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On the Relevance of the Parr−Pearson Principle of Absolute Hardness to Organic Chemistry

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The remarkable generality of extrathermodynamic correlations between rates, equilibria, enthalpies, and many spectral properties relevant to the making and breaking of covalent bonds is at the heart of modern thinking about organic chemistry and must be regarded as something more than just a fortunate and useful fact.[1] Structural changes on thousands[2] of widely different processes, including complicated biological ones, correlate closely with those for a few simple ionization[3−6] and radical-forming[7] processes as models. It is reasonable to suppose that the correlations between these apparently diverse patterns of behavior rest on some simple, although no necessarily obvious, causes.

The purpose of this communication is to point out that the concept of *absolute hardness* derived from density functional theory (DFT) by Parr[8] and Pearson[9] as $\eta = (I - A)/2$ (i.e., one-half the HOMO−LUMO energy gap), the softness $\sigma = 1/\eta$, and the electronegativity, $\chi = (I + A)/2$, are fundamental properties which lie behind the observed chemical behavior of organic compounds[10] and provide a simple, integrative way of thinking about them.

Extrathermodynamic correlations show that similar structural factors affect the stabilities/reactivities of an enormous range of carbocations (R^+) and related transition states in the same way irrespective of extensive structural changes in their neutral, tetracovalent precursors, and the same is true for radicals ($R^\bullet$) and carbanions (R^-). This is the basis for the customary practice of using the stabilities of trivalent R^+, R^-, $R^\bullet$ as criteria for ranking the reactivities of their tetracovalent precursors.[11] It is also widely recognized that a variety of ground state effects can complicate such simple interpretations.[12]

Close correlations are also found between energies for making/breaking bonds to carbon and the energies for transferring electrons between R^+, $R^\bullet$, R^- as represented by their respective redox potentials in solution or their ionization potentials and electron affinities in the gas phase. For example, excellent correlations with nearly unit slopes and $R^2 = 0.994$ and 0.985 are found for the gas phase hydride affinities of saturated and unsaturated carbenium ions versus the ionization potentials of their conjugate radicals.[13] Comparable relationships are also found in solution between the heats of reaction of various R^+s with cyanoborohydride ion and their first reduction potentials.[14] Several excellent correlations between pK_{HA}s of anions and their oxidation potentials have also been reported.[15]

Thus, it is just as appropriate to use the ionization potentials, electron affinities, or solution phase redox potentials for comparing structural effects on reactivities as it is to use the more familiar substituent parameters or energies of model bond breaking/making reactions such as σ, σ^+, σ^-, $\sigma^\bullet$, pK_{HA}, pK_{R^+}, or hydride affinities. This is because the stabilities of R^+s, R^-s, and $R^\bullet$s, which primarily determine the equilibrium or rates of the various model reactions, are determined primarily by the oxidation and reduction potentials of the conjugate trivalent Rs. In turn, these are determined by their HOMO−LUMO gaps; expressed as the free energies of electron transfer, which are approximately equal to -2η in solution. According to the principle of maximum hardness,[16,17] *chemical systems at equilibrium are as hard as possible*; i.e., the most stable structure of $R^\bullet$ is the one with the maximum HOMO−LUMO gap between the energies for oxidizing it to R^+ and reducing it to R^-. The well-known hard−soft acid−base generalization[9d,17,18]

$$\Delta G_{ET} = -23.06[E_{red}(R^+) - E_{red}(R^\bullet)] \qquad (1)$$

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(1) See forward by L. P. Hammett to the following: *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: London and New York, 1972; p vii.

(2) (a) Personal communications from Professors Corwin Hansch and Marvin Charton. (b) Hansch, C. *Acc. Chem. Res.* **1993**, *26*, 147. (c) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(3) (a) Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 96. (b) For a useful listing to the many reviews on the Hammett equation and its many varients, see: *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Lowry, T. H., Richardson, K. S., Eds.; Harper and Row Publishers: New York, 1987, footnote 28, p 143.

(4) Brown, H.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

(5) (a) Deno, N. C.; Evans, W. L. *J. Am. Chem. Soc.* **1957**, *79*, 5804. (b) Arnett, E. M.; Bushick, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1564. (c) *Carbonium Ions, An Introduction*; Bethell, D., Gold, V., Eds.; Academic Press: London and New York, 1967.

(6) (a) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456. (b) Mathews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006. (c) Arnett, E. M.; Moriarity, T. C.; Small, L. E.; Rudolph, J. P.; Quirk, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 1492.

(7) For a brief review of attempts to develop a set of substituent parameters for radical reactions, see: Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221.

(8) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(9) (a) Pearson, R. G. *J. Org. Chem.* **1989**, *54*, 1423. (b) Pearson, R. G. *J. Org. Chem.* **1987**, *52*, 2131. (c) Pearson, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 7684. (d) Pearson, R. G. *J. Mol. Struct.* **1993**, *300*, 519. (e) De Proft, F.; Langenacker, W.; Geerlings, P. *J. Phys. Chem.* **1993**, *97*, 1826. (f) Kneisler, J.; Zhou, Z. *Int. J. Quantum Chem.* **1994**, *49*, 309. (g) Komorowski, L.; Lipínski, J.; Pyka, M. J. *J. Phys. Chem.* **1993**, *97*, 3166. (h) Smith, D. W. *J. Chem. Educ.* **1990**, *67* (11), 911. (i) Collins, S. J.; O'Malley, P. J. *Chem. Phys. Lett.* **1994**, *228*, 246. (j) Carpenter, J. E.; Sosa, C. P. *J. Mol. Struct. (THEOCHEM)* **1994**, *117*, 325.

(10) The Parr−Pearson approach is not limited to organic chemistry although that is the context of this paper.

(11) (a) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley: New York, 1976. (b) McMillan, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 473. (c) O'Neal, H. E.; Benson, S. W. In *Free Radicals*; Kochi, J. L., Ed.; Wiley: New York, 1973; Vol. II.

(12) See the following key references to many articles on ground state effects. (a) Leroy, G. *J. Mol. Struct. (THEOCHEM)* **1988**, *168*, 77. (b) Bordwell, F. G.; Zhang, X.-M.; Satish, A. V.; Cheng, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 6605. (c) Rüchart, C. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 830. (d) Reference 7. (e) Richard, J. P. *Tetrahedron* **1995**, *51*, 1535.

(13) For data, see: *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. II, Table XII.

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(15) (a) Bordwell, F. G.; Zhang, X.-M. *Acc. Chem. Res.* **1993**, *26*, 510. (b) Bordwell, F. G.; Cheng, J.-P.; Satish, A. V.; Twyman, C. L. *J. Org. Chem.* **1992**, *57*, 6542. (c) Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635. (d) Kern, J. M.; Sauer, J. D.; Federlin, P. *Tetrahedron* **1982**, *38*, 3023. (e) Maran, F.; Vianello, E. *Tetrahedron Lett.* **1990**, *31* (40), 5803. (f) Arnett, E. M.; Harrelson, J. A.; *Gazz. Chim. Ital.* **1987**, *117*, 237. (g) Venimadhavan, S.; Amarnath, K.; Harvey, N. G., Arnett, E. M. *J. Am. Chem. Soc.* **1992**, *114*, 221. (h) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 344.

(16) (a) Parr, R. G.; Zhou, Z. *Acc. Chem. Res.* **1993**, *26*, 255. (b) Parr, R. G., Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512. (c) Chattaraj, P. K.; Parr, R. G. *Struct. Bonding (Berlin)* **1993**, *80*, 11−26. (d) Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 1854. (e) Chattaraj, P. K.; Lee, H.; Parr, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 1855.

(17) (a) Pearson, R. G. *Acc. Chem. Res.* **1993**, *26*, 250−255. (b) Pearson, R. G. *J. Mol. Struct. (THEOCHEM)* **1992**, *255*, 261. Note some special qualifications of the principle, especially nuclear repulsion effects. In the current context one way to consider the stablest structure is as the one that gives the "hardest" resistance to redistribution of its electrons.

(18) (a) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827. (b) Ho, T. L. *The Hard and Soft Acids and Bases Principle in Organic Chemistry*; Academic Press: New York, 1977. Parr's calculation of η and σ provides a *quantitative* basis for HSAB discussions.

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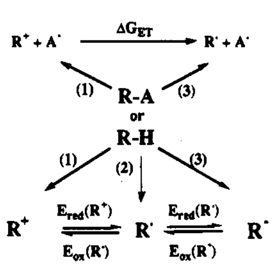
Scheme 1



[a] Processes refer to (1) hydride transfer to R^+, pK_{R^+} of ROH or heterolysis of RA, (2) bond dissociation energy of RH or homolysis of RA, and (3) heat of deprotonation or pK_{HA} of RH or HA.

then determine how ions or radicals of different η will react with each other.

Scheme 1 shows that ΔG_{ET} is the difference between the ΔH_{het} or ΔG_{het}[19] for heterolytic cleavage of an R−A or R−H bond and the corresponding homolytic bond energy (ΔH_{homo}). Thus, combination of pK_{HA}s with E_{ox} R^-s gives homolytic bond dissociation energies (BDEs) of R−H,[20] and E_{red} R^+ combined with pK_{HA}s and E_{ox} R^-s gives free energy hydride affinities of R^+.[21] ΔH_{homo}s of RA bonds can be calculated from ΔH_{het}s and ΔG_{ET}s.[19]

No general correlations are found between homolytic and heterolytic bond cleavage energies. Plot of BDEs *versus* gas phase acidities or of hydride affinities of R^+ *versus* η of $R^\bullet$ [22] are random scatters of points, as are plots of ΔH_{het}s vs ΔH_{homo} for R−As.[23] However, good linear relationships (average $R^2 = 0.95$) are found between the ΔH_{het}s for families of compounds generated from reaction of a single R^+ with a series of structurally related A^-s and the corresponding ΔG_{ET}s (i.e., -2ηs) from the redox potentials of the R^+, A^- combinations.[24] Each such line extrapolates to a nearly constant ΔH_{homo} for the series. Thus, an enormous range of heterolytic processes are governed by the hardness of the conjugate $R^\bullet$ of the R^+ or R^- produced by bond cleavage. It must be stressed that homolytic BDEs and ηs represent different criteria for radical stability. The former relates $R^\bullet$ to R−H; the latter relates $R^\bullet$ to R^+ and R^-. BDEs are related to the absolute electronegativities χ of the bonded radicals[9c] and are usually less sensitive to structure change than are ionization energies or ηs.[15a]

Good familial correlations also are found between ΔH_{het}s *versus* ($pK_{HA} - pK_{R^+}$)[25,26] for a wide variety of R^+, A^- combinations. The correlations cited above between ΔH_{het} and η suggest that it should also be appropriate to use the ($pK_{HA} - pK_{R^+}$) difference as a guide to ΔG_{ET} or the pair-hardnesses of the two ions relative to their radicals. Indeed, such correlations are found (average $r^2 = 0.95$) when data from ref 24 are plotted *versus* those in ref 26. The ($pK_{HA} - pK_{R^+}$) gap is thus a useful rough guide to the HOMO−LUMO gap, the hardnesses, and stabilities of $R^\bullet$s and $A^\bullet$s relative to their conjugate R^+s and A^-s. The hardness of $R^\bullet$ determines the interesting ($pK_{HA} - pK_{R^+}$) gap between the free energies for producing the conjugate R^+ and R^- from ROH and RH, respectively. However, there are only a few classes of compounds (e.g., triphenylmethanes) for which both ionization properties[27] are readily accessible in the same solvent.

The energy difference between R^+ and R^-, i.e., $-23.06[E_{red}(R^+) + E_{red}(R^\bullet)]$, is also of fundamental importance. In DFT terms this is approximately twice the "absolute" electronegativity, χ[28] a measure of the escaping tendency of electrons from $R^\bullet$. The use of reversible two-electron redox potentials of R^+ and R^-, when observable, has been invaluable for relating the stabilities of very weak carbon acids to those of their very stable carbenium ions and *vice versa*.[29]

The importance of the HOMO−LUMO gap to reactivity and to electronic transitions is well recognized.[30] However, the causal relationship between η and χ as the primary determining factors in bond making/breaking energies, and therefore of heterolytic and homolytic organic chemical reactions, has not previously been stated explicitly to our knowledge. The relationships between these fundamental properties provide an integrative perspective into the factors which underlie the observed behavior of organic and other covalent compounds.

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[19] Combination of calorimetrically determined ΔH_{het}s with electrochemical ΔG_{ET}s requires determination of ΔS_{ET}s from temperature coefficients of redox potentials. For cases examined in our laboratory $\Delta S_{ET} \approx 0$.

[20] See many references in ref 15a and the following: (a) Bordwell, F. G.; Zhang, X.-M.; Filler, R. *J. Org. Chem.* **1993**, *58*, 6067. (b) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287. (c) Griller, D.; Simões, J. A. M.; Mulder, P.; Sim, B. A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 7872.

[21] Cheng, J.-P.; Handoo, K. L.; Parker, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 2655.

[22] For example, using BDEs from ref 11a and ηs from ref 9a.

[23] Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 344.

[24] Chattaraj, P. K.; Cedillo, A.; Parr, R. G.; Arnett, E. M. *J. Org. Chem.*, in press.

[25] Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *Science* **1990**, *247*, 423.

[26] Arnett, E. M.; Chawla, B.; Amarnath, K.; Whitesell, L. G., Jr. *Energy Fuels* **1987**, *1*, 17.

[27] We have referred to compounds such as triphenylmethane whose R^+ and R^- are stable enough to be studied in solution by cleavage/formation of an R−H bond as *amphihydric*; see: Arnett, E. M.; Flowers, R. A., II; Meekhof, A. E.; Miller, L. *J. Am. Chem. Soc.* **1993**, *115*, 12603.

[28] ΔG_{ET} is based on a *difference* between observed electrode potentials, and hence any correction to standard potentials is substracted out. However, the sum of the potentials used to derive χ depends on the reference electrode and so cannot be considered as absolute in solution although it is absolute in the gas phase if referred to the electron at rest.

[29] This valuable approach and a seminal discussion of the application of cyclic voltammetry to physical organic chemistry are presented in the following: Breslow, R. *Pure Appl. Chem.* **1974**, *40*, 493.

[30] See, for example: (a) *Frontier Orbitals and Organic Chemical Reactions*; Fleming, I., Ed.; John Wiley: New York, 1978. (b) Reference 3b. (c) *Electron Transfer Reactions in Organic Chemistry*; Eberson, L., Ed.; Springer-Verlag: Berlin, Heidelberg, 1987. (d) Kochi, J. K. *Acc. Chem. Res.* **1992**, *25*, 39; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227.