

Bond Energies in Solution from Electrode Potentials and Thermochemical Cycles. A Simplified and General Approach¹

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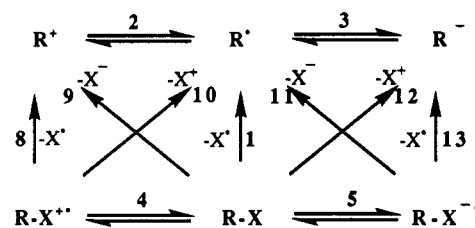
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A thorough understanding of reaction thermochemistry is essential in order to distinguish between mechanistic possibilities. In the gas phase, thermodynamic relationships between molecules, radicals, and their related ions are well understood in terms of familiar parameters (bond energies, ionization potentials, electron affinities). However, it is not always meaningful to apply properties derived in the gas phase to the vast majority of chemical reactions that are carried out in solution where differential solvation of reactants, intermediates, and products can be important. Thermochemical cycles incorporating electrode potentials provide a means of obtaining thermodynamic data for reactions in solution which are either difficult or impossible to obtain directly. This area of thermochemistry was stimulated by the seminal work of Breslow, who used thermochemical cycles to estimate relative pK_a values of weak carbon acids in aprotic solvents as well as pK_{R^+} values of alcohols.² More recently, significant contributions have been made by a number of groups. In particular, Arnold³ has devised three different thermochemical cycles to estimate the pK_a of radical cations, Bordwell⁴ has made estimates of a large number of C-H, O-H, and N-H bond dissociation energies as well as the pK_a 's of the radical cations, and Arnett⁵ has combined solution calorimetry and electrochemistry to estimate heterolytic and homolytic bond energies for a number of C-C, C-O, C-S, and C-N bonds. The purpose of this Account is not to provide a comprehensive review of this rapidly growing area but rather to demonstrate the utility of thermochemical cycles in organic and organometallic solution chemistry. We will show that all of the schemes and cycles that are used by others as well as by ourselves can, in fact, be combined into a simple, general approach. In addition, we will provide some practical information that will help those not experienced in the

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Scheme I. Thermochemical Mnemonic Describing All of the Homolytic and Heterolytic Cleavage Reactions of a Species R-X and of the Corresponding Radical Ions



area of electrochemistry to avoid many of the common pitfalls that can lead to erroneous estimates.

The relationships between the thermodynamic properties of ions and radicals derived from a molecule, R-X, can be represented conveniently in a thermochemical mnemonic which is completely defined by seven independent experimental measurements (Scheme I).⁶

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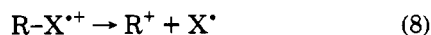
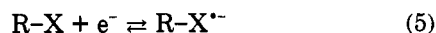
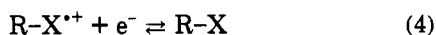
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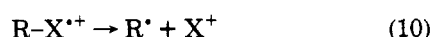
The thermochemistry for all of the possible homolytic and heterolytic cleavage reactions of RX and its corresponding ions (eqs 8–13) can be written simply as the sum of the homolytic bond dissociation energy (eq 1) with the difference between two potentials (eqs 2–7). These free energy relationships are given in eqs 8a–13a ($\Delta G^\circ = -F\Delta E^\circ$ with $F = 23.06 \text{ kcal mol}^{-1} \text{ eV}^{-1}$; the numbers appearing as subscripts refer to the corresponding equation number).



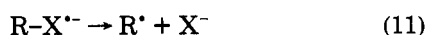
$$\Delta G^\circ_8 = \Delta G^\circ_1 + F(E^\circ_2 - E^\circ_4) \quad (8a)$$



$$\Delta G^\circ_9 = \Delta G^\circ_1 + F(E^\circ_2 - E^\circ_7) \quad (9a)$$



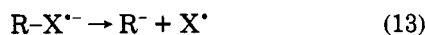
$$\Delta G^\circ_{10} = \Delta G^\circ_1 + F(E^\circ_6 - E^\circ_4) \quad (10a)$$



$$\Delta G^\circ_{11} = \Delta G^\circ_1 + F(E^\circ_5 - E^\circ_7) \quad (11a)$$



$$\Delta G^\circ_{12} = \Delta G^\circ_1 + F(E^\circ_6 - E^\circ_3) \quad (12a)$$



$$\Delta G^\circ_{13} = \Delta G^\circ_1 + F(E^\circ_5 - E^\circ_3) \quad (13a)$$

Although it is not in itself a thermochemical cycle (the oxidation state of the X fragment is not explicitly considered), the mnemonic in Scheme I is a useful device in that it clearly demonstrates the relationships between the properties of radicals and those of ions and radical ions. The bond dissociation energy of RX connects the thermochemistry of the molecule to that of the corresponding radical R[•] while electron transfer connects the thermochemistry of the neutral to that of the ionic species. This interconnectivity of thermochemical properties is not generally appreciated. Using an example where X = H, it is clear from Scheme I that a structural change that results in the weakening of the RH homolytic bond (eq 1) *must* also change the

reduction potential of R[•] (eq 3) and/or the pK_a (eq 12) of RH. Consequently, insights into the thermochemistry of ionic reactions can be obtained by studying the thermochemistry of radicals and vice versa even though these two areas of research are often perceived to be mutually exclusive.

Using Scheme I, the thermochemical data required to complete a thermochemical cycle can easily be visualized. For example, the estimation of the pK_a of a radical cation (eq 10, X = H) can be approached in one of two ways: by the combination of the pK_a of RH with the oxidation potential of RH (eq 4) and the oxidation potential of R[•] (eq 3), or by the combination of the homolytic bond energy of RH (eq 1), with the oxidation potential of RH and the oxidation potential of H[•] (eq 6). The first cycle is defined by the difference $\Delta G^\circ_{10} - \Delta G^\circ_{12}$ (eqs 10a–12a); the latter is defined explicitly by eq 10a. The choice of method, obviously, will depend on the availability of other thermodynamic data.

A similar approach for illustrating thermochemical cycles involving electrode reactions also has been used.⁸ Here, one or more reactions, usually bond dissociations, are written above a double line in such a way that the sum of these can be expressed as an electron-exchange reaction below the double line (see Schemes II–VI and VIII). This method can be applied to derive thermochemical cycles for all of the interconversions in Scheme I as well as any others involving electrode reactions.

Sources of Thermodynamic Data

From the point of view of this Account, the most commonly used thermodynamic data are electrochemical redox potentials, pK_a's, and bond dissociation energies, BDE (DH[•] is the symbol that is normally used in the gas-phase literature). Methodology for the determination of pK_a's is well established and beyond the scope of this paper.⁹ These values are solvent dependent so care must be taken to ensure that other thermochemical data apply to the same solvent system. Tables of BDEs in the gas phase are available from a number of sources.^{10,11} Since all of the energies in eqs 1–13 are free energies, an entropy correction must be applied to the BDE and the solvation of X[•] must be taken into account (the solvation energies of R–X and R[•] are often similar) when using these data in thermochemical cycles. The entropy correction is not always straightforward, and in most cases it is *preferable to determine relative values using the assumption that the entropy terms for similar cleavage reactions will cancel*. In the case of R–H cleavage reactions, most of the correction is associated with the gas-phase entropy and the solvation energy of the hydrogen atom since the entropies of R–H and R[•] are similar.¹³

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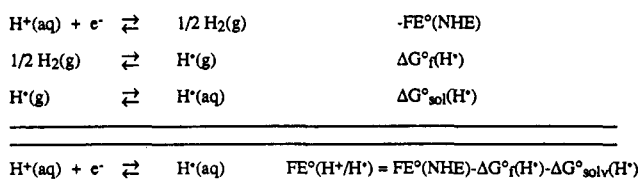
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Scheme II



Entropy and Solvation Energy Corrections for the Hydrogen Atom in Solution

In order to relate electrochemical potentials (eqs 2–5) to bond dissociation energies (eq 1) it is necessary that both be expressed either as free energy or enthalpy changes. In most cases it is more convenient to choose the former approach and to estimate ΔS° for eq 1. The entropy and solvation energy of the hydrogen atom in solution are of particular importance since thermochemical cycles are often used to determine ΔG° or ΔH° for the homolytic and heterolytic cleavage of R–H bonds. This, in effect, requires the determination or estimation of the entropy ($\Delta S^\circ_{\text{sol}}$) and enthalpy ($\Delta H^\circ_{\text{sol}}$) of solvation of H^\bullet . These values have been evaluated recently from a relationship between the van der Waals radii and the entropies and enthalpies of solvation of noble gases.¹⁴ From this analysis, it is found that the values of $\Delta G^\circ_{\text{f}}(\text{H}^\bullet)$, i.e., $\Delta G^\circ_{\text{f}}(\text{H}^\bullet)_{\text{g}} + \Delta G^\circ_{\text{sol}}(\text{H}^\bullet)$, for water, dimethyl sulfoxide, *N,N*-dimethylformamide, and acetonitrile are 52.8, 52.6, 52.0, and 51.8 kcal mol⁻¹, respectively (the gas-phase value is 48.58 kcal mol⁻¹).¹³

Standard Potential (E°) for the $\text{H}^+/\text{H}^\bullet$ and $\text{H}^\bullet/\text{H}^-$ Couples

The standard potential for the $\text{H}^+/\text{H}^\bullet$ couple in water is related to that of the normal hydrogen electrode (NHE) by the thermochemical cycle illustrated in Scheme II. The standard potential of the NHE is defined, by convention, to be 0.00 V, so $E^\circ(\text{H}^+/\text{H}^\bullet)$ is simply equal to the sum of $\Delta G^\circ_{\text{f}}(\text{H}^\bullet)_{\text{g}}$ and $\Delta G^\circ_{\text{sol}}(\text{H}^\bullet)$;¹⁴ in water, $E^\circ_{\text{NHE}(\text{aq})}(\text{H}^+/\text{H}^\bullet) = -2.29$ V vs NHE. Since the free energy changes for the transfer of the proton from water to other organic solvents, $\Delta G^\circ_{\text{tr}}(\text{H}^+)_{\text{sol}}$, are available,¹⁵ the standard potential of the $\text{H}^+/\text{H}^\bullet$ couple in other solvents also can be determined. These values are given in Table I. A similar scheme can be used to estimate E° for the $\text{H}^\bullet/\text{H}^-$ couple in various solvents (Table I).^{14c}

Reliability of Electrochemical Measurements

Reversible Electrode Potentials. The largest source of experimental error in the application of thermochemical cycles is often in the electrochemical measurements. The rigorous application of thermochemical cycles requires reversible electrode potentials (E_{rev}). These are thermodynamically significant quantities defined as the electrode potential at which equal concentrations of the reduced (red.) and oxidized (ox.) forms of the redox couple exist in equilibrium (eq 14). In order that the measurements actually reflect E_{rev} , it

Table I. Standard Potential of the $\text{H}^+/\text{H}^\bullet$ (E°_6) and the $\text{H}^\bullet/\text{H}^-$ (E°_7) Redox Couples in a Number of Solvents

solvent	E°_6 vs NHE ^a	E°_7 vs NHE ^b
water	-2.29	0.18
acetonitrile	-1.77	-0.60
dimethylformamide	-2.45	-0.60
dimethyl sulfoxide	-2.48	-0.55

^a Data from ref 14b. ^b $\Delta G^\circ_{\text{tr}}(\text{H}^\bullet)$ was estimated from the correlation of heats of hydration of halide ions with $\Delta G^\circ_{\text{tr}}(\text{X}^-)$; ref 14c.

is obvious that the equilibrium must be maintained. This implies that both red. and ox. must be long-lived and that the charge transfer must be rapid relative to the time scale of the measurement. The latter criterion is often referred to as “Nernstian” charge transfer.



The two criteria stated above for the measurement of E_{rev} may often appear to be incompatible; i.e., if it is necessary to use a very rapid technique (to ensure the existence of both red. and ox.), the charge transfer may not be Nernstian. As a result, a careful evaluation of electrode potentials obtained by voltammetric measurements is always necessary. In the following paragraphs the measurement of E_{rev} is discussed with reference to linear sweep voltammetry as the measurement tool since this is the most commonly used of the techniques. While the exact nature of the criteria for obtaining E_{rev} may differ, the conditions outlined above are common to all techniques.

Effect of Linear Sweep Voltammetry Kinetic Peak Shifts on Electrode Potential Measurements. Reversible electrode potentials, required for thermochemical cycles, are often inaccessible. Neglect of kinetic shifts of peak potentials obtained by linear sweep voltammetry (LSV) can give rise to significant errors in derived thermochemical quantities. For example, if the electrode-generated intermediate undergoes an irreversible first-order reaction (the EC mechanism, eqs 15–19) with a rate constant equal to 10^{10} s⁻¹, the peak potential measured at 298 K at a voltage scan rate (ν) of 0.1 V/s differs from the reversible peak potential by 287 mV. This corresponds to a 6.6 kcal mol⁻¹ error in any thermochemical quantity derived from the irreversible peak potential. Kinetic peak potential shifts ($\Delta E_{\text{p}} = E_{\text{p}}^{\text{obs}} - E_{\text{p}}^{\text{rev}}$) as a function of first-order rate constants for reaction 16, scan rate, and substrate concentration (C_A) may be calculated using eqs 17–19.^{8,16} Kinetic potential shifts for the related ECE mechanism are 9 mV greater than those for the EC mechanism.



$$\Delta E_{\text{p}}/(\text{mV}) = (E_{1/2} - E_{\text{p}})^{\text{rev}} - 780(RT/F) + (RT/2F) \ln[(RT/F)(k_{16}/\nu)] \quad (17)$$

$$\Delta E_{\text{p}}/(\text{mV}) = -38.4 + 12.85 \ln(k_{16}/\nu) \quad (\text{at } 298.15 \text{ K}) \quad (18)$$

$$\begin{aligned} dE_{\text{p}}/d \log \nu &= 29.6 \text{ mV/decade;} \\ dE_{\text{p}}/d \log C_A &= 0 \quad (\text{at } 298.15 \text{ K}) \quad (19) \end{aligned}$$

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Homogeneous chemical reactions following charge transfer which are second-order in the product of the electrode reaction give rise to the smaller ΔE_p . The second-order dimerization mechanism, EC(dim) (eqs 20–24), exemplifies second-order reactions. For example, with $C_A = 10^{-3}$ M and $\nu = 0.1$ V s⁻¹, a second-order rate constant of 10^{10} M⁻¹ s⁻¹ for reaction 21 gives rise to ΔE_p equal to 128 mV (3 kcal mol⁻¹) at 298.15 K. The EC(dim) mechanism is particularly relevant since this is the most common reaction pathway of free radicals formed upon oxidation or reduction of ions.



$$\Delta E_p / (\text{mV}) = (E_{1/2} - E_p)^{\text{rev}} - 902(RT/F) + (RT/3F) \ln [(2RT/3F)(k_{21}C_A/\nu)] \quad (22)$$

$$\Delta E_p / (\text{mV}) = -29.6 + 8.57 \ln (k_{21}C_A/\nu) \quad (\text{at } 298.15 \text{ K}) \quad (23)$$

$$dE_p/d \log \nu = 19.7 \text{ mV/decade}; \\ dE_p/d \log C_A = 19.7 \text{ mV/decade} \quad (\text{at } 298.15 \text{ K}) \quad (24)$$

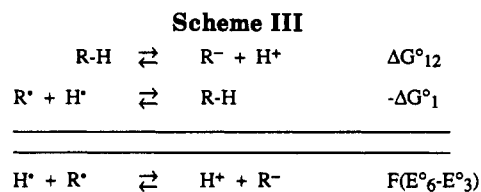
Two different strategies can be adopted to minimize the error due to ΔE_p . The first approach is to estimate the rate constant of the homogeneous follow-up reaction and make the appropriate correction, while the second is to increase the voltage scan rate in order to diminish the effect of the kinetic step on the peak potential. In principle, either method can provide the reversible peak potential required. However, the second approach requires an intimate understanding of electrochemical instrumentation and heterogeneous kinetics in order to account for the peak shifts associated with uncompensated cell resistance and quasi-reversible heterogeneous kinetics. The latter of these two effects can lead to significant errors at fast scan rates (>1000 V s⁻¹).

It is our opinion that, for the nonexpert, the most reliable method to minimize error due to ΔE_p is to carry out LSV studies at low ν and then apply a correction based upon a rate constant for the follow-up reaction which can be determined or estimated. In order to make this correction for ΔE_p it also is necessary to know the mechanism (or at least the reaction order in electrode-generated intermediate B). The importance of knowing the pertinent mechanism is obvious from comparing the peak potential data for the EC (eq 17) with that for the EC(dim) (eq 22) mechanism. However, distinguishing between first-order and second-order reactions of B is straightforward from the relationships in eqs 19 and 24.¹⁷

Standard Potentials for Transient Species. The determination of redox properties of radicals (eqs 2 and 3) is difficult because of their low steady-state concentrations. For cases in which it is possible to prepare stable solutions of the product ions, conventional cyclic voltammetry can be used, normally with

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the assumptions that the electrode mechanism is EC(dim) with a dimerization rate constant of ca. 10^{10} M⁻¹ s⁻¹ and that the measurements made in extremely acidic or basic media can be applied to reactions in neutral media. The development of the photomodulation voltammetry technique has allowed direct voltammetric detection of transient radicals that cannot be determined by other voltammetric techniques under mild, neutral conditions.^{6,18} In this experiment, radicals are generated by photolysis of suitable substrates with the light intensity varying sinusoidally in time. This causes the concentration of the radicals to vary at the same frequency as the modulated light intensity and produces a small alternating current that is easily detected using a lock-in amplifier. From simulation it is found that the oxidation wave shifts anodically by 20 mV for each decade increase in the rate of dimerization of the radical and cathodically by 35 mV for each decade increase in the rate of reaction of the product ion. The opposite is true for reduction waves.¹⁹

Bond Dissociation Free Energies (BDFE)

The combination of $pK_a(\text{R-H})$ and $E^\circ(\text{R}^-/\text{R}^\bullet)$ leads to an estimate of the homolytic bond dissociation free energy (BDFE), $\Delta G^\circ_1(\text{R-H})$ (eq 8, Scheme III).⁴ It has been assumed, generally, that differences in ΔG°_1 in solution will be the same as the differences in the gas-phase BDEs (i.e., the enthalpy of homolysis). The gas-phase BDE is related to ΔG°_1 by eq 25, which reduces to eq 26 if it is assumed that the energies and entropies of formation of R-H and R[•] cancel. For water, acetonitrile, and dimethyl sulfoxide the sums of the last two terms in eq 26 are equal to 3.9, 4.8, and 4.1 kcal mol⁻¹, respectively. Thus, the BDEs are expected to exceed ΔG°_1 by 4–5 kcal mol⁻¹. We have emphasized that it is preferable to determine ΔG°_1 values in solution in order to avoid the approximations necessary to reduce eq 25 to eq 26.¹⁴

$$\text{BDE}(\text{R-H})_g = \Delta G^\circ_1 - \Delta G^\circ_{\text{sol}}(\text{H}^\bullet) + TS^\circ_f(\text{H})_g - \Delta \Delta G^\circ_{\text{sol}}(\text{R}^\bullet\text{-RH}) + TS^\circ_f(\text{R}^\bullet\text{-RH}) \quad (25)$$

$$\text{BDE}(\text{R-H})_g \approx \Delta G^\circ_1 - \Delta G^\circ_{\text{sol}}(\text{H}^\bullet) + TS^\circ_f(\text{H})_g \quad (26)$$

Thermochemistry of Organic Species

Neutral Molecules. In cases where the pertinent BDFEs and E° values are known or can be estimated,

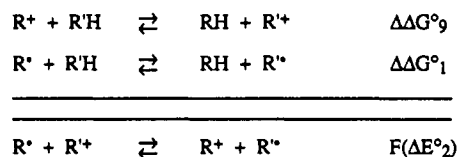
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Table II. pK_a and pK_H Values of Some Aromatic Hydrocarbons in Acetonitrile

R-H	E°_2 ^a	E°_3 ^a	ΔG°_1 ^b	pK_a ^c	pK_H ^d	ΔpK_R ^e
9H-fluorene	0.76	-0.76	75.0	37.7	77.6	-3.9
PhCH ₃	0.73	-1.45	84.0	55.9	83.7	-10.0
1-methylnaphthalene	0.47	-1.27	80.1	50.1	76.5	-2.8
PhCH ₂ CH ₃	0.37	-1.60	80.4	55.8	75.0	-1.7
Ph ₂ CH ₂	0.35	-1.14	79.0	47.1	73.7	0.0
1,1-dimethyl-1,4-cyclohexadiene	0.30	-1.70	68.0	48.5	64.8	8.9
Ph ₂ CHCH ₃	0.23	-1.34	76.0	48.2	69.4	4.2
9,9-dimethyl-9,10-dihydroanthracene	0.20	-1.36	72.0	45.7	66.0	7.6
PhCH(CH ₃) ₂	0.16	-1.73	79.4	57.3	70.7	2.9

^a Volts vs SCE measured by photomodulation, ref 18e (E° for ferrocene/ferrocenium was 0.387 V). ^b Evaluated using eq 26 with $\Delta G^{\circ}_{sol}(H^{\circ}) - TS^{\circ}(H^{\circ}) = -4.8 \text{ kcal mol}^{-1}$. ^c $pK_a = \Delta G^{\circ}_{12}/2.303RT$. ^d $pK_H = \Delta G^{\circ}_9/2.303RT$. ^e Based on pK_R of diphenylmethanol = -13.3 (Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* 1983, 105, 2889-2895).

Scheme IV



Scheme III can be used to estimate pK_a values for weakly acidic C-H bonds that cannot be determined by equilibrium studies.^{18b,e} The pK_a values for a number of carbon acids in acetonitrile are given in Table II along with the relevant E° and ΔG°_1 values. There is a relatively constant difference of about 11 pK_a units between values estimated in acetonitrile and those determined in DMSO (fluorene, 22.6; diphenylmethane, 32.2; toluene, 43⁹). This difference is about the same as the free energy of transfer of the proton between the two solvents. The implication is that the carbanion solvation free energies do not vary significantly between these two solvents.

The electrochemical oxidation potentials of the radicals can be used to determine hydride-transfer equilibrium constants, pK_H , using eq 9 (Table II). While these values are in themselves somewhat esoteric; if it is assumed that the free energy change for the conversion of RH to an alcohol, ROH, is essentially constant, then the ΔpK_H values represent more familiar ΔpK_R values.^{18e,g} In cases where the comparison is possible, the ΔpK_R values in Table II are within 1 pK unit of those determined in sulfuric acid.

Conversely, eq 9 can be used to estimate ΔG°_1 when the hydride-transfer equilibrium constants are known. We have used this approach to determine relative BDFEs ($\Delta\Delta G^{\circ}_1$) in a number of NADH model compounds (Scheme IV) using $\Delta\Delta G^{\circ}_9$ values for some substituted *N*-alkyl-1,4-dihydropyridines and *N*-alkyl-1,4-dihydroquinones versus that for 10-methylacridan.²⁰ The data in Table III show that the variation of the ΔG°_1 with structure is small and that the differences in the hydride affinities can be attributed to the variation in E°_2 .

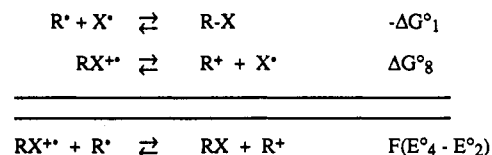
Ions and Radical Ions. The one-electron oxidation or reduction of a molecule can have a profound effect on the strength of σ bonds. This phenomenon is well-known in the gas phase, where the removal of an electron from a molecule results in a characteristic mass spectrometric fragmentation pattern. Recent work by Arnold²¹ [thermochemical cycles, eq 9, Scheme V] and Maslak^{7,22} (direct measurement using ESR) has pro-

Table III. Thermochemical Data for Some NADH Model Compounds^a

compound	E°_2 , V vs SCE	$\Delta\Delta G^{\circ}_9$, kcal mol ⁻¹	$\Delta\Delta G^{\circ}_1$, ^b kcal mol ⁻¹
<i>N</i> -methylacridan	-0.41	0 ^c	0 ^c
3-cyano- <i>N</i> -methylquinoline	-0.53	-0.2	2.7 ± 1.2
3-cyano- <i>N</i> -benzylquinoline	-0.49	1.72	3.5 ± 1.3
3-cyano- <i>N</i> -benzyl-1,4-dihydropyridine	-0.82	-6.61	3.0 ± 1.1
3-acetyl- <i>N</i> -benzyl-1,4-dihydropyridine	-0.97	-9.80	3.1 ± 1.2
<i>N</i> -benzyl-1,4-dihydropyridine	-1.08	-11.2	4.3 ± 1.5

^a In acetonitrile/0.1 M tetrabutylammonium perchlorate. Data from ref 20. ^b $\Delta\Delta G^{\circ}_1 \approx \Delta BDE(C-H)$. ^c Reference compound.

Scheme V



vided BDFE values of radical cations (ΔG°_8) in solution. Photomodulation voltammetry^{18,19} has provided some of the electrochemical data that are necessary to determine a large number of other radical cation bond energies that pertain to acetonitrile solution using eq 8 (Scheme V). While the thermochemistry in the gas phase is well understood, it is not obvious that even the trends will be the same in solution, where differential solvation of the reactants or products may be important. Some of the electrochemical and bond energy data for radical cations are given in Table IV. The last column represents the change in the BDFE in the radical cation ($RX^{+\cdot}$, ΔG°_8) compared to the neutral species (RX , ΔG°_1). Whenever possible, the solution data have been compared to BDE data in the gas phase (values in parentheses in Table IV).

In general it is found that there is reasonably good correspondence between the gas-phase BDE and solution BDFE differences, implying that the solvation energies of the radical cation and cation are similar, presumably because the extent of charge localization in the radical cation (reactant) and cation (product) are about the same. The fragmentation of $PhCH_2CH_2OCH_3^{+\cdot}$ is particularly interesting in this regard.²³ The energetics for the fragmentation to give

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(22) Maslak, P.; Asel, S. L. *J. Am. Chem. Soc.* 1988, 110, 8260-8261.

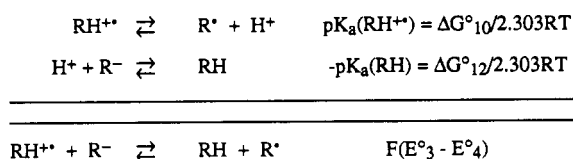
(20) Klippenstein, J.; Arya, P.; Wayner, D. D. M. *J. Org. Chem.* 1991, 56, 6736-6737.

Table IV. Oxidation Potentials (vs SCE) of Radicals and Bond Energy Differences for Molecules and Radical Ions in Acetonitrile/0.1 M Tetrabutylammonium Perchlorate

R	X	$E^\circ(\text{R}^+/\text{R}^\bullet)$, V vs SCE ^a	$E^\circ(\text{R-X}^{++}/\text{RX})$, V vs SCE ^a	$\Delta G^\circ_8 - \Delta G^\circ_{11}$, kcal mol ⁻¹ ^b
PhCH ₂	H	0.73	2.4	-38 (-37)
PhCH ₂	CH ₃	0.73	2.4	-38 (-36)
PhCH ₂	PhCH ₂	0.73	2.4	-38 (-41)
Ph ₂ CH	Ph ₂ CH	0.35	2.04	-37
1-NapCH ₂	1-NapCH ₂	0.47	1.59	-26
Me ₂ NCH ₂	H	-1.03	1.15	-50 (-49)
Me ₂ NCH ₂	Me ₂ NCH ₂	-1.03	0.70	-40 (-36)
PhCH ₂	Me ₂ NCH ₂	0.73	1.15	-10 (-11)
CH ₃ OCH ₂	PhCH ₂	-0.24	2.45	-62 (-43)
PhCH ₂	CH ₃ OCH ₂	0.73	2.45	-40 (-37)

^a Measured by photomodulation voltammetry, ref 18e. ^b $\Delta G^\circ_8 - \Delta G^\circ_{11} = -F[E^\circ(\text{R-X}^{++}/\text{RX}) - E^\circ(\text{R}^+/\text{R}^\bullet)]$. Values in parentheses are those calculated for the gas phase (Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* 1988, 17).

Scheme VI



the benzyl cation are the same both in acetonitrile and in the gas phase. However, the fragmentation to give $\text{CH}_3\text{OCH}_2^+$ is much more favorable in acetonitrile than in the gas phase. This is an example where *preferential solvation of one of the product ions provides an additional driving force* that determines the chemoselectivity of the reaction. In this case, the smaller and less delocalized methoxymethyl cation has a solvation energy that is about 15 kcal mol⁻¹ more exoergic than that of the benzyl cation.^{18h}

Reduction of a molecule also can have a profound effect on the σ BDFE(R-X). Maslak demonstrated that the BDFEs of substituted diarylethane radical anions are about 50% less than those of the neutral precursors^{7,24,25} and showed that the BDFEs estimated by eq 11 agreed with those values that were measured experimentally. The cycle described by eq 11 also has been used to address the important issue of BDFE(R-X) values of aromatic halide radical anions.²⁶ In the latter study the BDFE of $\text{PhF}^{\bullet-}$, $\text{PhCl}^{\bullet-}$, and $\text{PhBr}^{\bullet-}$ were estimated to be -10, -18, and -17 kcal mol⁻¹, respectively, in acetonitrile. The negative BDFEs simply mean that the radical anion is unstable with respect to the phenyl radical/halide ion pair, thus providing the driving force for the rapid fragmentation of these species.

pK_a 's of Radicals and Radical Cations. The pK_a 's of radical cations have been estimated by Nicholas and Arnold using eq 12³ and by Bordwell and his co-workers⁴ using an equation which can be derived from Scheme VI. The acidities of carbonium ions and the basicities of radical anions (i.e., the acidity of radicals) also can be derived from Scheme I.⁶ The mnemonic can be

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Scheme VII

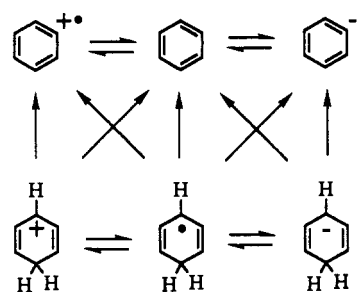


Table V. Acidities of Carbonium Ions and Radicals (Radical Anion Basicities) Based on Scheme VII

radical	$E^\circ_{3^a}$	$E^\circ_{4^b}$	$\Delta G^\circ_{11^c}$	$pK_a(\text{R}^+)^{c,d}$	$pK_a(\text{R}^\bullet)^e$
cyclohexadienyl	-3.4	0.30	20.5	-19.9	42.4
1,4-dihydronaphthalen-1-yl	-2.50	0.30	26.0	-15.5	31.3
9,10-dihydroanthracen-9-yl	-1.98	0.2	38.0	-5.4	31.3

^a Data from the following: Ebersson, L. *Electron Transfer in Organic Chemistry*; Springer-Verlag: Berlin, 1987. ^b Data from ref 18f. ^c Evaluated using eq 26 with $\Delta G^\circ_{\text{sol}}(\text{H}^\bullet) - \text{TS}^\circ(\text{H}^\bullet) = -4.8$ kcal mol⁻¹. ^d $pK_a = \Delta G^\circ_{10}/2.303RT$. ^e $pK_a = \Delta G^\circ_{12}/2.303RT$.

extended so that the species R-X is not necessarily a closed-shell neutral molecule. An example using cyclohexadienyl as RX is shown in Scheme VII. Data for the acidity of some arenium ions (protonated aromatics) and the acidity of the corresponding radicals are given in Table V. A similar approach has been used to estimate the thermochemical properties of dications and dianions in solution.^{27,28}

Thermochemistry of Organometallic Species

Application of Thermochemical Cycles To Estimate Metal-H BDEs and BDFEs. A few years ago it was pointed out that thermochemical data for the homolytic M-H bond dissociation energies of organo-transition-metal hydrides are scarce and that those available were derived from M-M bond dissociation energy estimates which vary over wide ranges.²⁹ A thermochemical cycle based on Scheme V was used to derive eq 27, which was applied to estimate gas-phase BDEs of a variety of carbon-hydrogen^{4e} and metal-hydrogen²⁹ bonds. The BDE estimated using eq 27 for a variety of M-H are summarized in Table VI. The M-H BDE of one of these compounds [M = C₅H₅Cr(CO)₃] was later determined by a direct calorimetric method.³⁰ A very close correspondence of BDE determined by the two methods was observed: 61.5 kcal mol⁻¹ by calorimetry and 62 kcal mol⁻¹ by the thermochemical cycle (eq 27).

$$\text{BDE} = 1.37 pK_a(\text{M-H}) + 23.06 E_{\text{NHE(AN)}}(\text{M}^+/\text{M}^\bullet) + 58.3 \text{ kcal mol}^{-1} \quad (27)$$

Having access to an experimental BDE for M₁-H suggested the use of the isodesmic reaction relationship illustrated in Scheme VIII to determine that value for any other compound, M₂-H.⁸ Data obtained from this relationship using H-Cr(CO)₃(C₅H₅) as M₁-H are

(27) Parker, V. D.; Tilset, M.; Hammerich, O. *J. Am. Chem. Soc.* **1987**, *109*, 7905.

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(29) (a) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2843.

(b) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711.

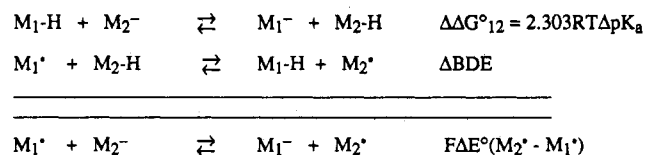
(30) Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Roper, G. C. *J. Am. Chem. Soc.* **1990**, *112*, 5657.

Table VI. Bond Dissociation Energies and Bond Dissociation Free Energies of Organometallic Species Derived from Thermochemical Cycles (kcal mol⁻¹)

compound (M-H)	BDE(M-H) ^a	BDE(M-H) ^b	ΔG°_1 (M-H) ^c	pK_a (M-H) ^d	pK_a (M-H ^{•+}) ^e
(η^5 -C ₅ H ₅)Cr(CO) ₃ -H	62	61.5	55.1	13.3	-9.5
(η^5 -C ₅ H ₅)Mo(CO) ₃ -H	70	69.2	62.9	13.9	-6.0
(η^5 -C ₅ H ₅)W(CO) ₃ -H	73	72.3	66.0	16.1	-3.3
(η^5 -C ₅ Me ₅)Mo(CO) ₃ -H	69	68.6	62.8	17.1	-2.5
(η^5 -C ₅ H ₅)W(CO) ₂ PMe ₃ -H	70	69.6	63.3	26.6	5.1
Mn(CO) ₅ -H	68	68.0	61.7	14.1	
Mn(CO) ₄ PPh ₃ -H	69	68.4	62.1	20.4	
Re(CO) ₅ -H	75	74.7	68.4	21.1	
(η^5 -C ₅ H ₅)Fe(CO) ₂ -H	58	57.1	50.8	19.4	
(η^5 -C ₅ H ₅)Ru(CO) ₂ -H	65	64.9	58.7	20.2	
Fe(CO) ₄ H-H	68	67.6	61.4	11.4	
Co(CO) ₄ -H	67	66.4	60.2	8.3	
Co(CO) ₃ P(OPh) ₃ -H	66	65.2	58.9	11.3	
Co(CO) ₃ PPh ₃ -H	65	65.0	58.7	15.4	

^a Calculated from eq 27 (ref 29). ^b Calculated from Scheme VIII with (η^5 -C₅H₅)Cr(CO)₃-H as the standard (BDE = 61.5 kcal mol⁻¹ ref 8). ^c Calculated from eq 28. ^d Data from the following: Jordan, F.; Norton, J. R. *J. Am. Chem. Soc.* 1982, 104, 1255. Kristjansdottir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* 1988, 7, 1983. Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* 1986, 108, 2257. ^e Calculated using eq 10a, ref 31.

Scheme VIII



summarized in the second data column of Table VI. The thermochemical cycle in Scheme VIII implicitly assumes that ΔBDE in the second line is equal to $\Delta G^\circ_1(M_2\text{-H}) - \Delta G^\circ_1(M_1\text{-H})$ in solution. This is probably a good approximation in this case since a cancellation or error is expected when one term is subtracted from the other.

Since $E^\circ_{\text{NHE(aq)}}(\text{H}^+/\text{H}^\bullet)_{\text{AN}}$ in acetonitrile is available (Table I), it is possible to make a direct comparison of BDE(M-H) with the corresponding $\Delta G^\circ_1(\text{M-H})_{\text{AN}}$ estimated with a thermochemical cycle comparable to that in Scheme III. These data can be calculated using eq 28 and appear in the third column of Table VI. The BDE(M-H) values in Table VI exceed $\Delta G^\circ_1(\text{M-H})_{\text{AN}}$ by 6.3–6.4 kcal mol⁻¹. This implies that the contribution of the terms following ΔG°_1 in eq 25 is equal to about 2 kcal/mol in acetonitrile for these organometallic species. The last two of these terms are commonly neglected in estimating BDE using thermochemical cycles.³¹

$$\Delta G^\circ_1(\text{M-H})_{\text{AN}} = 1.37 pK_a(\text{M-H})_{\text{AN}} + 23.06[E^\circ(\text{M}^+/\text{M}^\bullet) - E^\circ(\text{H}^+/\text{H}^\bullet)] \quad (28)$$

The pK_a 's of the metal hydride radical cations also could be estimated from Scheme V.³² It was found that the removal of an electron from M-H results in about a 20-unit decrease in the pK_a (Table VI). In a similar study, Tilset has estimated ΔG°_8 for a number of Cr-H complexes.³³ In this case it was found that the $\Delta G^\circ_1 - \Delta G^\circ_8$ was only ca. 10 kcal mol⁻¹, and it was concluded

(31) It is interesting to note that (BDE - ΔG°_1) is predicted (eq 26) to be 4.8 and 4.1 kcal mol⁻¹ in acetonitrile and dimethyl sulfoxide, respectively. The average values observed in the two solvents^{14b,d} were 6.3 and 4.1 kcal mol⁻¹, respectively. This strongly supports the usual assumption that the neglect of the last two terms in eq 25 does not lead to serious errors.

(32) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* 1990, 112, 2618.

(33) Tilset, M. *J. Am. Chem. Soc.* 1992, 114, 2740.

that, upon loss of an electron, M-H bonds are activated by approximately 3 times more toward heterolytic than homolytic cleavage. Both of these results are in sharp contrast to data for organic radical cations. For example, in the case of toluene, oxidation to the radical cation decreases the pK_a by 60 units (i.e., $\Delta G^\circ_{12} - \Delta G^\circ_{10} = 85$ kcal mol⁻¹) and decreases the BDFE (i.e., $\Delta G^\circ_1 - \Delta G^\circ_8$) by 40 kcal mol⁻¹.⁶ The implication of this observation is that there is a much smaller contribution of the M-H bond to the SOMO of the organometallic radical cations than there is of the R-H bond to the SOMO of the hydrocarbon radical cations.

Concluding Remarks

In this Account we have illustrated the intimate relationships between the energetics of heterolytic and homolytic bond dissociation of molecules (R-X) and their corresponding radical ions (R-X^{•+} and R-X^{•-} as well as the doubly charged ions) and the redox potentials of the derived radicals and their corresponding ions. These relationships can be expressed by the handy mnemonic illustrated in Scheme I from which a number of thermochemical cycles are readily derived for the energetics of the various processes in solution. For processes which involve breaking R-X bonds, the free energy relationships described by eqs 8–13, or related equations derived by combinations of these, are quite general and can be used to estimate the free energy changes of all of the reactions in Scheme I. The mnemonic, while not itself a thermochemical cycle, serves as a simple aid to visualize other thermochemical data needed to complete a given cycle.

Thermochemical cycles involving electrode reactions can readily and conveniently be expressed by another simple and general method. One or more reactions, usually bond dissociations, are written above a double line in such a way that the sum of these can be expressed as an electron-exchange reaction below the double line (see Schemes II–VI and VIII). The sum of the free energy changes for the reactions above and below the double line can then be equated.

The key to the recent and widespread use of the thermochemical cycles described in this Account is the availability of excellent commercial electrochemical instrumentation, thus allowing the redox potentials of

many ionic and free radical intermediates to be determined readily. These electrochemical data, however, may also represent the greatest source of error in derived thermochemical quantities, and care must be taken to ensure that the measured potentials reflect reversible potentials for the redox reactions.

The cycles also provide a means to estimate redox potentials which are not readily measured. Recently evaluated potentials for the (H^+/H^\bullet) and (H^\bullet/H^-) redox couples in a number of common solvents allow for the application of simple thermodynamic cycles involving heterolytic and homolytic cleavage of X-H bonds. The importance of solvation of H^\bullet is highlighted in this regard. The free energy of formation of H^\bullet is significantly greater in solution than in the gas phase. While this has no effect on derived relative bond energies in solution versus the gas phase, the absolute bond energies in these media will vary.

Applications of redox potentials in thermochemical cycles to estimate experimentally inaccessible ther-

modynamic data have been made in only a few areas of chemistry. A wide variety of heterolytic and homolytic bond dissociation energies of relevance to physical organic chemistry, inorganic chemistry, organometallic chemistry, and biochemistry are potentially available by the methods discussed in this Account. Of particular importance is the need to address the dearth of bond energy data for organometallic species that are relevant to homogeneous catalysis and enzyme-catalyzed processes (e.g., cytochrome P-450, vitamin B-12). Future applications of thermochemical cycles are expected to make significant contributions to these areas.

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