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Appraisal of Chemical Bond Making, Bond Breaking, and Electron Transfer in Solution in the Light of the Principle of Maximum Hardness

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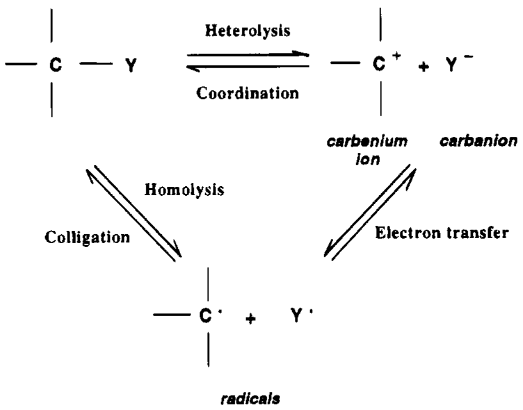
Experimental heats of heterolysis (ΔH_{het}) and homolysis (ΔH_{homo}) and free energy changes ΔG_{ET} associated with the electron transfer process are investigated theoretically for several series of compounds that have been produced by the direct reaction of resonance-stabilized carbenium ions with a variety of organic anions to produce C−C, C−N, C−O, and C−S bonds. Various empirical linear relationships show that the stabilities of molecules toward heterolysis can be analyzed in terms of the maximum hardness principle. The relationship between ΔH_{het}, ΔH_{homo}, and ΔG_{ET} for some symmetrical compounds, 9,9′-diphenylbixanthyl, bibenzyl, tetramethylbutane (bis-*tert*-butyl), and ethane, are established from published data which show the increasing strength of the central C−C bond in response to the stabilities of the cations, anions, and radicals produced by cleavage. The hypothetical pK_{HA} of isobutane is discussed.

1. Introduction

The making and breaking of covalent bonds is the most fundamental process in organic chemistry. Although there are now homolytic bond dissociation energies and heterolytic Brönsted acidities for thousands of C−H, N−H, O−H, S−H, and other Y−H bonds in solution[1] and the gas phase,[2] there is a relative paucity of information on the homolytic and heterolytic energies for corresponding bonds between carbon and other elements than hydrogen. However, recently it has been possible[3−8] to study a large number of organic reactions involving heterolysis, homolysis and electron transfer around C−C, C−N, C−O, and C−S bonds. The basic relationships between all these reactions can be depicted as shown in Scheme 1.

Scheme 1



Heats of heterolysis (ΔH_{het}) for a variety of compounds have been determined calorimetrically[3] as the negative of the measured heats of reaction between carbenium ions and the various types of anions in solution to form C−C or C−Y bonds. The changes in free energy associated with the electron transfer processes (ΔG_{ET}) have been obtained[3] from the reversible reduction potentials of the radicals in equilibrium with the anions and the reduction potentials of the carbocations to the radicals in solution using cyclic voltammetry. Heats of homolysis (ΔH_{homo}) can be calculated using ΔH_{het}s and ΔG_{ET}s provided that the entropy changes of the electron transfer processes (ΔS_{ET}) are negligible: $\Delta G_{ET} \approx \Delta H_{ET}$ and $\Delta H_{homo} = \Delta H_{het} - \Delta H_{ET}$. This has been shown to be true for several of the reactions cited above using the temperature coefficients of the redox potentials. All the processes referred to here have been carried out in sulfolane at 25 °C,[3−8] wherein all components (cation, anion, radical, and the neutral precursor) are amenable to study. It has been observed[3] that ΔH_{het}s correlate well with properties that involve conversion of a neutral species into ions or *vice versa* while ΔH_{homo} values correlate well with other properties involving conversions between neutral species, but there is little if any correlation between these two types of data.

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(1) For references to many measurements of acidities in DMSO and to an extensive review of Brönsted acidities in solution, see: Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(2) (a) For review of gas phase BDEs, see: McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493. (b) See: Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2. (c) NIST Database 19B, *Negative Ion Energetics*. (d) Bordwell, F. G.; Zhang, X.-M. *Acc. Chem. Res.* **1993**, *26*, 510.

(3) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *Science (Washington, D.C.)* **1990**, *247*, 423. $\Delta G_{ET} = -23.1[E_{red}(C^+) - E_{red}(Y^\bullet)]$.

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In order to obtain a better understanding of this situation, we concentrate on three established facts[3,4] for the series of reactions discussed here (for a fixed cation, if we vary anions): (A) ΔH_{het} is related linearly to ΔG_{ET},[5] (B) ΔH_{het} does not correlate with ΔH_{homo},[5] (C) structural changes affect ΔH_{het}s and ΔG_{ET}s much more than they do the related ΔH_{homo}s.[5] In this paper we attempt to analyze these correlations critically in terms of the relative stabilities and hardnesses of the various species involved. For this purpose, we begin with experimental data[5,8] for representative systems involving the making or breaking of C–C, C–N, C–O, and C–S bonds. We also explore whether the "maximum hardness principle"[9] or some variant of it is operative.

The term *hardness* in the original sense of Pearson,[10] as refined by later developments,[11] is best thought of qualitatively as the resistance of a species to electron transfer, as initiated by electronegativity differences and is the reciprocal of softness. For an isolated molecule or a piece of a molecule in a ground state, hardness is $(I - A)/2$, where I and A are its ionization potential and electron affinity respectively. In solution, I and A are obtained from reversible redox potentials of the species under study, in the present case the radicals and ions in Scheme 1.[9a,10c] When the electron number N is variable, the hardness is $^1/_2(\partial^2E/\partial N^2)$ for a fixed external potential, for which $(I - A)/2$ is the finite difference approximation. The maximum hardness principle (MHP) asserts that "there seems to be a rule of Nature that molecules arrange themselves so as to be as hard as possible".[12] In the following discussion we consider the hardness of radicals relative to their conjugate ions.

2. Theory

We apply Hess's law of thermochemistry to understand the relationship of ΔH_{het} to ΔG_{ET}. Rewrite the relevant cycle in its most general form as follows:

$C{-}Y \rightarrow C^+ + Y^-$	heterolysis		ΔH_{het}
$C^+ + e^- \rightarrow C^\bullet$	reduction	electron transfer	$-\Delta H_{\text{ET}}$
$Y^- \rightarrow Y^\bullet + e^-$	oxidation		
$C{-}Y \rightarrow C^\bullet + Y^\bullet$	homolysis		ΔH_{homo}

Then

$$\Delta H_{\text{het}} = \Delta H_{\text{homo}} + \Delta G_{\text{ET}} \qquad (1)$$

provided that the entropy change is small for the electron transfer process. Further, if it happens that for reaction of a series of anions with a given cation ΔH_{homo} is roughly a constant, then ΔH_{het} will be linear in ΔG_{ET}. In section 3 we will establish this linear behavior with specific examples. We will find straight lines with slopes close to unity and intercepts close to constant ΔH_{homo} values for each series of compounds. Generally, ΔH_{homo} vs ΔH_{het} produces a completely uncorrelated scatter diagram.[7]

For an ideal symmetric situation, the electron transfer process may be written as

$$R^\bullet + R^\bullet \rightarrow R^+ + R^-$$

The enthalpy change associated with this process is $I - A$, which is simply the hardness η of $R^\bullet$ (atom in case of a homonuclear diatomic molecule),[11] and is approximately the same as the HOMO–LUMO gap.[13] Since ΔH_{homo} is found experimentally not to change much for the reactions considered here, if we vary the reactions of a series of related anions with a given carbocation,[5] we define an effective hardness (η^*) for the pair of radicals even if the two are different. This corresponds to the legitimate definition of the pair hardness of the system R--R′ when R and R′ are widely separated[14]

$$\eta_{R\text{--}R'} = (I_{\min} - A_{\max})/2 \qquad (2)$$

where $I_{\min}$ is the smaller of the two ionization potentials (I_R and $I_{R'}$) and $A_{\max}$ is the larger of the two corresponding electron affinities. Then, when the fragments are different in the electron transfer process in Scheme 1, we have

$$\Delta G_{\text{ET}} \approx \Delta H_{\text{ET}} = I_C - A_Y = 2\eta^* \qquad (3)$$

where η^* is the pair hardness of eq 2. Making use of eqs 1 and 3 we have

$$\Delta H_{\text{het}} = \text{constant} + 2\eta^* \qquad (4)$$

That is, the higher the value of the pair hardness, the greater the stability toward heterolytic cleavage, which is consistent with the maximum hardness principle.[9,12] Note that in some cases, $I_{\min}$ can be less than $A_{\max}$ and the pair hardness need not necessarily be positive.

When both radicals are treated individually, consider the heterolytic dissociation

$$C{-}Y \rightarrow C^+ + Y^- \qquad (\Delta H_{\text{het}})$$

for which, from eqs 1 and 3,

$$\Delta H_{\text{het}} = \Delta H_{\text{homo}} + I_C - A_Y \qquad (5)$$

For the other conceivable heterolytic dissociation one has

$$C{-}Y \rightarrow C^- + Y^+ \qquad (\Delta H_{\text{het}'})$$

and

$$\Delta H_{\text{het}'} = \Delta H_{\text{homo}} + I_Y - A_C \qquad (6)$$

Subtracting eq 6 from eq 5, and recognizing that there is only one possible mode of homolysis,

$$\Delta H_{\text{het}} - \Delta H_{\text{het}'} = (I_C + A_C) - (I_Y + A_Y)$$

or

$$\Delta H_{\text{het}} - \Delta H_{\text{het}'} = 2(\mu_Y - \mu_C) \qquad (7)$$

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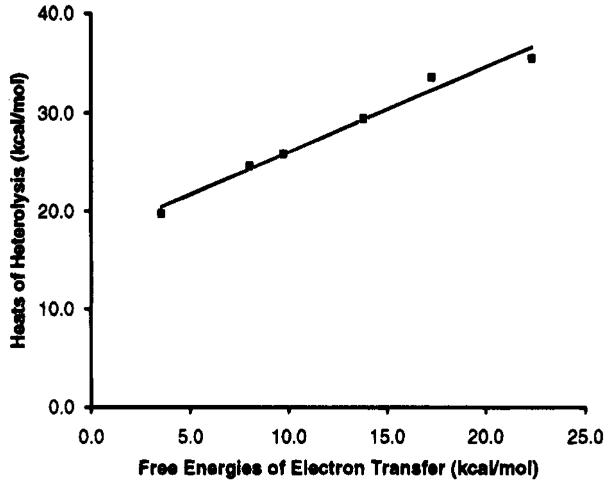

Figure 1. Correlation of ΔH_{het} (y) of C−C bonds with ΔG_{ET} (*x*) for trityl ion with 9-PhFl$^-$, 9-PhSFl$^-$, 2-Br-9-PhSFl$^-$, 9-COOMeFl$^-$, 9-CNFl$^-$, and 2,7-Br$_2$-9-CO$_2$MeFl$^-$. Omitted from this graph is the datum for 9-PhSO$_2$Fl$^-$: $y = 28.35$, $x = 5.97$. See ref 21 for a discussion of this case.

where $\mu_{Y(C)}$ is the electronic chemical potential of Y(C) (which is the negative of the electronegativity).[15]

Adding eq 6 to eq 5,

$$\Delta H_{het} + \Delta H_{het'} - 2\Delta H_{homo} = (I_C - A_C) + (I_Y - A_Y)$$

or

$$\Delta H_{het} + \Delta H_{het'} - 2\Delta H_{homo} = 2(\eta_C + \eta_Y) \qquad (8)$$

Because of the enormous differences that usually exist between the stabilities of C$^+$ vs C$^-$ and of Y$^+$ vs Y$^-$, it is so difficult to measure $\Delta H_{het'}$ from the direct reaction of very unstable Y$^+$ and C$^-$ that we know of no examples to date. However, I_C, I_Y, A_C, and A_Y may often be obtained by cyclic voltammetry from the two-electron reduction potential of a stable C$^+$ or the two-electron oxidation potential of a stable Y$^-$. Therefore, it should be possible to calculate the enthalpy changes associated with *both* heterolytic processes whenever ΔH_{het}, I_C, I_Y, A_C, and A_Y are available from thermochemical and electrochemical measurements (and they often are measurable). To test this approach one might employ pairs of amphihydric compounds,[16] both of which are capable of conversion to C$^+$, C$^-$ and Y$^+$, Y$^-$ in the same solvent and measure the heats of reaction of C$^+$ with Y$^-$ and of Y$^+$ with C$^-$. Exploratory experiments are currently underway.

3. Results and Discussion

Figures 1 −4 depict the variation of $\Delta H_{het}(y)$ with $\Delta G_{ET} \sim \eta^*(x)$ for molecules undergoing cleavage of C−C,[5] C−N,[6] C−O,[7] and C−S[8] bonds, respectively. For a given cation, the anions were chosen to give the maximum number of data points. For linear behavior involving other cations, see refs 5−8. For the C−C bond,[5] the cation is trityl and the anions are substituted fluorenides: 9-PhFl$^-$, 9-PhSFl$^-$, 2-Br-9-PhSFl$^-$, 9-COOMeFl$^-$, 9-CNFl$^-$, and 2,7-Br$_2$-9-CO$_2$MeFl$^-$. The linear relation between ΔH_{het} and $\Delta G_{ET} \sim \eta^*$ is given by $y = 0.86x + 17.39$ with $r^2 = 0.98$. The range of ΔH_{homo} values is $13.18 \le \Delta H_{homo} \le 16.60$. For the C−N bond,[6] the cation is tropylium and the anions are succinimide, 3,6-dibromocarbazole, and carbazole. The linear relation is $y = 1.01x + 37.15$ with $r^2 = 0.97$ and $36.60 \le \Delta H_{homo} \le 37.52$. For the C−O bond,[7] the cation is trityl and the anions are 4,6-dinitro-*o*-cresol, *p*-nitrophenol, *p*-cyanophenol, 3,5-dichlorophenol, *p*-carbomethoxyphenol, and *p*-chlorophenol. The linear relation is $y = 1.06x + 40.06$ with $r^2 = 0.998$ and $37.81 \le \Delta H_{homo} \le 40.13$. For the C−S bond,[8] the cation is perinaphthenium and the anions are 4-bromothiophenol, 4-chlorothiophenol, thiophenol, 4-methylthiophenol, and 4-methoxythiophenol. The linear relation is $y = 0.91x + 13.00$ with $r^2 = 0.96$ and $11.60 \le \Delta H_{homo} \le 12.80$. Four easily discernible conclusions are clear: (A) good linear correlations exist between ΔH_{het} and ΔG_{ET} ($\sim\eta^*$), (B) ΔH_{homo}s are nearly constant for each set, (C) the slopes are close to unity, and (D) the intercept is close to ΔH_{homo} in each series. This is in accordance with eq 1 and the MHP (eq 4) for the heterolytic cleavages.

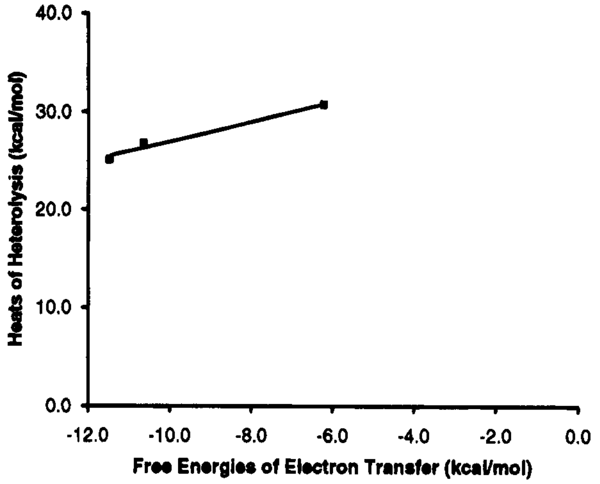

Figure 2. Correlation of ΔH_{het} (*y*) of C−N bonds with ΔG_{ET} (*x*) for tropylium ion with succinimide, 3,6-dibromocarbazole, and carbazole. Omitted from this graph is the datum for phthalimide: $y = 23.05$, $x = -10.28$.

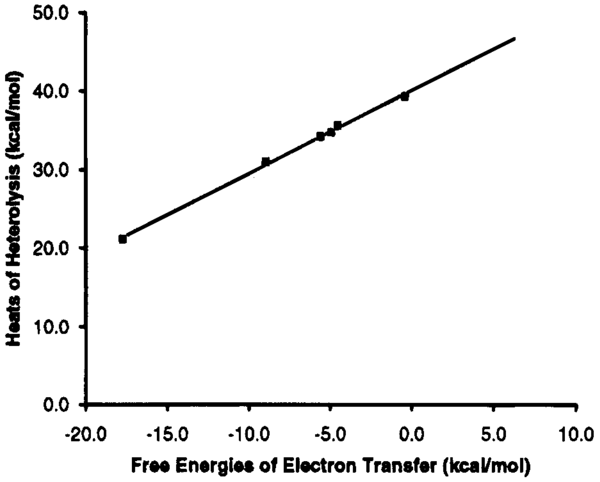

Figure 3. Correlation of ΔH_{het} (*y*) of C−O bonds with ΔG_{ET} (*x*) for trityl ion with 4,6-dinitro-*o*-cresol, *p*-nitrophenol, *p*-cyanophenol, 3,5-dichlorophenol, *p*-carbomethoxyphenol and *p*-chlorophenol. Omitted from this graph are the data for *p*-fluorophenol ($y = 38.29$, $x = 3.71$) and for *p*-*tert*-butylphenol ($y = 40.59$, $x = 6.30$).

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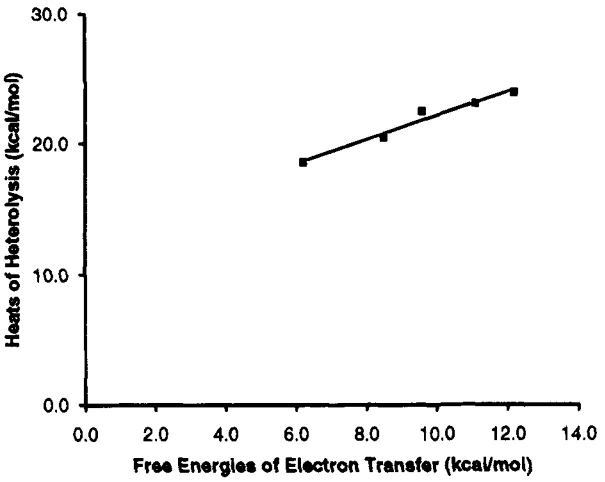

Figure 4. Correlation of ΔH_{het} (y) of C–S bonds with ΔG_{ET} (x) for perinaphthenium ion with 4-bromothiophenol, 4-chlorothiophenol, thiophenol, 4-methylthiophenol, and 4-methoxythiophenol.

Bond Cleavage and Electron Transfer. The relationships between ΔH_{het} and ΔG_{ET}, or η^*, discussed here are not intuitively obvious. However, there are so many precedents from the current literature that it seems likely they are part of a general and quite reasonable pattern that is based on well-known principles. The recent availability of appropriate instruments and the appreciation that redox potentials, ionization potentials, and electron affinities can be used to relate heterolytic energies of C-H bonds (as protonic acids or hydride donors) to corresponding homolytic bond dissociation energies have resulted in many correlations of these properties in solution and the gas phase. Excellent correlations of Brönsted acidities (e.g., pK_{HA}) vs the first oxidation potentials of the conjugate anions have often been noted[2d,5,7,8,17] and of the hydride affinities of carbenium ions vs their first reduction potentials.[18] Especially noteworthy are Parker's recent excellent correlations of free energy hydride affinities for Me^+, Et^+, i-Pr^+, and t-Bu^+ vs their affinities for Cl^-, Br^-, I^- and the electron in the gas phase.[19]

We propose that these many correlations involving the heterolytic breaking (or making) of C–H, Y–H, and C–Y bonds vs redox potentials, or the corresponding free energies and the ΔH_{het} vs ΔG_{ET} correlations discussed here have a common origin. It is a commonplace practice to compare bond cleavage energies, or the related rates, in terms of the stabilities of the radicals or ions that are formed. Unless there is some unusual strain energy[20] or other factor[2d] in the initial state of the reacting precursor, differential bond energies or rates are analyzed entirely in terms of the reactive species produced by homolysis or heterolysis. Usually, heterolysis energies are much more sensitive to structure modification than are homolytic processes. It is therefore entirely reasonable that the relative energies for producing a related series of cations or anions from neutral precursors should be correlated closely to the energies required to convert them into their conjugate (neutral) radicals. Bordwell[21] has demonstrated for an extensive series of flourenes, including those plotted on Figure 1, that in the absence of unusual "radical stabilizing effects", structural changes which have considerable effects on anion stability have virtually none on the radical.

Although there are many precedents for comparing heterolytic bond energies of C–H or Y–H bonds to redox energies of C^+ or Y^-, there are none we known of, except those cited here,[3–8,13b] that involve heterolytic cleavage of C–Y bonds and the ΔG_{ET} relating C^+ and Y^- to $C^\bullet$ and $Y^\bullet$. Since C^+ and $C^\bullet$ are constant for each series and structure affects on Y^- are much larger than on $Y^\bullet$ and C–Y, the linear plots of ΔH_{het} vs ΔG_{ET} are understood.

Related Studies on Homolysis/Heterolysis. Attempts to relate the stabilities of molecules to inherent additive properties of their components have a long history. Of particular appeal is the notion of electronegativity which Pauling offered in his classic text[22] as a quantitative guide to the strengths and polarities of a wide variety of bonds. Recently, Luo and Benson[23] have reviewed their development of the covalent potential (V_x) as a measure of valence state electronegativity which shows a powerful correlative ability for the molecular energetics of CY compounds in the gas phase. V_x compares favorably against 20 other electronegativity scales and receives powerful theoretical support from density functional theory,[24] where notions of absolute electronegativity and absolute hardness appear naturally. Luo has applied the V_x scale to correlating heats of formation,[25] adiabatic ionization energies of organic molecules,[26] and homolytic[27] and heterolytic bond dissociation energies[28] and reviewed the extensive literature on these properties. These studies demonstrate that all of the above *gas phase* properties for a wide variety of inorganic and *relatively small* organic C–Y molecules can be predicted with high precision by means of simple empirical equations based on the V_x of Y.

The present studies of *large complex* C–Y molecules *in solution* extends the discussion of the two modes of bond cleavage and the stabilities of the radicals and ions produced relative to each other as expressed by ΔG_{ET} and η^*s of the radicals. As discussed below these properties may vary considerably in their interactions with solvents as the size and nature of C–Y is varied.

Role of Solvent in Homolysis/Heterolysis. There is a classical dilemma in attempts to relate bond energetics in the gas phase to those in solution. The small, simple radicals and ions whose formation and electron transfer are best studied in the gas phase[2a–c] are mostly too unstable for investigation in common solvents at room temperature. Large radicals and ions, such as those used

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in this report, may be so stabilized by resonance, or other means, that they can be studied at leisure in appropriate solvents. They and their precursors are mostly of such low volatility that they cannot be studied in the gas phase in the way that their low molecular weight counterparts can be. Heats of ionization of a wide range of C−Y, including many that ionize in the gas phase, have been studied in superacids at low temperature in non-nucleophilic solvents.[29] Again, Brönsted acidities (pK_{HA}s) of over 2000 anions of greatly varied size and stability, some of which overlap those in the gas phase, have been compared in DMSO.[1] Important advances have been made using laser pulse technology to produce highly reactive carbenium ions and carbanions in solution.[30] Still, we know of no case where ions, as unstable as *tert*-butyl cation or its carbanion, have been produced directly by this method. However, a wide variety of unstable, transient radicals have been produced by modulated photolysis and their redox properties examined.[17c,31] Some of these (e.g., *tert*-butyl) are small enough to overlap those investigated in the gas phase so that the redox potentials for converting *tert*-butyl radical to both its carbenium ion and carbanion have been measured in acetonitrile.[31a]

It is well-established that carbocation−anion reactions which are the subject of this report are controlled heavily by solvent polarity. As evidence, a close correlation of ΔG_{het} with the reciprocal of the dielectric constant[32] was reported. Thus, some C−C bonds can actually be heterolyzed simply by increasing solvent polarity.[33] Alternatively other stable solutions of C^+, Y^- were converted to $C^\bullet$, $Y^\bullet$ simply by reducing the solvent polarity.[34] Some C−Ys have been heterolyzed in MeCN by laser photolysis through complicated mechanisms.[35] Thus, it is reasonable to suppose that if the rather large C−Y molecules under discussion above could be volatilized, gas phase photolysis would probably produce $C^\bullet Y^\bullet$ radical pairs in that low dielectric medium with no dissociation to C^+Y^- ions.

The effect of solvation on organic reactions has been of subject of many discussions,[36,37] but exact treatments for the ionization of large molecules do not yet exist. Ritchie's speculations on the free energies of transfer for large ions, such as C^+ and Y^- from the gas phase to polar solvents,[38,39] and Pearson's more general discussion[10c] are especially noteworthy efforts. A very recent article analyzes molecular charge distribution and solvation of 29 small neutral molecules through high-level *ab initio* calculations including continuum dielectric theory with excellent results[40] but does not consider ions. Hynes has attacked the case of *tert*-butyl−Y solvolysis through an extensive theoretical analysis[41] which also reviews the large literature on this classical problem.

Most relevant to the present discussion is the study of homolysis−heterolysis−electron transfer on five 2-naphthyl-CH_2-Ys which attempts to compare bond cleavage (in kcal/mol) in the gas phase to acetonitrile solution.[42] $\Delta G_{homo}/\Delta G_{het}$ in the gas phase is calculated for the following $Y^\bullet/Y^-$ to be H = 85.9/234.5, Cl = 67.8/151.0, Br = 52.8/141.6, *I* = 40.0/136.1, OAc = 68.2/163.8; while in acetonitrile, H = 85.9/105.1, Cl = 67.8/30.3, Br = 52.8/24.5, *I* = 40.0/23.2, OAc = 68.2/43.3 assuming, as is reasonable, that ΔG_{homo} would be little affected by transfer to solution. The calculated ratios for electron transfer energies in the two phases, $\Delta G_{ET}^{gas}/\Delta G_{ET}^{MeCN}$, are: H = 148.6/19.2, Cl = 83.2/−37.5, Br = 88.8/−28.3 (sic), *I* = 96.1/−16.8, OAc = 95.6/−24.9. These values of ΔG_{het} produce a random scatter when plotted vs ΔG_{ET} in contrast to the cases we have presented.

Using data from a variety of sources, Wayner[31c] has calculated solvation energies for several relatively large (e.g., diphenylmethyl) cations and concludes that they have about the same solvation energy of 40 kcal/mol from the gas phase to acetonitrile. However, this may be affected significantly by charge distribution. Parker[18c] has calculated solvation free energies from the gas phase to DMSO and MeCN for 15 carbenium ions, all of which fall between 39 and 47 kcal/mol. Tropylium ion (40 kcal/mol) is especially important since its hydride ion affinity can be studied both in solution[18c,42] and the gas phase.[2b] This is directly relevant to the data presented in Figure 2. Also of relevance is the laser flash photolysis study of some diphenylmethyl halides.[43] The gas phase homolysis of Ph_2CHCl is estimated as 64 kcal/mol, the corresponding heterolysis as 150 kcal/mol, and the solvation energy of Ph_2CH^- into acetonitrile is 67 kcal/mol.

Presumably, the solvation energies of large charge-delocalized carbanions in nonhydroxylic solvents are not very different from those of their conjugate carbenium ions if electrostatic factors dominate. Taft and Bordwell[44] have demonstrated that solvation energies for large, delocalized anions from the gas phase to DMSO are essentially constant. Clearly, the differentiation between solvation energies of a given ion pair and its conjugate radical pair is a sensitive function of solvent polarity and charge delocalization. In sulfolane the large delocalized ions under discussion here appear to be completely dissociated under our experimental conditions. Since most of the solvent−solute interaction terms such as cavity volume, van der Waals forces, etc. should be nearly the same for solvating large C−Y, $C^\bullet Y^\bullet$, C^+Y^- in non-

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(42) Milne, P. H.; Wayner, D. D. M.; DeCosta, D. P.; Pincock, J. A. *Can. J. Chem.* **1992**, *70*, 121. Note that the tabulated value for ΔG_{ET}^{gas} = 138.8 kcal/mol for the bromide should be 88.8 kcal/mol based on the ΔG_{homo} and ΔG_{het} in the same Table 3.

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hydrogen bonding solvents, it is not surprizing that simple electrostatic factors play the leading role in differentiating homolysis from heterolysis in solution. For small C^+ solvation free energies are very sensitive to size, for example: $\Delta G2_{\mathrm{solv}}^{\mathrm{gas}\rightarrow\mathrm{H_2O}}$ Me^+ (96), Et^+ (78), *i*-Pr^+ (59), *t*-Bu^+ (54), $benzyl^+$ (59).[19] Not surprizingly, hydrogen bonding plays a major role in differential solvation of ammonium, oxonium ions.[45]

The conclusion that should be drawn from the above discussion is that ΔG_{ET}, η^*, and ΔH_{het} are highly sensitive to solvent dielectric constant for large resonance-stabilized C^+Y^- and that $C^\bullet Y^\bullet$ and ΔH_{homo} will be virtually insensitive. However, the type of correlations between ΔG_{ET} and ΔH_{het} reported here for large C−Y do not apply to small C−Y where solvation energy differences are much larger and depend more specifically on details of size and charge distribution for the ions and a large variety of characteristic solvation parameters for the solvent.

Concerning the Homolysis/Heterolysis Energy of Symmetrical Compounds. The combination of reaction calorimetry and electrochemistry that we have applied to the C−Y compounds, formed from relatively stable C^+ carbenium ions and Y^- anions, can be extended directly to a limited number of amphihydric[16] compounds whose carbenium ion and carbanion can both be handled in the same solvent. This is a rare situation since the conjugate carbanion of a stable cation is usually such a strong base that it will deprotonate any solvent that is polar enough to dissolve and dissociate the salts of both types of conjugate ions. Conversely, the conjugate carbocations of very stable carbanions are usually too reactive or unstable to handle in solvents such as sulfolane, DMSO, or acetonitrile.

The pioneering studies of Breslow[46] established the power of electrochemistry for relating very unstable carbon ions of both types to their stable conjugate ions and radicals. Triarylmethyl and some other polycyclic systems have just the right balance of stability for both their carbocations and carbanions to permit study of their ΔH_{het}s through direct reaction of C^+ with C^- in sulfolane by reaction calorimetry and of their ΔG_{ET}s by cyclic voltammetry. The following four cases exemplify increasingly stable symmetrical C−C bonds.

9-Phenylxanthene yields a very stable carbenium ion ($pK_{R^-} = 1.01$) and a strongly basic, but readily accessible, carbanion in DMSO ($pK_{HA} = 27.9$).[16,47] These react in sulfolane at 25 °C to give the presumably[48] symmetrical 9,9′-diphenylbixanthyl whose $\Delta H_{\mathrm{het}} = 42.15$ kcal/mol. Cyclic voltammetry of the cation and anion yields a $\Delta G_{\mathrm{ET}} = 26.5$ kcal/mol for conversion of the radical to the ions and thus $\Delta H_{\mathrm{homo}} = 15.65$ kcal/mol. These values have no direct precedent from those above based on combinations where both the cation and anion are highly stable[3−8] and reflect the relative instability of the 9-phenylxanthenide anion on ΔH_{het}, η, and ΔG_{ET}. A correlation equation based on the proportionality of ΔH_{het}s with pK_{R^-}s and pK_{HA}s[49] closely predicted the measured ΔH_{het} for 9,9′-diphenylbixanthyl.

Bibenzyl ($PhCH_2CH_2Ph$) is a model compound for the thermolysis of aromatic fossil fuels such as coals[50] and is the symmetrical dimer from coupling of benzyl radicals. It would be out of the question to apply calorimetry to measuring ΔH_{het} for this compound by mixing solutions of the benzyl cation ($pK_{R^+} \approx -23$) and carbanion ($pK_{HA} \approx 42$) in sulfolane. Both ions are so unstable (see below) that they have defied production in all types of superacidic or superbasic solutions except as very short-lived species. They would surely react immediately with sulfolane, DMSO, or acetonitrile at 25 °C.

However, the bond dissociation energy (BDE) for homolysis of the central C-C bond in the gas phase can be estimated as 64.8 kcal/mol from the heats of formation of bibenzyl[51] and of the benzyl radical.[2a] Assuming that the heats of solvation of reactants and products into acetonitrile will be equal, we can convert this ΔH_{homo} value to the corresponding ΔH_{het} in acetonitrile using the values of Wayner, McPhee and Griller[31a] for $E_{\mathrm{ox}} = 0.73$ V and $E_{\mathrm{red}} = -1.45$ V of the benzyl radical from which $\Delta G_{\mathrm{ET}} = 50$ kcal/mol and $\Delta H_{\mathrm{het}} = 115$ kcal/mol is obtained.

This value can be used to test the correlation equation referred to above[49] using the data of Wayner et al.[31a] who interpolate a $pK_{R^-} = -22.6$ for the benzyl cation and $pK_{HA} = 41-42$ for producing the benzyl anion by deprotonation of toluene. These values are in good agreement with Parker's[18c] more recent estimate of −23.8 for the benzyl cation and Bordwell and Algrim's[52] estimate of 43 for the pK_{HA} of toluene. Using the correlation equation[49] for relating pK_{R^-}s of secondary stabilized cations, such as xanthylium or tropylium, to the ΔH_{het}s of their reactions with anions of known pK_{HA}s, one obtains $\Delta H_{\mathrm{het}} = 13.48 - 0.434pK_{R^-} + 1.302pK_{HA} = 76$ kcal/mol which falls drastically short of the value obtained from ΔH_{homo} and ΔG_{ET}.

A third estimate combines the gas phase $\Delta H_{\mathrm{homo}} = 65$ kcal/mol with the gas phase $\Delta G_{\mathrm{ET}} = 155$ kcal/mol from Pearson's[12d] estimate of η for converting benzyl radical to the cation and anion to give $\Delta H_{\mathrm{het}} = 217$ kcal/mol in the gas phase. If we accept Parker's estimate[19] of 44 kcal/mol for the free energy of solvation of the benzyl cation, and assume that the same estimate can be used for solvating the carbanion, one obtains 129 kcal/mol for the ΔH_{het} of bibenzyl in acetonitrile.

The second and third approaches used above involve increasingly dubious assumptions which include neglect of a variety of large (but conceivably cancelling) entropy terms; differential hydrogen bonding of cations and anions; specific solvation differences between cations and anions; and differences between the acidity/basicity behavior, ion pairing, and activity coefficients of relatively

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(48) The symmetrical structure for this compound is based on tradition and (in our laboratory) NMR and mass spectrometry data. We have tried repeatedly to obtain a suitable crystal for an X-ray structure determination but without success. The demonstration by Lankamp, H.; Nauta, W. Th.; MacLean, C. *Tetrahedron. Lett.* **1968**, 249, that coupling of trityl radicals does not give a symmetrical product justifies skepticism in the present case.

(49) Arnett, E. M.; Chawla, B.; Amarnath, K.; Whiteshell, L. G., Jr. *J. Energy Fuels* **1987**, *1*, 17. Several equations of the form: $\Delta H_{\mathrm{het}} = A - BpK_{R^-} + CpK_{HA}$ fit a wide variety of carbocation-anion reactions, where *A*, *B*, and *C* depend on the types of ions. We have used the equation for secondary resonance-stabilized carbenium ions simply because it should be better than the one for tertiary ions, and there is none for primaries.

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(52) Bordwell, F. G.; Algrim, D. J. *J. Am. Chem. Soc.*, **1988**, *110*, 2964.

stable ions compared to tightly charge-localized ones. Of the three methods for estimating ΔH_{het} of strong C−C bonds in solution, the first is closest to reliable experimental data, involves the fewest assumptions, and is probably correct within 3−4 kcal/mol.

Comparing bibenzyl with 9,9′-diphenylbixanthyl, one sees, as might be expected, a much larger ΔG_{ET} for the former separating ΔH_{het} from ΔH_{homo} and much more endothermic values for C−C bond cleavage reflecting the much reduced stability of its cation, radical, and carbanion which can enjoy delocalization over only one benzene ring instead of three.

2,2,3,3-Tetramethylbutane (Me_3C-CMe_3). The dimerization of *tert*-butyl radicals leads to this methylated analog of hexaphenylethane. Its homolysis has been discussed in terms of strain developed through an extensive series of substituted ethanes.[20] The ΔH_{homo} may be related to its hypothetical heterolysis through the results of Wayner, McPhee, and Griller[31a] who were able to measure the half-wave potentials (referred to SCE) for reversible reduction (0.09 V) of the carbocation and reduction (−2.00 V) of the *tert*-butyl radical in acetonitrile. From these values $\Delta G_{ET} = 23.1 \times 2.09 = 48.2$ kcal/mol may be calculated, which is closely comparable to that for the benzyl radical. The corresponding value in the gas phase, calculated from the ionization potential and electron affinity, is 166 kcal/mol for *tert*-butyl radical, only slightly harder than the benzyl radical.[12d] The large stabilizing effects of solvent on the ions are demonstrated by the differences between ΔG_{ET}^{gas} and ΔG_{ET}^{MeCN}.

The above results answer the essential question of the hardness of the radical, its ΔG_{ET}, and the size of the gap between ΔH_{homo} and ΔH_{het} (if ΔS_{ET} is neglected), but a reliable value for the bond dissociation energy of the C−C bond is needed in order to estimate the actual values of these energies. This is a matter of some controversy. A wide choice of older values is available.[53] More recently, Luo and Holmes obtain $\Delta H = 72.6$ kcal/mol through their interpolation equation[53d] which agrees well with 72.7 kcal/mol proposed by Griller and Kanabus-Kaminska[54] whose careful review of the problems of calculating bond dissociation energies carries the warning *caveat emptor* to would-be users of such data. The problem of assigning a correct ΔH_f to the *tert*-butyl radical is discussed at length by McMillen and Golden,[2a] who choose a value of 8.7 kcal/mol from a range of 4 kcal/mol. Combination with $\Delta H_f = -53.83$ kcal/mol for tetramethylbutane[51] gives 71.2 kcal/mol for ΔH_{homo}. Faced with these possibilities, we favor 72 kcal/mol for the gas phase heat of homolysis of tetramethylbutane into two *tert*-butyl radicals and expect that it would be virtually unchanged in a solvent such as acetonitrile.

If these assumptions are correct, $\Delta H_{het} = 71.2 + 48.2 = 119.4$ kcal/mol which is drastically greater than the modest endothermic values (10−40 kcal/mol) that we have measured in sulfolane for heterolysis of the weak C−C , C−N, C−O, and C−S bonds to produce large, resonance-stabilized ions and the identical value for heterolysing the C−C bond in bibenzyl under similar conditions.

This estimate for heterolysis of "bis-*tert*-butyl" can be compared with that derived from the correlation equation[49] relating ΔH_{het}s with pK_{R^+}s and pK_{HA}s used above. A pK_{R^+} of −15 has been suggested for *tert*-butyl cation from an extensive correlation of heats of formation for a variety of carbenium ions in superacids vs their known pK_{R^+}s.[29d] This value lies close enough to measurable ones that it is probably within one or two pK_{R^+} units from the correct, but inaccessible, value in aqueous sulfuric acid solutions. It is not clear why this value should be 7−8 pK units more positive than the estimates given above for the pK_{R^+} of the benzyl cation.

The most serious problem for correlating[49] ΔH_{het} with pK_{R^+} and pK_{HA} for tetramethylbutane is the choice of a suitable pK_{HA} for the *tert*-butyl carbanion in DMSO. Breslow's classic value of 70.7[55] was obtained from the oxidation potentials of trityl and *tert*-butyl carbanions, the BDEs of isobutane and triphenylmethane, and the pK_{HA} of triphenylmethane. Over the past two decades there has been some revision[54,56] of all of these measurements.

Using revised values in Breslow's calculation, a $pK_{HA} = 54$ is obtained for isobutane.[57] This is close to 58.1 obtainable by applying Bordwell's empirical equation for relating pK_{HA}s, BDEs and E_{ox,R^-}[57,58] directly to the BDE of isobutane[54] and its oxidation potential in acetonitrile.[31a] However, when included in the correlation equation[49] for relating pK_{HA} and pK_{R^-} to heterolysis energies, a low value of $\Delta H_{het} = 94.5$ kcal/mol is obtained, as was the case for bibenzyl.

Bordwell and Algrim[52] estimate pK_{HA}s for methane = 56 and toluene = 43 in DMSO with the former not far from the revised value for isobutane given above. The gas phase acidities of these three hydrocarbons are[2c] methane = 408.4 kcal/mol, isobutane = 405.7 kcal/mol, and toluene = 373.7 kcal/mol. Clearly, on the basis of the gas phase as precedent, one might expect the pK_{HA} for isobutane in DMSO, or sulfolane, to lie not far from that of methane and both of them to be about 25 pK units above toluene, close to 70[59] and to Breslow's proposal. Bordwell's estimate for toluene is probably much better than that for methane since the extrapolation is only a few units above well-substantiated values for di-and triphenylmethanes.

Parker[19] estimates the solvation free energy for methyl, *tert*-butyl, and benzyl cations into water from the gas phase to be 96, 54, and 59 kcal/mol, respectively. If these same values were used for heats of solvation into DMSO (an admittedly poor substitution), the large gap between the basicity of *tert*-butyl and benzyl anions would be unaffected while that between methyl and *tert*-butyl carbanions would be greatly widened. If we use a pK_{HA} of 70, a ΔH_{het} of 112 kcal/mol is predicted by the correlation equation[49] in rough agreement with the value derived directly from ΔH_{homo} and ΔG_{ET}.

From the gas phase ΔG_{ET} of the *tert*-butyl radical and ΔH_{homo} for the central C-C bond of tetramethylbutane, one obtains 237 kcal/mol (71 + 166) for its ΔH_{het} in this low dielectric medium. Applying Parker's hydration

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(53) (a) Tsang, W. *J. Chem. Phys.* **1966**, *44*, 4283. (b) Tsang, W. *Int. J. Chem. Kinet.*, **1978**, *10*, 821. (c) Beckham, H.-D.; Rüchardt, C. *Chem. Ber.* **1977**, *110*, 878. (d) Luo, Y.-R.; Holmes, J. L. *J. Mol. Struct.* (THEOCHEM) **1993**, *281*, 123. (e) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; Table A22.

(54) Griller, D.; Kanabus-Kaminska, S. M. *J. Mol. Struct.* (THEOCHEM) **1988**, *163*, 125.

(55) Breslow, R.; Goodin, R. *J. Am. Chem. Soc.* **1976**, *98*, 6076.

(56) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X.-M. *J. Am. Chem. Soc.* **1991**, *113*, 9790.

(57) We are indebted to Dr. Y. Zhao and Professor F. G. Bordwell for this estimate and providing the following calculation.

(58) Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1994**, *116*, 904. Applying this equation, 93.6 + 23.1(2.27 + 0.3) − 73.3)/1.37 = 58.1.

(59) (406 − 374)/1.37 = 23 pK units.

energy for the *tert*-butyl cation (and the assumptions applied above to the bibenzyl case) we arrive at 129 kcal/mol for $\Delta H_{\rm het}$ in water, in rough agreement with 119 kcal/mol obtained directly or the 112 kcal/mol using Breslow's $pK_{\rm HA}$ in the correlation equation.

Thus, a wide variety of estimates can be made for the $pK_{\rm HA}$ of isobutane and for the $\Delta H_{\rm het}$ of tetramethylbutane. Using the clearly inappropriate correlation equation, use of Parker's solvation energies with the gas phase $\Delta H_{\rm homo}$ gives an estimate of $\Delta H_{\rm het}$ in water that is *ca.* 10 kcal/mol higher than the correct one of 119 ± 3 kcal/mol in acetonitrile. Although ground-state strain could be invoked as a special factor in tetramethylbutane, it is probably no more than 6 or 7 kcal/mol[20b] which is inadequate to explain any large discrepancies between the various estimates.

Ethane. The ultimate symmetrical hydrocarbon is ethane, for which we have a gas phase BDE = 85.8 kcal/mol[2a] and $\Delta G_{\rm ET}$ = 224 kcal/mol,[12d] from which $\Delta H_{\rm het}$ = 310 kcal/mol in this medium is calculated. Using Parker's[19] hydration free energy for methyl cation, 96 kcal/mol, and the assumptions used above, one arrives at $\Delta H_{\rm het}$ = 118 kcal/mol for ethane in water. The close agreement between this number and that for bibenzyl (120) and tetramethylbutane (130) reflects primarily cancellation of the much greater hardness, $\Delta G_{\rm ET}$, of the methyl radical by the much larger solvation energies of its conjugated ions compared to the comparable properties for the benzyl or *tert*-butyl radicals and ions. Pearson[12d] has discussed the interesting fact that the *local hardness* parameter (58 kcal/mol) for the *tert*-butyl cation is superior to that of CH_3^+ (53) in the gas phase. The equivalent property for benzyl cation is 56 kcal/mol.

If the above estimate for $\Delta H_{\rm het}$ of ethane in water is used with Bordwell's[52] estimate of $pK_{\rm HA} = 56$ for methane in a clearly far-fetched use of the correlation equation,[49] an estimate of $pK_{\rm R^+} = -59$ can be obtained for CH_3^+ in equilibrium with CH_3OH at a molar standard state at infinite dilution in water at 25 °C. If instead we consider that $pK_{\rm HA}$ of methane as an acid is close to that of Breslow's value of 71 for isobutane, $pK_{\rm R^+} = -28$ is found for CH_3^+. As another approach to this interesting value consider the increasingly negative $pK_{\rm R}$-s through the series $Ph_3C^+ = -6.63$, $Ph_2CH^+ = -13.2$,[60] $PhCH_2^+ = -22.6$.[31a] Extrapolating this series, a $pK_{\rm R^+}$ of −40 ± 5 seems intuitively plausible for CH_3^+—*caveat emptor*!

Finally, we draw attention to the large differences between the important bond-breaking parameters for making the carbenium ions and carbanions of these symmetrical compounds. For the 9-phenylxanthyl species $pK_{\rm HA} - pK_{\rm R^+} = 27$ pK units compared to 65 for benzyl and either 71 or 85 for *tert*-butyl depending on the choice of $pK_{\rm HA}$, and 115, 111, 109, or 96 for the gap between these properties for CH_3^- and CH_3^+. This interesting difference[18b] is a direct result of the energies required to make the carbanion and carbenium ion of each system from well-standardized precursors, RH and ROH, under well-standardized conditions in DMSO and aqueous strong acid, respectively. It is related closely to the energies for converting the radical to the conjugate ions or vice versa, e.g. $\Delta G_{\rm ET}$ or η. Not surprisingly, the difference is largest for methyl anion and cation.

Summary

The principle of maximum hardness derived from density functional theory provides a useful and very simple way of thinking about the relationships between fundamental processes of bond making/breaking and electron transfer which lie at the basis of observed processes in organic chemistry and which are usually considered quite separately. From various published data we have calculated the hypothetical heats of heterolysis of bibenzyl and tetramethylbutane (bis-*tert*-butyl) in DMSO. Two alternative approaches have been discussed and various estimates for the $pK_{\rm HA}$ of isobutane in this solvent. Rough estimates for the $\Delta H_{\rm het}$ of ethane in water and the $pK_{\rm R^+}$ of CH_3^+ have been made. Attention has been drawn to the important difference $pK_{\rm HA} - pK_{\rm R^+}$ as it relates to the electron transfer free energy, $\Delta G_{\rm ET}$, for creating the cation and anion from their conjugate radical, i.e., the absolute hardness η of the latter.

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