropoulos, J. N., Meyer, G. R. and Goel, A. B. *J. Am. Chem. Soc.* 104 (1982) 6788.
100. Scamehorn, R. G. and Bunnett, J. F. *J. Org. Chem.* 42 (1977) 1449.
101. Russell, G. A. and Janzen, E. G. *J. Am. Chem. Soc.* 89 (1967) 300.
102. Kornblum, N., Cheng, L., Kerber, R. C., Kestner, M. M., Newton, B. N., Pinnick, H. W., Smith, R. G. and Wade, P. A. *J. Org. Chem.* 41 (1976) 1560.
103. Kerber, R. C., Urry, G. W. and Kornblum, N. *J. Am. Chem. Soc.* 87 (1965) 4520.
104. Kalinkin, M. I., Parnes, Z. N., Puzanova, V. E., Khmelinskaya, A. D., Shein, S. M. and Kursanov, D. N. *J. Org. Chem. USSR* 9 (1973) 2354.
105. Ebersson, L. and Greci, L. *J. Org. Chem.* 49 (1984). *In press.*
106. Bartoli, G., Basco, M., Pozzo, R. D. and Ciminale, F. *J. Org. Chem.* 47 (1982) 5229.
107. a. Kaim, W. *Angew. Chem. Int. Ed. Engl.* 21 (1982) 140; b. *J. Am. Chem. Soc.* 104 (1982) 3833; for the $\lambda(0)$ value of pyrazine/(pyrazine)⁻, see Rüsse, C. and Jaenicke, W. *Electrochim. Acta* 27 (1982) 1745.
108. Taylor, S. K., Bennett, S. G., Heinz, K. J. and Lashley, L. K. *J. Org. Chem.* 46 (1981) 2194.
109. Guthrie, R. D. and Nutter, D. E. *J. Am. Chem. Soc.* 104 (1982) 7478.
110. Bethell, D. and Bird, R. *J. Chem. Soc. Perkin Trans 2* (1977) 1856.
111. Blyumenfel'd, L. A., Bryukhovetskaya, L. V., Fomin, G. V. and Shein, S. M. *Russ. J. Phys. Chem.* 44 (1970) 518.
112. Prousek, J. *Collect. Czech. Chem. Commun.* 47 (1982) 1334.
113. Abe, T. and Ikegami, Y. *Bull. Chem. Soc. Jpn.* 51 (1978) 196.
114. Rico, I., Cantacuzene, D. and Wakselman, C. *J. Org. Chem.* 48 (1983) 1979.
115. Sosonkin, I. M., Polynnikova, T. K., Kaminskii, A. Y., Gitis, S. S., Ivanov, A. V. and Kumantsov, V. I. *J. Org. Chem. USSR* 11 (1975) 113.
116. Hanzlik, R. P. *Biochem. Pharmacol.* 30 (1981) 3027.
117. Rechnagel, R. D., Glende, E. A. and Hruskawycz, A. M. In Pryor, W. A., Ed., *Free Radicals in Biology*, Academic, New York 1977, Vol. 3, p. 97.
118. Sakurai, H., Okada, A., Umino, H. and Kiro, M. *J. Am. Chem. Soc.* 95 (1973) 955; Russell, G. A., Malatesta, V., Morita, T., Osuch, C., Blankespoor, R. L., Trahanovsky, K. D. and Goettert, E. *J. Am. Chem. Soc.* 101 (1979) 2112.
119. *Selected Values of Chemical Thermodynamic Properties, Natl. Bur. Stand.*, Circular 500, Washington 1952.
120. Benson, S. W. *Thermochemical Kinetics*, 2nd Ed., Wiley, New York 1976.
121. Pedley, J. B. and Rylance, J. *Sussex - N. P. L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*, Univ., Sussex, England 1977.
122. Stull, D. R., Westrum, E. F. and Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York 1969.
123. Barner, H. E. and Scheuerman, R. V. *Handbook of Thermochemical Data for Compounds & Aqueous Species*, Wiley, New York 1978.
124. Nangia, P. S. and Benson, S. W. *J. Phys. Chem.* 83 (1979) 1138.

125. Fine, D. H. and Westmore, J. B *Can. J. Chem.* 48 (1970) 395.
126. Perdue, E. M. *Thesis*, Georgia Institute of Technology, August 1973 (Univ. Microfilms No. 74-7631).
127. Wadsö, I. *Acta Chem. Scand.* 14 (1960) 561.

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