Chemical Bond-Making, Bond-Breaking, and Electron Transfer in Solution

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A method is described for determining heats of heterolysis, ΔH_{het} , from the heats of reaction of resonancestabilized carbenium ions with carbanions in solution. These results can be converted into heats of homolysis, ΔH_{homo} , for the same bonds by combining ΔH_{het} values with electron transfer energies, ΔG_{ET} ($\Delta G_{ET} \approx \Delta H_{ET}$), obtained from redox potentials of the reacting ions. The results provide a comprehensive tabulation of ΔH_{het} , ΔH_{homo} , and ΔG_{ET} values for an extended series of organic compounds and are examined in terms of their interrelationships and a number of related properties of the ions and radicals.

THE ELECTRONIC THEORY OF ORGANIC CHEMISTRY PROvides an extraordinarily powerful intellectual structure for describing the reactivities of the roughly 6 million presently known organic chemicals from methane to DNA, in terms of the breaking and reforming of electron pair bonds (1). Furthermore, these principles relate reactivity to structure in terms of thermodynamics and kinetics within an elegantly simple general framework, which requires only the elaboration of details to describe the most complex reactions.

Because chemical reactions take place through the redistribution of bonding electron pairs, it follows that bond rupture can occur in two ways (Scheme 1, where we use C_a and C_c to refer to the



covalently bound carbons that will become the carbanion C_a^{\ominus} and the carbenium ion C_c^{\oplus} , respectively) and that a detailed knowledge of the energies associated with bond-making and bond-breaking lies at the heart of modern chemical theory. If we consider the electron

pair bond between a carbon atom and some other type of atom X (C:X), the linkage may be broken symmetrically (homolysis) to provide a pair of free radicals (C \cdot and \cdot X) whose reactivity is derived from the unpaired spins of their single electrons, or the bond may be broken unsymmetrically (heterolysis) to produce a pair of ions (C^{\oplus} and X^{\oplus}) or C^{\oplus} and X^{\oplus}), one of which is electron deficient and the other of which is electron rich. Homolysis is favored for the cleavage of nonpolar, relatively symmetrical covalent bonds in the gas phase or in nonpolar solvents (2–5). In contrast, heterolysis is favored for the rupture of highly polar unsymmetrical bonds in polar solvents, especially if there are electrophilic species present to coordinate with the departing anion or strongly nucleophilic ions to displace it by attack on the incipient cation.

Despite the fundamental importance of homolysis and heterolysis for the quantitative treatment of organic reactivity, few data are available for the wide variety of bonding situations encountered in the broad range of organic compounds (6, 7). An inherent problem for the quantitative study of both homolysis and heterolysis is the high reactivity of the free radicals and ions that are produced by the two processes, so that it is difficult to separate the energetics of the initial bond cleavage from secondary processes. However, if one uses ions and radicals that are stabilized by resonance, it is quite feasible to obtain complete quantitative comparisons for a wide range of homolytic and heterolytic processes that are relevant to many processes ranging from biochemistry to the fossil fuels and polymer industries.

Since carbocations, carbanions, and radicals can be stabilized by resonance, quantitative criteria are needed for comparing the tendency of any given bond to choose the more likely pathway for its fragmentation. This article describes a straightforward experimental approach that can provide both homolysis and heterolysis energies in solution for compounds that can cleave to resonance-stabilized ions and radicals. We show that the key to relating the two different types of bond cleavage processes is the electron-transfer energy, a quantity that is readily accessible in many cases through modern electrochemical techniques. With an abundance of these data in hand, we will discuss a few generalizations that relate different types of bond-making and bond-breaking properties to each other.

A Calorimetric Approach

Thermodynamics, unlike kinetics, deals with the difference between two clearly defined states, reactants and products. However, unless the process taking place in the calorimeter is clearly defined, the resulting heat change (and there almost always is one) may lead the investigator to erroneous conclusions. The research leading up to that described below was stimulated by the great interest of

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physical-organic chemists in the relative stabilities of carbenium ions (often referred to as carbonium ions) (8), and carbanions, two of the three most important classes of organic reactive intermediates. Two decades ago the classic investigations of Olah (9–11) demonstrated by a variety of spectroscopic techniques that even quite unstable carbenium ions could be maintained indefinitely in solution provided that very weakly basic, non-nucleophilic solvents (such as SO_2CIF) were used at low temperature and that a powerful Lewis acid (such as SbF_5) was used to dislodge the halogen from an organic halide RX and maintain it as a stable complex anion:

$$RX + SbF_5 \xrightarrow{SO_2CIF}_{-80^{\circ} \text{ to } -120^{\circ}C} R^{\oplus} \stackrel{\Theta}{\to} SbF_5X$$
(1)

Building on this work we succeeded in measuring the heats of formation of a large series of carbenium ions covering an enormous range of stabilities (12-17). Concurrently, Bordwell and his group (18) and Arnett *et al.* (19, 20) developed conditions for comparing the stabilities of anions in dimethyl sulfoxide (DMSO) solution by the abstraction of protons from a wide range of carbon, oxygen, and sulfur acids. We have therefore developed the necessary techniques for making and handling many carbenium ion and carbanion salts in solution and for measuring both their heats of formation and heats of reaction with other species.

Against this background there finally arose the question of whether we could use our calorimetric techniques to measure directly the reactions between carbenium ions and carbanions in solution to form carbon-carbon bonds. If heats of reaction for such processes could be measured, it was only necessary to change the sign of the measured heat change to obtain the heats of heterolysis for breaking the bond under the same conditions (Scheme 1).

An obvious obstacle to this approach was that most carbenium ions with which we had had experience could only be made and stored in superacidic media and all of our experience with carbanions was limited to superbasic systems. Nonetheless, there was precedent going back to the early 1900s showing that highly stabilized species of either type could be made and handled in aqueous solution, and we soon demonstrated to our satisfaction that aqueous solutions of carbenium ions did undergo reaction with aqueous carbanion solutions. Clearly, what was needed to expand the study to less stable members of each species was an appropriate solvent that was stable to attack by strongly basic carbanions and also by highly reactive carbenium ions. After considerable trial and error we settled on sulfolane (tetramethylene sulfone)



as a remarkably robust solvent, which has allowed the reaction of an enormous range of members of both species with each other.

Heterolysis Energies

In our initial studies of the direct reactions between carbenium ions and carbanions, the goal was to find systems in which the mixed ions were actually at equilibrium with their covalent products. This goal was reached by Troughton and co-workers (21, 22), who studied the remarkable reaction between substituted cyclopropenylium ions and anions of *p*-substituted phenylmalononitrile. Equation 2 leads to the formation of a white crystalline product that may be isolated from such nonpolar solvents as ether or pentane, and whose x-ray structure demonstrates the formation of a covalent bond between the cation and the anion:



 $R = CH_3, C_6H_5$

When this material is redissolved in ether and a polar solvent, such as acetonitrile, is titrated into the solution, the purple color of the anion gradually reappears, demonstrating that the carbon-carbon covalent bond is actually being broken simply by the change of solvent from a nonpolar to a polar one. The reaction is reversible and can actually be run back and forth by adding ether or acetonitrile. Thus the principal driving force for heterolysis in solution is the solvation energy of the ions produced by cleavage of the neutral species.

Experimental Methods

Equilibrium constants for the reaction of several combinations of resonance-stabilized carbenium ions and carbanions were obtained at a series of temperatures and provided a tabulation of the basic thermodynamic properties (standard free energy ΔG^0 , standard enthalpy ΔH^0 , and standard entropy ΔS^0) for the forward coordination reaction between the ions and their reversed heterolysis (23, 24). In several cases the enthalpy of reaction, determined by application of the van't Hoff equation to the temperature coefficient of the equilibrium constant, was checked by direct measurement of the heat of reaction of the cation and the anion in a calorimeter. The two types of determination agreed within experimental error.

The facile determination of free energies of reaction is limited to processes that are close to equilibrium. In contrast, calorimetric determination of heats of reaction is usually easier for reactions that go completely and cleanly to products. Accordingly, our extensive investigation of heats of heterolysis for a wide range of carbenium ions and carbanions, including relatively unstable members, has been limited only by the stability of the solvent, the solubility of appropriate salts of the ions, and clean formation of a single product.

As stated before, sulfolane is a nearly ideal solvent, permitting the study of ions over a range of acidity and basicity of nearly 45 orders of magnitude. In addition, this liquid has a high dielectric constant $(36.42 \text{ at } 30^{\circ}\text{C})$ (25, 26) and is a surprisingly good solvent for ions as well as the nonpolar reaction products. A slight drawback lies in its high freezing point (26°C). However, the addition of 5% 3-methylsulfolane reduces the freezing point well below 25°C, a convenient temperature for calorimetry, without affecting its stability to acids and bases. Although several types of solution calorimeters are appropriate for most of the reactions we have studied, the Tronac model 450 (TRONAC Corporation, Orem, Utah) is a convenient, relatively inexpensive, off-the-shelf and reliable, commercial product that we have used for virtually all of this study.

In order to measure a heat of reaction, solutions of the cation and anion are prepared within a high-quality argon-filled dry box. Usually the potassium salt of the carbanion is used, and the tetrafluoroborate salt of the cation is prepared by standard methods (27-29). The solution of one of the ions is charged to the argonpurged calorimeter vessel inside the dry box and transferred to the calorimeter under argon pressure. The solution of the other reacting ion is transferred within the dry box to a syringe, which is affixed to a constant-drive mechanism for delivery as a thermometric titrant to the calorimeter. Heat is detected with an appropriate thermistor in the well-stirred calorimeter vessel and is presented as a strip chart thermogram—a plot of temperature change versus time. The heat output is calibrated with a small electric heater in the calorimeter vessel, and the time coordinate of the strip chart is calibrated in terms of pumping rate and the concentration of the titrant being pumped into the calorimeter. Experimental errors are given as standard deviations on the basis of five to seven replica measurements with the same batch of solution in the calorimeter. In many cases the complete experiment was repeated with completely new batches of materials many months later.

More than 200 heats of heterolysis have been derived from the heats of reaction of ten resonance-stabilized carbenium ions with a variety of resonance-stabilized carbanions, oxanions, thianions, and

Table 1. Structures of cations and anions. The counterion for the cations is tetrafluoroborate and for anions is potassium. Abbreviations: Me, methyl; Ph, phenyl; G = phenyl or phenylthio or cyano or methoxycarbonyl or phenylsulfonyl.



nitranions (27–29), providing an extensive picture of the effects of molecular structure change on the stabilities of a wide variety of covalent bonds to heterolytic cleavage. A crucially important component in authenticating the above results has been the analysis of the reaction products by high-pressure liquid chromatography. In a number of cases the products have been isolated and examined by nuclear magnetic resonance (NMR). The structures of the carbenium ions and carbanions used in this study are shown in Table 1. In Table 2, typical results are shown for some of the reactions of several carbenium ion–carbanion combinations and the energies for breaking the bond that was formed. [A complete tabulation of data for carbenium ion–carbanion coordinations is given in (28).] Corresponding results for C–O, C–N, and C–S bonds are being prepared for publication.

Prediction Equations

With the heats of heterolysis having been obtained, it is reasonable to ask what other properties are related to these values. Intuition suggests that heats of heterolysis, ΔH_{het} , should be related to the stabilities of the cation and anion being produced—the stabler the ions, the lower the heterolysis energy (30). In fact, remarkably successful prediction equations follow from this notion.

The appropriate criterion for anion stability is the pK_a of its acid precursor. The pK_a values of more than 1300 organic acids have been determined by Bordwell and his group by an elegant indicator method that uses DMSO as solvent and its potassium salt as the base (18). The traditional measure of carbenium ion stability is the pK_{R^+} (the negative logarithm of the equilibrium constant for ionizing the carbinol at a standard state of high dilution in water). Unfortunately, there is only a limited number of such values, and they are obtained in many cases by a long, linear, free-energy extrapolation based on the use of a special acidity function, H_R , constructed in a series of aqueous acid solutions covering the range from about 1 to



Fig. 1. Relations of heats of heterolysis for C–C bonds with ion stabilization properties. Equation 1: $\Delta H_{het} = 8.895 + 1.294pK_a - 0.648pK_{R^+}$; standard error of estimate = 0.932. Equation 2: $\Delta H_{het} = 13.18 + 1.307pK_a - 0.324pK_{R^+}$; standard error of estimate = 1.576. Equation 1: \Box , trimethylcy-clopropenylium; \blacklozenge , triphenylcyclopropenylium; \diamondsuit , 9-phenylxanthylium; \blacksquare , trimethylcyclopropenylium; \bigtriangleup , y, 9'-dimethyl-10-phenyl-9,10-dihydroantracenium. Equation 2: \blacktriangle , tropylium; \bigtriangleup , xanthylium; \Box , 4,4'-dimethoxydiphenylmethyl. [Adapted from (28) with permission of the American Chemical Society]

Table 2. Various measures of the stabilities of carbenium ions and their corresponding radicals; pK_{R^+} is the negative logarithm of the equilibrium constant for carbinol and carbenium ion in aqueous acids; E_{V_2} is the reduction potential of the cation in sulfolane/3-methylsulfolane (5%) at 25°C; CRP is the bond dissociation energy of the carbinol C–OH bond; ΔH_{cmf} , ΔH_{cmp} , and ΔH_{tp} are, respectively, the heats of heterolysis of the carbocations with 9-methoxycarbonylfluorenide, 4-methoxycarbonylphenoxide, and thiophenoxide in sulfolane/3-methylsulfolane (5%), measured in the calorimeter at 25°C.

Cation	pK _{R⁺}	$E_{\frac{1}{2}}$ (V)	CRP (kcal/mol)	$\frac{\Delta H_{\rm cmf}}{\rm (kcal/mol)}$	$\frac{\Delta H_{\rm cmp}}{\rm (kcal/mol)}$	$\Delta H_{ m tp}$ (kcal/mol)	
Trityl	-6.63	-0.133	12.2	25.8 ± 0.4	35.6 ± 3.1	29.3 ± 0.6	
4,4'-Dimethoxydiphenylmethyl	-5.65	-0.450	18.1	27.3 ± 0.7	41.5 ± 1.9	26.5 ± 1.2	
9,9'-Dimethyl-10-phenyl-	-5.49	-0.133	10.6	26.2 ± 0.5	32.4 ± 0.5	27.1 ± 0.4	
9,10-dihydroanthracenium					,		
Xanthylium	-0.84	-0.347	9.15	27.3 ± 0.8	24.5 ± 0.3	26.4 ± 0.4	
9-Phenylxanthylium	1.1	-0.352	6.84	22.4 ± 0.9	18.3 ± 0.1	26.1 ± 0.4	
Triphenylcyclopropenylium	3.1	-1.304	25.8	20.6 ± 0.1	16.3 ± 0.3	20.1 ± 0.4	
Tropylium	4.7	-0.622	7.90	24.9 ± 0.5	14.2 ± 0.4	20.2 ± 0.1	
Trimethylcyclopropenylium	7.4	-1.375	21.6	16.5 ± 0.2			
Perinaphthenium		-0.013		25.0 ± 0.2	36.4 ± 0.8	22.4 ± 0.6	
2,4,6-Triphenylpyrylium		-0.770		9.03 ± 0.30	7.67 ± 0.42	9.05 ± 0.12	

96% sulfuric acid. Nonetheless, as shown in Fig. 1, ΔH_{het} values for a number of compounds formed by combinations of the cations and anions listed in Table 1 are predicted extraordinarily well with the stabilities of the product ions by simple equations of the form:

$$\Delta H_{\rm het} = {\rm const.} + apK_{\rm a} - bpK_{\rm R^+} \tag{3}$$

Such a simple equation is, in fact, too good to be true for all the varied systems we have studied. Not surprisingly, the cause of its breakdown lies in the weakness of the pK_{R^+} values determined in aqueous acidic media for the cleavage of carbon-oxygen bonds as a model for the reaction of many other types of species in anhydrous sulfolane. A variety of alternative carbenium ion stability parameters have been used, some with good success, with equations no more complicated than Eq. 2. See, for example, Fig. 2, where the heat of heterolysis of the carbenium ions with 9-methoxycarbonylfluorenide ion (ΔH_{cmf}) has replaced $-pK_{R^+}$.

Electron Transfer Energies—the Key to Relating Heterolysis to Homolysis

As their names imply, the essential difference between homolytic and heterolytic processes for the cleavage of covalent bonds lies in whether the electron pair is divided evenly to produce a pair of free radicals or whether one of the participating atoms in the bond departs with both the electrons as an anion to leave behind an electron-deficient carbenium ion. Only in the rarest cases will these two processes have equivalent energies, which would result in an equal number of (i) carbenium ions plus carbanions and (ii) radicals from cleavage of a given compound under a given set of conditions. In fact, the types of species and conditions that produce radicals are usually so different from those that lead to ionization that they are normally treated as totally different areas of organic chemistry, appearing in widely separated sections of introductory textbooks and involving totally different communities of scientists. Nonetheless, there are many well-documented cases where free radicals are produced by electron transfer between carbenium ions and carbanions, as well as examples of the reverse process (31, 32).

Under carefully chosen circumstances it is feasible to maintain a system in which all three types of reactive intermediates are at equilibrium with electrons shuttling around between the cations, anions, and radicals (31). As another demonstration of the same principle, we have reported a simple electrolytic cell (Fig. 3) with a solution of carbenium ions on one side and carbanions on the other, with electron flow from one compartment to another to produce an electrical current (33).

More formally, the energy of single electron transfer from the cation to the anion determines exactly the differences between the energies of homolysis and heterolysis (Scheme 2).

$$C_{c} - C_{a} \rightleftharpoons C_{c}^{\ominus} + C_{a}^{\ominus} \qquad \Delta H_{het}$$
(4)

$$C_{c}^{\oplus} + e \rightleftharpoons C_{c}^{\bullet} \qquad \qquad E_{red}(C_{c}^{\oplus}) \qquad (5)$$

$$C_a^{\ominus} \rightleftharpoons C_a^{\bullet} + e \qquad E_{ox}(C_a^{\ominus}) \qquad (6)$$

$$C_c - C_a \rightleftharpoons C_c^{\bullet} + C_a^{\bullet} \qquad \Delta H_{homo}$$
(7)

Scheme 2

Putting all values in units of kilocalories per mole gives the heat of homolysis:

$$\Delta H_{\text{homo}} = \Delta H_{\text{het}} - 23.06[E_{\text{red}}(C_{\text{c}}^{\oplus}) - E_{\text{ox}}(C_{\text{a}}^{\ominus})]$$
(8)

Thus the difference between the heterolysis and homolysis energies is the Gibbs free energy of electron transfer, ΔG_{ET} , obtained from the redox potentials of the cation and anion.

If any two of three processes ΔH_{het} , ΔH_{homo} , and ΔG_{ET} are



Fig. 2. Correlation of heats of heterolysis for C–C bonds with modified ion stabilization properties. $\Delta H_{het} = -11.893 + 1.335pK_a + 0.925 \Delta H_{cmf}$, standard error of estimate = 1.055. Symbols plotted are as listed for Fig. 1, plus the following: X, perinaphthenium; +, 2,4,6-triphenylpyrylium. [Adapted from (28) with permission of the American Chemical Society]

known, the other may be calculated precisely. This principle has been used extensively to relate gas-phase acidities, bond dissociation energies, and electron affinities (34–36). Recently Bordwell and Bausch (37) have calculated the bond dissociation energies (BDEs) for many carbon-hydrogen bonds from the pK_a of the carbon acid and the oxidation potential of the resulting carbanion. This approach is extended in Scheme 2, where a variety of carbenium ions rather than just the proton can be the acid.

One can obtain the necessary electron-transfer energy by measuring the oxidation potential of the anion and the reduction potential of the carbenium ion in solution. This is achieved experimentally with commercial cyclic voltammetry equipment, which frequently requires use of second-harmonic ac voltammetry (SHACV) in order to obtain reversible redox potentials. Scheme 2 also implies the questionable mingling of enthalpies of heterolysis with redox potentials, which are free-energy terms. These different thermodynamic properties can be used together provided that a correction is made for the redox entropies, which in turn may be evaluated by determining the redox potentials at several different temperatures T, since $\Delta S = -(\partial \Delta G/\partial T)$. If the requirements of reproducibility and entropy correction are met, ΔH_{homo} values can be calculated directly from the calorimetrically obtained ΔH_{het} values and the redox potentials. A sampling of the complete set of data for one carbenium ion and seven carbanions is shown in Table 2. At present we now have in hand a total data set comparing ΔH_{homo} , ΔH_{het} , and ΔG_{ET} $(\approx \Delta H_{\rm ET})$ values for more than 118 carbenium ion-anion combinations.

The comparison of heterolysis and homolysis energies for the cleavage of covalent bonds between carbon and other atoms is an extension of the more familiar properties for breaking the bond from carbon to hydrogen. Removal of a proton to produce an anion is a common heterolytic process that can be described theoretically in the same way as the pK_a for ionization. Hundreds of such values have been tabulated (18, 38). The energy of equivalent homolytic process for removal of hydrogen as an atom is referred to as the BDE (2–5, 37). There are so few data for homolysis energies of other types of bonds that the energy of hydrogen atom removal is widely referred to as the BDE, although it is only one member of a large class of bond dissociation energies.

Relations Between Properties

With a good supply of energies for homolysis, heterolysis, and electron transfer in hand, what can be said about their relations to each other and to other important properties of the cations, anions, and radicals? In Fig. 4 we plot ΔH_{het} versus ΔH_{homo} for 60 systems that we have analyzed by the above method. Clearly there is no significant relation between the effect of structure on these two properties, nor is there any good reason to expect one. Homolysis converts a neutral covalent compound to a pair of neutral free radicals. In contrast, heterolysis takes a neutral species to a pair of charged ions. Because of the enormous contribution of solvation energy to the stabilization of ions and its negligible effect on radicals, it is reasonable to formulate a general rule that processes that involve the formation of ions from neutral species or vice versa will correlate well with each other, whereas processes that do not involve the creation or loss of charge will correlate with $\Delta H_{\rm homo}$

For example, we have described above the strong relations, such as those in Fig. 1, that are obtained by relating ΔH_{het} to the pK_a values for ionization of the neutral precursors of the anions formed from heterolysis and the pK_{R^+} values for creation of the carbenium ions from their parent carbinols. Here also, oxidation potentials

apply to the conversion of carbanions to their neutral free radicals and reduction potentials to the conversion of carbenium ions to radicals. Strong linear relations have been found between the pK_a and E_{ox} values of the anions (39). All of these properties, ΔH_{het} , pK_a , E_{ox} , and E_{red} , give linear plots against each other. The same factors that contribute to differential stabilization of the ions internally by substituent factors, or externally by solvation, contribute in similar ways to each one of these properties. Unfortunately, so few data are available for the generation of the radicals discussed here from neutral precursors that we have few properties to compare with our ΔH_{home} measurements.

Acidity Oxidation Potentials and Carbinol Reduction Potentials

Bordwell and Bausch (37) proposed the concept of acidity oxidation potential (AOP) for a wide variety of anions to evaluate



Fig. 3. Carbocation-carbanion cell showing taps at the bottom for removal of samples. [Adapted from (*33*) with permission of *Tetrahedron Letters*]



Fig. 4. Plots of heats of heterolysis versus heats of homolysis for seven fluorenide ions with nine cations. Symbols are as listed for Figs. 1 and 2. [Adapted from (28) with permission of the American Chemical Society]

Table 3. Heats of heterolysis, homolysis, and free energy of electron transfer (in kilocalories per mole) of trityl cation with fluorenides in sulfolane/3methylsulfolane (5%) at 25°C. For the trityl cation, $pK_{R^+} = -6.63$ and CRP = 28.88 (see Table 2). pK_a is the negative logarithm of the equilibrium constant of the reaction C–H \Rightarrow C⁻ + H⁺ in DMSO. E_{V_2} of oxidation from anion to radical measured in sulfolane/3-methylsulfolane at 25°C by cyclic voltammetry or second harmonic alternating current voltammetry. SD = ± 0.025 V. AOP is defined by the equation AOP = $1.37pK_a + 23.06E_{ox}(C^-)$. We measured ΔH_{het} in a calorimeter at 25°C, using $\Delta H_{het} = -\Delta H_{rxn}$. ΔH_{homo} was calculated by use of the equation $\Delta H_{homo} = \Delta H_{het} + \Delta G_{ET}$, where $\Delta G_{ET} = 23.06 [E_{V_2}(C^-) - E_{V_2}(C^+)]$; SD = ± 3.5 kcal/mol.

Anion	pK _a	$\begin{array}{c}E_{\frac{1}{2}}\left(\mathrm{ox}\right) \\\left(\mathrm{V}\right) \end{array}$	AOP	$\Delta H_{ m het}$	$\Delta G_{\rm ET}$	$\Delta H_{ m homo}$
9-Phenylfluorenide	17.9	-1.101	-0.87	35.51 ± 0.56	-22.32	13.18
9-Phenylthiofluorenide	15.4	-0.882	0.76	33.61 ± 0.34	-17.27	16.34
2-Bromo-9-phenylthio- fluorenide	13.2	-0.732	1.20	29.41 ± 0.52	-13.81	15.60
9-Phenylsulfonylfluorenide	11.55	-0.392	6.78	28.35 ± 0.59	-5.97	22.38
9-Methoxycarbonylfluorenide	10.35	-0.555	2.83	25.81 ± 0.42	-9.73	16.08
9-Cvanofluorenide	8.30	-0.481	0.28	24.62 ± 0.62	-8.02	16.60
2,7-Dibromo-9-methoxycarbonylfluorenide	6.52	-0.286	2.34	19.76 ± 0.85	-3.53	16.23



Fig. 5. Plots of heats of homolysis for C–C bonds versus radical stabilization properties. $\Delta H = 8.74 + 1.05(\text{AOP} + \text{CRP})$; standard error of estimate = 4.767. Symbols are as listed for Figs. 1 and 2, plus the following: *, triphenylcyclopropenylium and trimethylcyclopropenylium in acetonitrile.

the effects of structural change on the stabilities of their corresponding radicals:

$$C_a - H \rightarrow C_a^{\ominus} + H^+ \qquad pK_a$$
 (9)

$$C_{a}^{\ominus} \rightarrow C_{a}^{\bullet} + e \qquad E_{ox}(C_{a}^{\ominus})$$
 (10)

$$C_a - H \rightarrow C_a^{\bullet} + H^{\bullet}$$
 AOP (11)

$$AOP = 1.37pK_a + 23.06E_{ox}(C_a^{\ominus})$$
 (12)

The differential AOPs for a series of related carbon acids, C_a-H , provide the relative BDEs for the C–H bonds, which, in turn, compare the stabilities of their radicals relative to their respective acid precursors. This type of analysis may now be extended to the other half of the homolysis problem, to C_a-C_c bonds in which a series of C_a^{\bullet} radicals are formed rather than just a hydrogen atom. We define the carbinol reduction potential (CRP) as the homolytic bond energy for the C_c –OH bond in one of the carbinols used to prepare its corresponding carbenium ion in the series that was used to measure ΔH_{het} values:



Fig. 6. Plot of heats of homolysis for C–C bonds versus modified radical stabilization properties. $\Delta H = -14.70 + 1.01$ [AOP + $\Delta H_{cmf} - E_{1/2}$ (red)]; standard error of estimate = 1.375. Symbols are as listed in Figs. 1, 2, and 5.

$$C_{c}^{\oplus} + H_{2}O \rightarrow C_{c} - OH + H^{+} \qquad pK_{R^{+}} \qquad (13)$$

$$H^+ + OH^- \to H_2O \qquad -pK_{auto} \qquad (14)$$

$$C_c - OH \rightarrow C_c^{\oplus} + OH^{\ominus} - pK_{R^+} + pK_{auto}$$
 (15)

$$OH^- \rightarrow {}^{\bullet}OH + e \qquad E_{ox}(OH^-) \qquad (16)$$

$$C_{c}^{\oplus} + e \rightarrow C_{c}^{\bullet} \qquad -E_{red}(C_{c}^{\oplus}) \qquad (17)$$

$$C_c - OH \rightarrow C_c^{\bullet} + {}^{\bullet}OH \qquad CRP \qquad (18)$$

$$CRP = -1.37pK_{R^+} - 23.06E_{red}(C_c^{\oplus})$$
(19)

Because $E_{\rm ox}(\rm OH^-)$ and $pK_{\rm autoprotolysis}$ ($pK_{\rm auto}$) are both constants for the series of carbenium ions and their C[•]_c radicals, their CRPs are a measure of their radical stabilities relative to each other and to their carbinol precursors. Thus, CRPs are relative C_c–OH bond dissociation energies. Unlike the AOPs of Bordwell and Bausch (37), for which both the $pK_{\rm a}$ and $E_{\rm ox}(\rm C_{a}^{\ominus})$ were measured under a single set of conditions in DMSO, the CRPs presented here combine $pK_{\rm R^+}$ values measured in aqueous sulfuric acid solutions (from 0.75 to



Fig. 7. Plot of heats of homolysis versus radical stabilization properties for C-C, C-S, and C-O bonds. $\Delta H = 11.70 + 0.82(AOP + CRP)$; standard error of estimate = 4.566. [Adapted from (28) with permission of the American Chemical Society]

65% aqueous H_2SO_4) with $E_{red}(C_c^{\oplus})$ measured in sulfolane/3methylsulfolane and so are inherently more complex.

Our previous "master equations" provided extrathermodynamic equations for relating ΔH_{het} values to the pK_{R^+} and pK_a values for generation of their component ions. In a similar manner, ΔH_{homo} values are related to estimates of the stabilities of their component radicals through their AOPs and CRPs (28). Such relations provide independent means for predicting the heterolysis and homolysis energies in solution for the cleavage of bonds that produce either resonance-stabilized radicals or carbenium ions and carbanions. Following Eqs. 8, 12, and 19, it may be shown (28) that

$$\Delta H_{\text{homo}} = a \text{ (AOP)} + b \text{ (CRP)} + \text{ const.}$$
(20)

This is the formal relation between the energy required to cleave the C_a-C_c bonds to C_a^{\bullet} and C_c^{\bullet} and the corresponding estimates for cleavage of C_a -H and C_c -OH bonds based on pK_a and pK_{R^+} values.

The relation between ΔH_{homo} values and AOP + CRP is shown in Fig. 5 for 48 C_a - C_c bonds, with the pK_{R^+} parameter used as the measure of carbocation stability as defined in Eq. 19. The trend is clearly in the right direction, but the deviations are large (SD = 4.767 kcal/mol). If we scale all carbocation stabilities against their heats of reaction with a single standard carbanion, that is, the methoxycarbonylfluorenide ion as we did for Fig. 2, there is a marked improvement (SD = 1.375 kcal/mol) when we apply this treatment again to the homolysis data by substituting $\Delta H_{\rm cmf}$ for $-1.37pK_{R^+}$ for each cation (Fig. 6).

In Fig. 7 we show the result when all of the homolysis energies for the 118 combinations of carbenium ions with carbanions, phenoxide, and thiophenoxide ions are treated by Eq. 20. Most of the points fall within 5 kcal/mol of the regression line, which is quite good, considering the error involved in the ΔH_{homo} calculation (±3) kcal/mol).

Conclusions

During the last decade homolysis and heterolysis energies in solution have been determined, as well as their relation to each other through the energy of electron transfer between carbenium ions,

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carbanions, and free radicals. Although all chemical reactions take place through the breaking and making of bonds, there has been a dearth of experimental values for the energies of homolytic and heterolytic bond cleavage or, conversely, the corresponding energies for bond formation through coordination and colligation.

The key to the present study is the calorimetric determination of the direct reaction between resonance-stabilized carbenium ions and carbanions to form covalent products in solution at room temperature. The necessary requirement of a solvent that is stable against attack both by strongly basic and strongly acidic media is met by sulfolane. More than 200 ΔH_{het} values have been determined $(\Delta H_{\text{het}} = -\Delta H_{\text{rxn}}, \text{ where } \Delta H_{\text{rxn}} = \Delta H_{\text{reaction}}), \text{ and } 118 \text{ of them}$ have been converted quantitatively into the corresponding ΔH_{homo} values through the redox potentials of the carbenium ion and various anions, as determined in sulfolane by cyclic voltammetry techniques.

In general, ΔH_{het} values are well correlated with properties that convert a neutral species into ions or vice versa, such as the pK_a of the carbanion, the pK_{R^+} of the carbenium ion, or the redox potentials of the ions. Such correlations reflect the important role of electrostatic solvation to the stabilities of the resonance-stabilized ions. However, these properties are not correlated with ΔH_{homo} values or other properties by which neutral species (covalent molecules) are converted into other neutral species such as the radicals.

These results provide a comprehensive collection of experimental values for bond-breaking processes under mild conditions for complex compounds that are of relevance to a wide area of chemistry ranging from polymerization and fossil fuel conversion to biophysical processes.

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"Now, think about that, if rhino horn is really an aphrodisiac, would we really be an endangered species?"