Thermodynamics for C–H bond-breaking of some amphihydric compounds by transfer of protons, hydride ions, H-atoms and electrons

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Abstract: Carbenium ions, radicals, and carbanions can be generated by transfer of a hydride ion, hydrogen atom or proton from a R-H bond to an appropriate Lewis acid, radical or base. When all three of these reactive species are stable enough to be generated in solution a compound is referred to as "amphihydric" (e.g., triphenylmethane). Energetics for R-H cleavage in these ways are the most generally useful criteria for the stabilities of R^+, $R^•$, and R^-. In addition, their stabilities relative to each other can be established by electron transfer if redox potentials are reversible.

Stabilities of R^+, $R^•$ and R^- for several series of amphihydric compounds (e.g., 9-arylxanthenes, 2-aryl-1,3 dithianes) are reported as determined by the four methods referred to above. Relationships between these normally unrelated properties will be discussed.

Carbenium ions, (R^+), radicals, $(R^•)$, and carbanions, (R^-), are generally encountered under such drastically different conditions that it is unusual for them to be discussed in a single symposium. I am very pleased to participate in one where they are all treated together. This paper will discuss the stabilities of these primary types of reactive intermediates in terms of two apparently different, but fundamentally related types of criteria.
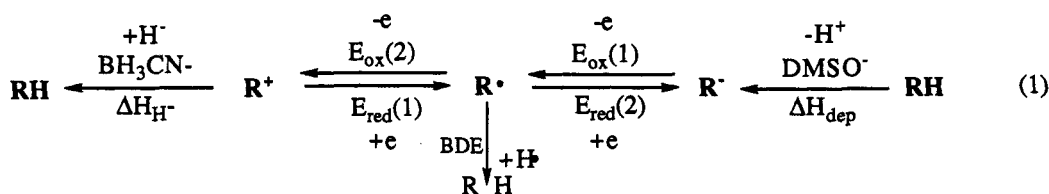
Bond Cleavage - The stabilities of these three species, and the transition states that are close to them in structure and energy, are usually referred to appropriate bond-making/breaking (heterolytic or homolytic) processes in solution with a variety of leaving groups, for example; proton transfer to a standard base (e.g. K^+DMSYL^- in DMSO), loss of water from $Ar_3COH_2^+$ in aqueous acid solution, ionization of RX, or hydrogen atom transfer from RH under many conditions. In the gas phase (1) hydrogen transfer to or from RH is involved in all three primary stability criteria--proton affinity, hydride affinity, and the bond dissociation energy (BDE). Since the majority of chemical processes take place in solution, the ionization constants, pK_{HA} and pK_R^+, have been the preferred properties for comparing the operational stabilities of R^- in DMSO (2) and R^+ (3) in aqueous acid respectively. Recent estimations of BDE's from $pK_{HA}s$ and the oxidation potentials of R^- in DMSO (4) show that the experimental gas phase values can be reproduced within ±2 kcal/mol (henceforth kcal). Correspondingly, many good correlations have been found between gas phase and solution values for processes which generate R^+ and R^- despite the importance of differential solvation energies (5).

Oxidation-Reduction Processes - A different approach to relating the stabilities of R^+, R^- and $R^•$ is in terms of their affinities for electrons rather than through their affinities for other atoms in a bond. In the gas phase this is usually expressed by electron affinities or oxidation potentials. In solution, electrochemistry provides the key to relating these three primary species as "different oxidation states of trivalent carbon" (6).

Free radical chemistry owes its discovery to Gomberg's attempt to prepare hexaphenylethane by coupling of the trityl cation through reduction (7) and several reversible cells have been constructed where stable R^+s (8) or R^-s (9) are in equilibrium with their conjugate radicals and coupling products. However, modern cyclic voltammetric techniques are required to "outrun" the coupling of highly reactive radicals by cycling through the redox stages so rapidly that reversible electrode potentials can be obtained (or approached) which represent the free energy differences between highly reactive R^+, $R^•$, and R^-, when multiplied by 23.06 kcal/Volt and referred to an appropriate standard state. These electrochemical methods provide the key to a fundamental understanding of the stabilities of the three conjugate species *relative to each other* without complications from leaving groups or other variable conditions. They also help to illuminate what lies behind the more familiar bond cleavage criteria for relating their thermodynamic stabilities to neutral precursors RH, RX or ROH.

Physical organic chemists are indebted to Breslow for introducing them to the power of electrochemistry in combination with thermodynamic cycles as a means for estimating pK_{HA}s of very weak RH acids from the pK_R^+s of the corresponding ROHs or vice versa (6). His pioneering studies are still bearing fruit in Bordwell's use of oxidation potentials, E_{ox}s, of R^-s to derive BDEs from pK_{HA}s of RHs (4), Parker's use of reduction potentials, E_{red}s, of R^-s to derive hydride (10) and halide (5c) affinities in solution, and the results to be described below from our laboratory. What then are the relationships between electrochemical criteria for stability and those based on bond/making and breaking?

Amphihydric Compounds - To deal directly with this question we draw attention to several classes of RH compounds whose R^+s and R^-s are stable enough to be studied by bond cleavage/formation in some of the solvents which also can be used for intercoverting them and their conjugate $R^{\bullet}$ by cyclic voltammetric techniques. We have called such compounds *amphihydric* (11) because they are capable of producing all three of the primary oxidation states of carbon by loss of hydride ions, hydrogen atoms, or protons from the same RH bond. Clearly this term should not be confused with the familiar one *amphiprotic* which refers to compounds that can function both as Brönsted bases and Brönsted acids. Almost all organic compounds are amphiprotic if exposed to strong enough Brönsted acids and bases, but relatively few are amphihydric. The study of amphihydric compounds is clearly contingent upon finding solvents which are weak enough Lewis bases to resist attack by R^+ and are also too weakly acidic to be deprotonated by R^-. After considerable experimentation we have settled on sulfolane (tetramethylene sulfone) as the solvent of choice for reaction calorimetry and electrochemistry of resonance-stabilized R^+ and R^- (12). We assume that for most purposes relevant to these studies sulfolane is interchangeable with DMSO although the former is a slightly weaker Lewis base towards R^+ but is a slightly stronger Brönsted acid (11). The fundamental bond making/breaking and electron-transfer processes discussed in this paper are shown below.

$$RH \xleftarrow[\Delta H_{H^-}]{\substack{+H^- \\ BH_3CN^-}} R^+ \underset{E_{red}(1)}{\overset{\substack{-e \\ E_{ox}(2)}}{\rightleftarrows}} R^{\bullet} \underset{E_{red}(2)}{\overset{\substack{-e \\ E_{ox}(1)}}{\rightleftarrows}} R^- \xleftarrow[\Delta H_{dep}]{\substack{-H^+ \\ DMSO^-}} RH \qquad (1)$$

Substituted triphenylmethanes are the most familiar series of amphihydric compounds since they can be deprotonated to stable R^- in DMSO and many of their conjugate R^+ can be handled in this solvent which is also convenient for their electrochemical study. Much of Breslow's original work used DMSO, as has virtually all of the extensive research by Bordwell's group on the pK_{HA}s of hundreds of C, O, N, S anions and their conjugate radicals, and many of the electrochemical studies by Parker, Wayner and Griller (13). The R^+ and R^- of many 9-substituted xanthenes (11) can also be generated and handled in sulfolane and DMSO as also can some six-membered ring 2-substituted 1,3-dithiolanes.(14) The corresponding R^+ from 1,3-dioxolanes and 1,3-oxythiolanes are stable but the parent neutrals are too weakly acidic to be rapidly and cleanly deprotonated to R^- by $DMSYL^-/DMSO$. In our hands the working range of amphihydric compounds in sulfolane is represented roughly by triphenylmethane; $pK_R^+ = -6.44$, $pK_{HA} = 31$. The majority of stable R^+ have RH too weakly acidic to give stable R^- by deprotonation in DMSO while the majority of R^- that are stable in DMSO have R^+ that are such strong Lewis acids that they cannot be handled in DMSO or sulfolane. It was the fact that electrochemistry can produce very unstable R^+ from stable R^- or unstable R^- from stable R^+ and thereby allow estimation of their otherwise inaccessible pKs that has motivated most of the physical organic chemistry in this area.

A recurrent problem which has raised doubts (4a,6,13b,c) about many such studies is the irreversibility of electrode processes. A special virtue of amphihydric compounds is the ability to approach the same redox potentials both by the two electron reduction of R^+ and the two electron oxidation of R^- in many cases in the series reported here this check can be applied and holds well. (see also ref 5d).

Calorimetric Heats of Deprotonation and Hydride Affinities in Solution - Reaction calorimetry has been the method of choice in our laboratory for measuring a wide variety of energy changes. For most purposes the equipment is inexpensive and techniques are learned easily. For reactions that are fast (complete in 5 min.) and clean, meaningful results are available almost immediately, often within an error of ±0.2 kcal which is adequate for combining or correlating with other properties of interest to physical organic chemistry without the laborious construction of ladders of equilibrium constants or acidity functions. Unlike free energy measurements, enthalpy changes are usually easily measured for systems far from equilibrium. Differential entropies of reaction are usually not a serious problem when

comparing free energy terms with the corresponding heats of reaction or other enthalpy changes. For present purposes, heats of deprotonation ($\Delta H_{dep}s$) obtained by injecting or titrating a DMSO solution of RH into a calorimeter vessel containing a solution of $K^+DMSYL^-/DMSO$, correlate with $R^2>0.99$ and unit slope against corresponding free energies of deprotonation ($1.37 \times pK_{HA}$) (15). In an analogous manner we have used reaction calorimetry to determine the heats of formation of RHs by reduction of stable R^+s i.e., the hydride affinity (ΔH_{H^-}) in sulfolane or other appropriate solvents. Calorimetric heats of formation of a wide range of R^+s in superacids at low temperatures have been reported (16) and correlated with gas phase ΔH_{H^-} and solvolysis rates (17). The new technique for measuring ΔH_{H^-} of stable R^+ in non-hydroxylic solvents used for electrochemistry removes the necessity for using pK_{R^+} values in aqueous acid as the criterion for their stabilities.

Although many R^+ may be produced from their RHs by H^- transfer to trityl cation, that reaction is too slow for good reaction calorimetry and is not a practical general means for relative free energies by equilibration. Instead we have settled on measuring hydride ion affinities of R^+ directly in sulfolane using their heats of reaction with sodium cyanoborohydride as the reducing agent, with crown ether to suppress any ion-pairing. Several correlations demonstrate its relation to other criteria for R^+ stabilities.

<u>Correlation of ΔH_{H^-} with Other Criteria of R^+ Stability</u> - Of particular relevance to heats of hydride transfer measurements in sulfolane is the elegant NMR study of Freedman et al. (18) who equilibrated about twenty resonance-stabilized cations with their neutral precursors in acetonitrile, a solvent which is also amenable to calorimetric heats of hydride transfer and electrochemistry of carbenium ions. An excellent correlation between data from their study and ours is demonstrated by equation 2.

$$\Delta G^{OMe} = 39.0 + 0.69 \times \Delta H_{H^-} \quad R^2 = 0.995, n = 5 \quad (2)$$

A less directly suitable comparison is with the pK_R^+s for trityl, xanthylium, 9-phenyl xanthylium and tropylium cations which correlate with $R^2 = 0.969$ and a slope of 1.148. Considering the difference in media (aqueous acid and sulfolane) and that free energies are compared with enthalpies the agreement seems to be reasonable.

Parker's group has derived free energy hydride affinities from the equation

$$\Delta G_{H^-} = 1.37\, pK_{HA} + 23.06\, E^0_{NHE}\left[\left(R^\cdot / R^-\right) + \left(R^+ / R^\cdot\right)\right] + Const \quad (3)$$

where the electrode processes correspond to $E_{ox}(1)$ and $E_{ox}(2)$ for the carbanion in Scheme 1. When compared with measured $\Delta H_{H^-}s$ the correlation equation

$$\Delta G_{H^-} = 34.7 - 1.18\, \Delta H_{H^-} \quad R^2 = 0.836.\ n = 5 \quad (4)$$

is obtained. For this correlation equation, and most of the others reported here, no significance should be attached to the intercepts because of differences in processes and standard states, it is the slopes and R^2s that count. Also, concern may be raised about using free energy terms ($pK_{HA}s$, E_{redox}) to obtain enthalpies such as BDEs (4), or mixing calorimetric ΔH terms with redox potentials. We have frequently tested the magnitude of redox entropies for systems discussed here and found them to be insignificant for this purpose. In view of the difference in medium and thermodynamic property referred to above we have revised Parker's free energy equation to use calorimetric $\Delta H_{dep}s$ and E_{ox} values from this laboratory in an equation of similar form. Correlation of the ΔH_{H^-} calculated in this way with the calorimetrically one gives:

$$\Delta H_{H^-}(calc) = 65.8 + 1.05\, \Delta H_{H^-}(measured)\ R^2 = 0.989, n = 5 \quad (5)$$

We are continuing these studies with other cations examined by Freedman and Parker which should provide a more extensive test of ΔH_{H^-} as a criterion for carbenium ion stability in nonhydroxylic media.

Somewhat surprisingly, ΔH_{H^-} for the reduction of six *p*-substituted 9-phenylxanthenium ions correlates much better with Hammett sigma constants ($R^2 = 0.981$) than with sigma$^+$ constants ($R^2 = 0.776$). We consider that this result taken at face value is consistent with evidence (19) that overlap between the 9-phenyl appendage and the well-delocalized xanthylium system is poor, not only because modest demand for electrons is made on the 9-phenyl system but because it is constrained from becoming planar with the xanthylium system.

<u>Correlations of Bond Cleavage with Electron Transfer</u> - Numerous authors have noted close correlations ($R^2 > 0.98$) between $pK_{HA}s$ for producing R·s and their first oxidation potentials, $E_{ox}(1)s$. Bordwell (4) has emphasized that the unit slopes of such plots, when converted into ΔG terms, imply that the observed substituent effects operate primarily on the anions while their influence on most radicals are very small. Departures from such correlation lines are a direct measure of radical stabilization energies (RSEs). This is thoroughly consistent with the widespread (and usually unstated) assumption that the effects of substituents on rates and equilibria of ionogenic process are entirely a reflection of the stabilities of the ions formed unless there is a special ground state effect such as strain which can be relieved by going to the ion or radical. In fact, the well-established value of Benson's method for calculating heats of formation and reactivity parameters by the method of group equivalents depends upon the insignificant effect of remote substituents on these properties for neutral molecules and radicals. Again, Breslow's successful use of redox potentials for estimating $pK_{HA}s$ and pK_R^+s of unstable R·s and R⁺s depends on substituent effects on ground states being negligible. Accordingly, substituent effects on BDE's are usually small compared to those on $pK_{HA}s$, $H_{dep}s$, pK_R^+s or H_H^-s.

In view of the close correlation between free energies for producing R⁻ by deprotonation of their neutral precursors, RH, and oxidation of their R⁻ to their radicals {since $E_{red}(1)=E_{ox}(2)$} one would expect to find excellent correlation between processes for making R⁺s by bond cleavage from a suitable neutral precursor versus $E_{red}(1)$ for reduction of R⁺ to the conjugate radical. Figure 1 demonstrates the close relationship between H_H^- for the reduction of a diverse group of R⁺s by hydride transfer from BH_3CN^- and their first reduction potentials. Parker's recent study of halide affinities of R⁺ (5c) reports close correlations with their reduction potentials.
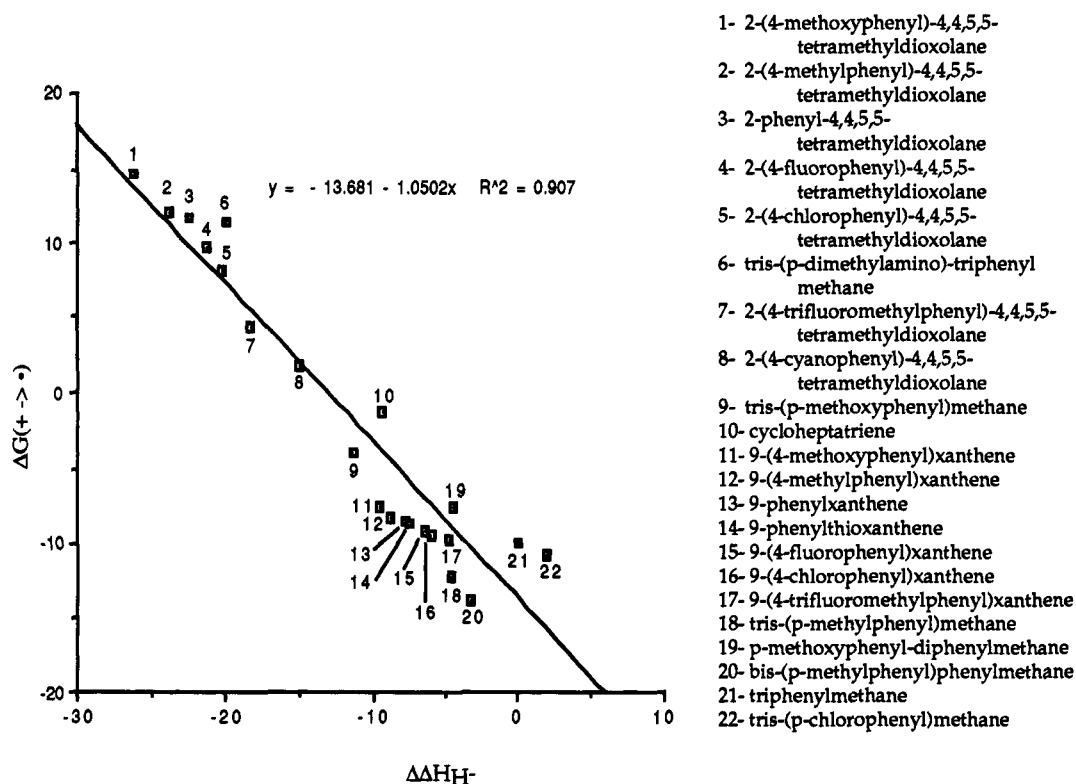

1- 2-(4-methoxyphenyl)-4,4,5,5-
      tetramethyldioxolane
2- 2-(4-methylphenyl)-4,4,5,5-
      tetramethyldioxolane
3- 2-phenyl-4,4,5,5-
      tetramethyldioxolane
4- 2-(4-fluorophenyl)-4,4,5,5-
      tetramethyldioxolane
5- 2-(4-chlorophenyl)-4,4,5,5-
      tetramethyldioxolane
6- tris-(p-dimethylamino)-triphenyl
      methane
7- 2-(4-trifluoromethylphenyl)-4,4,5,5-
      tetramethyldioxolane
8- 2-(4-cyanophenyl)-4,4,5,5-
      tetramethyldioxolane
9- tris-(p-methoxyphenyl)methane
10- cycloheptatriene
11- 9-(4-methoxyphenyl)xanthene
12- 9-(4-methylphenyl)xanthene
13- 9-phenylxanthene
14- 9-phenylthioxanthene
15- 9-(4-fluorophenyl)xanthene
16- 9-(4-chlorophenyl)xanthene
17- 9-(4-trifluoromethylphenyl)xanthene
18- tris-(p-methylphenyl)methane
19- p-methoxyphenyl-diphenylmethane
20- bis-(p-methylphenyl)phenylmethane
21- triphenylmethane
22- tris-(p-chlorophenyl)methane

Figure 1. Free Energies of Reduction for Various Carbenium Ions versus their Heats of Reduction Relative to Trityl tetrafluoborate ($\Delta H_H^- = 52.7$ kcal/mole) at 25°C, see Table 1.

The Fundamental Significance of Redox Potentials to Substitutent Effects - We have emphasized the close correlation between substituent effects on the bond making/breaking processes so important to chemical interconversions and those on the redox potentials of the R⁺s, R·s, and R⁻s which are the primary reactive intermediates in organic chemical reactions. We have measured many heats of reaction of various R⁺ with a variety of R⁻ and other anions to give directly the heats of heterolysis ($\Delta H_{het}s$) of the bonds formed. These $\Delta H_{het}s$ correlate closely with the pK_R^+ and pK_{HA} of the reacting species and are converted into the heats of homolysis $\Delta H_{homo}s$ by combination with their redox potentials (20).

It should now be clear that *the energies for heterolytic and homolytic bond-cleavage are totally dominated by the stabilities of* R^+, $R^·$ R^- *and for many purposes of comparing structural effects on the energies of these species the method of choice is electrochemistry rather than the more familiar rates or equilibrium constants.*

Since virtually all of the influence of substituents is on the R^+s and R^-s, how are they related? Table 1 provides a typical sample of redox potentials for R^+, $R^·$ and R^- derived from several amphihydric precursors which demonstrate the relative energies required to contribute one electron to a R^+ as compared to that for reducing the resulting $R^·$ with a second electron.

TABLE 1. Thermodynamic[a] and Electrochemical[d] Data (SHE) for Representatives of Seven Structural Types

Cation/ Radical/ Anion	$\Delta\Delta H_{H^-}$[b]	pK_{R^+}[g]	pK_{HA}[+e]	ΔH_{dep}[c]	BDE[h]	$\Delta G^{+\to·}$ kcal (V)	$\Delta G^{·\to-}$ kcal (V)	$\Delta G^{+\to-}$ kcal (v)	ΔG_{ET}[i]
[structure]	1.0	-10.5	17.9	-25.7	74	-13.6[i] (0.59)	11.3[i] (-0.491)	-2.3 (0.099)	-24.9 (1.07)
[structure]	0	-6.6	30.6	-9.4	81	-13.9 (0.604)	18.2 (-0.792)	4.4 (-0.188)	-32.2 (1.39)
[structure]	-7.62	1.1	27.9	-13.29	76.7	-8.57 (0.372)	17.8 (-0.773)	9.23 (-0.400)	-26.4 (1.14)
[structure]	-9.30	4.7	36	2.7	71.6	-0.9 (0.04)	32.5[i] (-1.41)	31.6 (-1.37)	-33.4 (1.45)
[structure]	-11.53	3.1	47[f]	11.1	85	8.9 (-0.386)	34.6 (-1.50)	41.5 (-1.799)	-25.7 (1.11)
[structure]	-12.59	-2.0[f]	30.7	-10.37	74.5	2.05 (-0.089)	22.0 (-0.956)	24.1 (-1.04)	-19.95 (0.87)
[structure]	-21.28	1.4	56[f]	22	85	11.7 (-0.509)	42.7 (-1.856)	54.5 (-2.36)	-30.9 (1.33)

a) Calorimetry was performed with a Tronac 450 titration calorimeter at 25C. b) ΔH_{H^-} values were determined by titrating a 0.1M sulfolane/ 5% 3-methylsulfolane solution of the cation-tetrafluoborate salt into a solution of sulfolane/ 5% 3-methylsulfolane which was 0.6 M in both 18-crown-6 and $NaBH_4CN$. Values reported are referenced to trityl tetrafluoborate ΔH_{H^-} = 52.7 kcal/mole. c) ΔH_{dep} were determined by titrating a 0.1M solution of the appropriate carbon acid in DMSO into a 0.1M solution of K^+DMSYL^- in DMSO. Positive values were obtained by extrapolation of data correlation's between ΔH_{dep} and pK_a. d) Electrochemistry was performed on a BAS-100 A Electrochemical Analyzer. $E_{1/2}$ values were determined using a Pt working electrode, silver auxiliary electrode, and an Ag/AgI reference electrode in DMSO with 0.1 M tetrabutylamonium tetrafluoborate as the electrolyte. The $E_{1/2}$ of Fc/Fc^+ relative to Ag/AgI was checked before each experiment and values recorded during that experiment were then referenced to Fc/Fc^+. The oxidation potentials measured in this way were referenced to the standard hydrogen electrode by adding 0.75V. e) pK_{Ha} values determined in DMSO; Bordwell, F.G. *Acc Chem Res*, **1988**, *21*, 456-463. f) pK_{Ha} values calculated as by Breslow, R.; Chu, W. *J. Am. Chem. Soc.*, **1973** *,95* ,411-418. g) Values obtained from Bethell, D.;Gold, V. <u>Carbonium Ions</u> Academic Press, New York, 1967. h) Calculated from BDE = 1.37(pKa) + 23.06($\Delta G^{·\to-}$) + 56; Bordwell, F.G.; Cheng,J.-P.; Satish, A.V.; Twyman, C.L. *J. Org. Chem.*, **1992**, *57*, 6542-6546. i) $\Delta G_{ET} = (\Delta G^{+\to·}) - (\Delta G^{·\to-})$. i) Value reported by Cheng,J.-P.; Handoo, K. L.; Parker, V.D. *J. Am. Chem. Soc.* **1993**,*115*,2655-2660.

Not surprisingly, the energy for adding the first electron into the open orbital of the R^+ is considerably less than that for forcing the second electron into the half filled orbital of $R^·$ to make R^-. The free energy difference between these processes is the electron transfer energy, ΔG_{ET} = -23.06[E_{ox} R^- - E_{red} R^+], that is required to convert both R^+ and R^- into free radicals (20) and corresponds to the negative of the HOMO-LUMO gap, or absolute hardness, η, a crucial quantity in density function theory (21). Note that this property does not depend upon the reference electrode convention since any correction term which is added to one of the measured potentials is subtracted off in taking the difference. In all cases that we know of ΔG_{ET} is exergonic indicating the strong positive driving force to oxidize R^- compared to reducing R^+. $\Delta G^{+\to-}$ is the free energy change for converting the R^+ to the R^- by two electron reduction passing through $R^·$. Since it is the sum of $\Delta G^{+\to·}$ and $\Delta G^{·\to-}$ it is doubly dependent on the choice of reference electrode (in the case of Table 1, the Normal Hydrogen Electrode). $\Delta G^{+\to·}$ corresponds to the electron chemical potential (21).

We hope that this report makes it clear that for many purposes fundamental structure/energy interpretations for the three primary reactive intermediates are probably approached better through electrochemistry than through the more familiar bond cleaving/making processes with which they are related directly.

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