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Determination and Interrelation of Bond Heterolysis and Homolysis Energies in Solution

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Abstract: Heats of homolysis (ΔH_{homo}) for a variety of carbon–carbon bonds have been determined by combining heats of heterolysis with redox potentials for a series of resonance-stabilized carbenium ions and carbanions by means of a simple thermodynamic cycle. The heats of heterolysis (ΔH_{het}) were derived from calorimetrically measured heats of reaction by changing the sign ($\Delta H_{\text{het}} = -\Delta H_{\text{rxn}}$). Redox potentials were determined by cyclic voltammetry and second harmonic alternating current voltammetry (SHACV), which produced excellent reversible electrochemical data. The difference between ΔH_{het} and ΔH_{homo} is the enthalpy of electron transfer, which for the systems studied here is approximated closely by the free energy of electron transfer (ΔG_{ET})—the difference between the free energy of oxidation of the carbanion and the free energy of reduction of the cation. In order to obtain ΔH_{homo} values from ΔH_{het} and ΔG_{ET}, it is necessary for ΔS_{ET} to be negligible. This is shown to be true for the systems reported here. The heats of homolysis and heats of heterolysis determined under this project are the first available thermodynamic data that allow comparison of the two primary modes of bond cleavage in solution for the bonds linking the component fragments of the types of large molecules that are important to the polymer and fossil fuel industries. A variety of correlations are presented between the pK_a's of the carbanions, the pK_{R^+}'s of the carbenium ions, the redox potentials of both types of ions, the ΔG_{ET}'s, the ΔH_{het}'s, and the ΔH_{homo}'s. Good linear correlations are obtained between most of the properties that involve the conversion of ions to neutral products or vice versa. Thus, ΔH_{het} correlates well with ΔG_{ET}. However, ΔH_{homo}, which involves the conversion of a neutral molecular species to a pair of electrostatically neutral free radicals, correlates poorly with these types of data. In general, ΔH_{het}'s and ΔG_{ET}'s are much more sensitive to structural change in the carbenium ions and carbanions than are the ΔH_{homo}'s to the formed radicals. The carbinol reduction potential (CRP) is defined as the free energy of homolysis for the carbon–oxygen bonds in triarylcarbinols (and related compounds). The CRP is the sum of the pK_{R^+} of the carbenium ion and its reduction potential. It is analogous to the acid oxidation potential (AOP) as defined by Bordwell and Bausch for the free energy of homolysis (relative bond dissociation energies) of carbon–hydrogen bonds in carbon acids. It is shown that to a good approximation $\Delta H_{\text{het}} = a\text{p}K_a + b\text{p}K_{R^+} + \text{constant}$ and $\Delta H_{\text{homo}} = c\text{AOP} + d\text{CRP} + \text{constant}$. Thus, heterolysis and homolysis energies can be determined experimentally from heats of reaction of resonance-stabilized ions and their redox potentials or estimated from their pK_a's, pK_{R^+}'s, and redox potentials. This work indicates that carbon–carbon bond cleavage may proceed with greater selectivity when resonance-stabilized ionic species rather than free-radical species are the initially formed reactive intermediates. Further research should expand insight as to the generality of these results as well as the factors that control the magnitude of bond cleavage selectivity differences.

Interactions between cations and anions can produce ion pairs of various degrees of intimacy, charge-transfer complexes, free radicals, or covalent bonds. Extensive studies[1-10] of the reactions of resonance-stabilized carbenium ions with inorganic anions have contributed to the understanding of nucleophilicity since the direct reaction of electrophile and nucleophile takes place without the complications of displacing a leaving group. Several years ago we undertook an investigation of the kinetics and thermodynamics of the direct reaction between resonance-stabilized carbanions and carbenium ions in nonacidic, nonbasic media.[11-20] Approaches similar to ours have recently demonstrated the existence of equilibria between resonance-stabilized cations, anions, radicals, and covalently bonded species in solution.[21-23] Although there was clear evidence that radicals had been formed by single electron transfer (SET) in some cases, the main emphasis of our study was on the two-electron processes to form a covalent bond by coordination and the reverse process—bond heterolysis.

Subsequently, we have extended the original study of relatively stable carbanions and carbocations to much more reactive ones. With the use of the robust solvent tetramethylenesulfone (sulfolane), heats of reaction have been measured for over 245 combinations of carbenium ions and a variety of carbanions, phenoxy, thiophenoxy, and nitrogen anions. Most of these reactions are so far from equilibrium that it would be impossible to determine free energies of reaction, but the instantaneous and clean reactions in sulfolane at 25 °C are ideal for reaction calorimetry. By changing the sign ($-\Delta H_{\text{rxn}} = \Delta H_{\text{het}}$), an extensive table of heats of heterolysis was developed,[19] and these were related in a very simple manner to the stabilities of the carbenium ions and carbanions as represented by their pK_{R^+}'s and pK_a's.

The present paper now provides a methodology for the quantitative evaluation of the energies required for the *homolysis* of

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(1) Ritchie, C. D. *Can. J. Chem.* **1986**, *64*, 2239.
(2) Ritchie, C. D. In *Nucleophilicity*; Harris, J. M., McManns, S. P., Eds.; American Chemical Society: Washington, DC, 1987; p 169.
(3) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348.
(4) (a) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1986**, *108*, 7023. (b) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929. (c) McClelland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 6913. (d) McClelland, R. A.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 5860.
(5) Katritzky, A. R.; Musumarra, G. *Chem. Soc. Rev.* **1984**, *13*, 47.
(6) Kessler, H.; Fiegel, M. *Acc. Chem. Res.* **1982**, *15*, 2.
(7) Okamoto, K.; Takeuchi, K.; Komatsu, K.; Kubota, Y.; Ohara, R.; Arima, M.; Takahashi, K.; Waki, Y.; Shirai, S. *Tetrahedron* **1983**, *39*, 4011.
(8) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *98*, 8238.
(9) Richard, J. P.; Rothenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361.
(10) Feldman, M. R.; Flythe, W. C. *J. Org. Chem.* **1978**, *43*, 2596.
(11) Arnett, E. M.; Troughton, E. B. *Tetrahedron Lett.* **1983**, *24*, 3229.
(12) Arnett, E. M.; Troughton, E. B.; McPhail, A.; Molter, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 6172.
(13) Troughton, E. B.; Molter, K. E.; Arnett, E. M. *J. Am. Chem. Soc.* **1984**, *106*, 6726.
(14) Arnett, E. M.; Chawla, B.; Molter, K.; Amarnath, K.; Healy, M. *J. Am. Chem. Soc.* **1985**, *107*, 5288.
(15) Arnett, E. M.; Molter, K. E. *J. Phys. Chem.* **1986**, *90*, 471.
(16) Arnett, E. M.; Molter, K. E. *Acc. Chem. Res.* **1985**, *18*, 339.
(17) Arnett, E. M.; Molter, K. E.; Marchot, E. C.; Donovan, W. H.; Smith, P. *J. Am. Chem. Soc.* **1987**, *109*, 3788.
(18) Arnett, E. M.; Chawla, B.; Amarnath, K.; Whitesell, L. G., Jr. *Energy Fuels* **1987**, *1*, 17.
(19) Arnett, E. M.; Whitesell, L. G., Jr.; Amarnath, K.; Cheng, J.-P.; Marchot, E. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 21.
(20) Arnett, E. M.; Whitesell, L. G., Jr.; Cheng, J.-P.; Marchot, E. *Tetrahedron Lett.* **1988**, *29*, 1507.
(21) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Takahashi, K. *J. Chem. Soc., Chem. Commun.* **1985**, 173.

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many of the carbon–carbon, carbon–oxygen, carbon–nitrogen, and carbon–sulfur bonds for which we have previously measured ΔH_{het}'s. By combining the ΔH_{het}'s and the redox potentials of the resonance-stabilized product ions through a simple thermodynamic cycle, homolysis energies may be calculated for production of the corresponding radicals and the complete set of energetics for homolytic, heterolytic, and electron-transfer reactions related to each other.

These data provide the first available quantitative criteria for the selective cleavage of such bonds in any system that can be cleaved to give resonance-stabilized cations, anions, or radicals. The results should help in the development of basic principles for understanding and predicting the conditions for replacing high-temperature homolytic processes with mild, selective heterolytic ones, providing fundamental comparisons between the factors that stabilize radicals, carbenium ions, and carbanions.

Despite the importance of homolysis energies to the fossil fuel industries[24] and many other areas of free-radical chemistry, there are relatively few experimental determinations of the heterolytic or homolytic bond energies for carbon–carbon, carbon–oxygen, carbon–sulfur, carbon–nitrogen, etc., bonds. The principal reason for this deficiency lies in the extreme instability of the simple reactive species that would result from bond cleavage so that they are very difficult to study directly, and their formation is often circumvented by more energetically favorable displacement reactions.

The sparse literature on homolysis energies is limited to Gomberg-type equilibria between resonance-stabilized radicals and their dimers;[24-28] homolysis energies derived from photolysis or pyrolysis of small, symmetrical compounds such as hydrocarbons and peroxides;[29-38] or values estimated by Benson's method of group equivalents.[39] Again, by analogy to proton-transfer pK_a values, homolytic energies for bonds from main-group elements to hydrogen form a special subset of bond dissociation energies (BDE's), which have been measured and calculated by a variety of methods.[40-43] Recently Bordwell and his students have successfully attacked the conversion of their many pK_a values in dimethyl sulfoxide to BDE's through measurement of oxidation potentials of the appropriate anions using cyclic voltammetry and combining these with pK_a's of the conjugate acids of the anions in an appropriate cycle.[44] Such a cycle has been used by Arnold to calculate pK_a's of radical cations from gas-phase BDE's.[45] Our method is analogous to that of Bordwell[44] and Brauman[46] but differs in that a series of carbocations takes the place of the proton.

Following a preliminary communication,[47] a full presentation of data obtained to date for cleavage of carbon–carbon bonds will be given in this paper. Comparable results for C–O, C–N, and C–S bonds will be presented in later reports.

Use of ΔH_{het}'s for determining the heat of homolysis (ΔH_{homo}) employs a strategy similar to that of Bordwell[44] and Brauman[46] for estimating the corresponding BDE's. We combine the redox potentials of the carbenium ions (C_c^+) and carbanions (C_a^-) with the heats of heterolysis for the C_c–C_a bonds to give the corresponding heats of homolysis for production of the resonance-stabilized radicals.

Scheme I

$$C_c\text{–}C_a \rightleftharpoons C_c^+ + C_a^- \qquad \Delta H_{het} \qquad (1)$$

$$C_c^+ + e^- \rightleftharpoons C_c^\bullet \qquad E_{red}(C_c^+) \qquad (2)$$

$$C_a^- \rightleftharpoons C_a^\bullet + e^- \qquad E_{ox}(C_a^-) \qquad (3)$$

$$C_c\text{–}C_a \rightleftharpoons C_c^\bullet + C_a^\bullet \qquad \Delta H_{homo} \qquad (4)$$

Finally, to put all values in units of kilocalories per mole

$$\Delta H_{homo} = \Delta H_{het} - 23.06[E_{red}(C_c^+) - E_{ox}(C_a^-)] \qquad (5)$$

Scheme I shows that *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. In contrast to using DMSO, which has been an appropriate solvent for Bordwell's studies of weak acids and carbanions, we have had to use sulfolane, a high-polarity medium that is remarkably impervious to attacks, by both carbanions and carbenium ions. Most of our measurements have been made at 25 °C in 95% sulfolane. 3-Methylsulfolane (5%) was added to lower the freezing point.

Two obstacles stand in the way of applying this approach: First is the requirement of obtaining reversible redox potentials for the carbocations and carbanions. Bordwell has encountered this difficulty with many carbanions but has provided good reasons why it should not be a serious problem.[44] We have used second-harmonic ac voltammetry (SHACV)[48] to obtain reversible potentials in many cases and can confirm values obtained by Bordwell's group for a number of anions.

The second problem is more fundamental—the mingling of ΔH_{het} enthalpic measurements with redox free energy terms. For the favorable case where entropy terms associated with electron transfer are negligible, ΔG_{ET} may be combined directly with ΔH_{het}: if $\Delta S_{ET} = 0$, then $\Delta G_{ET} = \Delta H_{ET}$. Otherwise, ΔS_{ET} must be evaluated and corrected for by the familiar expression $\Delta H_{ET} = \Delta G_{ET} + T\Delta S_{ET}$, where ΔS_{ET} can be determined through the temperature coefficient of the redox potential. We are unaware of such published data for ions of the types reported here but have

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(22) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Miyabo, A. *J. Chem. Soc., Chem. Commun.* **1988**, 923.

(23) Komatsu, K.; Aonuma, S.; Takeuchi, K.; Okamoto, K. *J. Org. Chem.* **1989**, *54*, 2039.

(24) Stein, S. E. In *The Chemistry of Coal Conversion*; Schlosberg, R. H., Ed.; Plenum Press: New York, 1983; Chapter 2, pp 13–44.

(25) Manka, M. J.; Brown, R. L.; Stein, S. E. *J. Phys. Chem.* **1985**, *89*, 5421.

(26) Bachmann, W. E.; Wiselogle, F. Y. *J. Org. Chem.* **1936**, *1*, 354.

(27) Coops, J.; Galenkamp, H.; Haantjes, J.; Luirink, K. L.; Nauta, W. T. *Recl. Trav. Chim. Pays-Bas* **1948**, *67*, 469.

(28) Coops, J.; Nauta, W. T.; Ernsting, M. J. E.; Faber, A. C. *Recl. Trav. Chim. Pays-Bas* **1940**, *59*, 1109.

(29) Benson, S. W.; O'Neal, H. E. *Kinetic Data on Gas Phase Unimolecular Reactions*; National Standard Reference Data Series 21; U.S. National Bureau of Standards; Washington, DC, 1970.

(30) Robaugh, D. A.; Stein, S. E. *Int. J. Chem. Kinet.* **1981**, *13*, 445.

(31) Poutsma, M. L. *Fuel* **1980**, *59*, 335.

(32) Brower, K. R. *J. Org. Chem.* **1980**, *45*, 1004.

(33) Cronauer, D. C.; Jewell, D. M.; Shah, Y. T.; Kueser, K. A. *Ind. Eng. Chem. Fundam.* **1978**, *17*, 29.

(34) Miller, R. E.; Stein, S. E. *J. Phys. Chem.* **1981**, *85*, 580.

(35) Stein, S. E.; Robaugh, D. A.; Alfieri, A. D.; Miller, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 6567.

(36) Rüchardt, C.; Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 529.

(37) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(38) Kanabus, J. M.; Gilbert, B. C.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 3311.

(39) (a) Benson, S. W. *Thermochemical Kinetics*, 2nd ed., John Wiley & Sons: New York, 1976; p 272. (b) Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502. (c) Benson, S. W.; Buss, J. *J. Chem. Phys.* **1958**, *29*, 546.

(40) (a) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125. (b) McMillan, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493. (c) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279. (d) Eggers, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516. (e) Tsang, W. *J. Am. Chem. Soc.* **1985**, *107*, 2872.

(41) (a) Catelhano, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655. (b) McLoughlin, R. G.; Traeger, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5791. (c) Lossing, F. P.; Traeger, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 1579. (d) Lossing, F. P. *Can. J. Chem.* **1971**, *49*, 357.

(42) Wentrup, C. *Reactive Molecules: The Neutral Reactive Intermediates in Organic Chemistry*; John Wiley & Sons: New York, 1984; pp 23–26.

(43) Pearson, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 7684.

(44) (a) Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229. (b) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979.

(45) Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1982**, *20*, 2165.

(46) (a) Brauman, J. I. In *Frontiers of Free Radical Chemistry*; Pryor, W. A., Ed.; Academic Press: New York, 1980; p 23. (b) Janousek, B. K.; Brauman, J. I. In *Gas Phase Ion Chemistry, Vol. 2*; Bowers, M. T., Ed.; Academic Press: New York, 1979; p 53.

(47) Arnett, E. M.; Harvey, N. G.; Amarnath, K.; Cheng, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 4143.

(48) (a) McCord, T. G.; Smith, D. E. *Anal. Chem.* **1969**, *41*, 1423. (b) Bond, A. M.; Smith, D. E. *Anal. Chem.* **1974**, *46*, 1946.

made appropriate measurements in several cases from which we have found that the entropies of electron transfer are small.

It is not obvious why ΔS_{ET} should be negligible. In an earlier study[13] entropies of heterolysis were shown to be small for the neutral, covalent compounds that yield trisubstituted cyclopropenylium cations and arylmalononitrile anions. In that case it was argued that the gain in translational entropy to make two ions from one neutral molecule was being canceled by the loss of entropy of solvent molecules as they were oriented around the ions. In the present case, two ions are being converted to a pair of radicals and one should expect a large gain in entropy as solvent molecules are released from electrostriction.

Possibly the low ΔS_{ET} that we have obtained from the temperature coefficient of $\Delta G_{\mathrm{redox}}$ is an artifact of our method by which electron-transfer processes take place at an electrode surface rather than between ions (or in an ion pair) in solution. Insofar as our assumptions about ΔS_{ET} are incorrect, there will be an error (hopefully a systematic one) in the ΔH_{homo} values reported herein.

In the following report we shall describe our experimental methods, shall present our complete tabulation of ΔH_{het} values for carbon–carbon bonds (many of which have been determined or updated since our last listing),[19] the E_{ox} and E_{red} values for the carbanions and carbocations as measured *reversibly* in sulfolane/3-methylsulfolane solvent by the SHACV method, and the derived ΔG_{ET} and the calculated ΔH_{homo} values, and shall discuss various interrelations between these properties and their pK_a's and pK_{R^+}'s.

Experimental Section

Materials. Commercially available (Aldrich) fluorene was purified by recrystallization from hexane (mp 116–118 °C). Substituted fluorenes were prepared and purified according to procedures reported in the literature.[49-55] The remaining anion precursors were available commercially (Aldrich and Trans World Chemicals) and were purified by standard procedures.[56] The purity of these materials was confirmed by melting point, ^{1}H NMR, and HPLC.

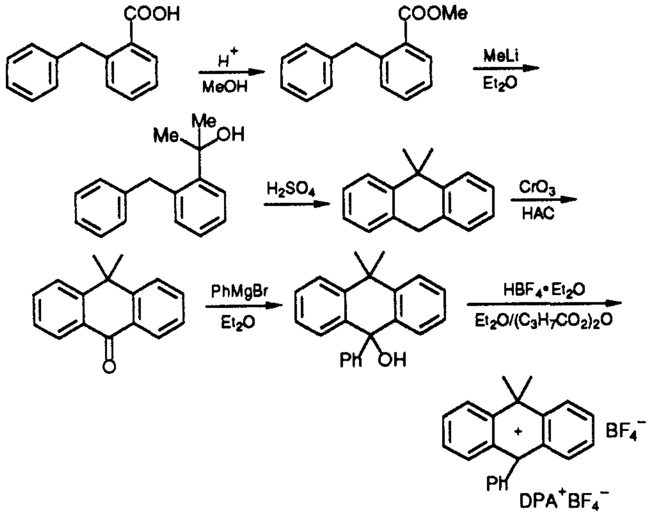
Sulfolane (Phillips Petroleum Co.) was stirred with NaOH pellets overnight at 100–150 °C, while argon was bubbled through the solvent. The sulfolane was decanted from the NaOH and stirred with warming overnight with CaH_2 under an argon atmosphere. The dry solvent was then vacuum distilled [bp = 110–111 °C (1 Torr)] and the first 10% of the distillate discarded. Upon solidifying, the pure dry sulfolane (mp = 28.5 °C[57]) formed a colorless, transparent glass, which was protected from contact with air.

3-Methylsulfolane (Aldrich) was stirred overnight at room temperature with CaH_2 under an argon atmosphere and then vacuum distilled [bp = 101–102 °C (1 Torr)]. The purified solvent was transferred to an argon-filled drybox where the melted sulfolane and 3-methylsulfolane were mixed to form a 5% 3-methylsulfolane/95% sulfolane solvent mixture. This mixture was stirred over CaH_2 for 1 day, filtered, and degassed by the freeze–thaw method. A water content of less than 60 ppm was considered acceptable.

An oil dispersion of potassium hydride was washed thoroughly with dry pentane under an argon atmosphere to remove the mineral oil.[58] The resulting hydride powder was dried under vacuum and then transferred to an argon-filled drybox.

Triphenylcarbinol (Aldrich), triphenylcyclopropene (Alpha), 9-phenyl-9-xanthenol (Fluka), and xanthene (Aldrich) were converted to their corresponding tetrafluoroborate salts by the procedures described by Dauben et al.[59] These carbocations were washed with anhydrous ethyl ether and dry, ice-cold chloroform under an argon atmosphere.

Scheme II



Commercially available tropylium tetrafluoroborate (Aldrich) was recrystallized from CH_3CN/Et_2O. Trimethylcyclopropenylium tetrafluoroborate was prepared following the procedure of Closs et al.[60]

The dianisylmethyl cation was prepared by a modified version of Dauben's[59] procedure. 4,4′-Dimethoxybenzhydrol (1.974 g, 8 mmol) was dissolved in a mixture of 25 mL of dry ether and 5.1 mL (~40 mmol) of propionic anhydride. An 85% ether solution of $HBF_4 \cdot OEt_2$ complex (3.05 g, ~16 mmol) was added to it. The solution was stirred at room temperature for 20 min and then in an ice bath for 10 min. The resulting reddish purple precipitate was filtered under argon and washed with cold dry ether and then cold dry pentane. The product (2.33 g, 93%) decomposes at 97–98 °C but is stable inside the drybox up to 1 week.

9,9-Dimethyl-10-phenyl-9,10-dihydroanthracenium cation (DPA^+) was synthesized by a six-step procedure from *α*-phenyl-*o*-toluic acid in overall yield of 33% (including all purifications) (Scheme II).

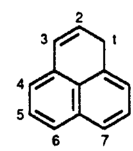
A literature method[61] was modified to make the 9,9-dimethyl-10-anthrone; a general Grignard procedure as followed to make the carbinol, mp 164.5–165.5 °C (lit.[62] mp 167.5–168.5 °C). A similar procedure as in the preparation of dianisylmethyl cation was followed in the last step.

The NMR spectrum of the cation was determined in $CDCl_3$ (300 MHz): δ 1.98 (s, CH_3), 7.60–8.38 (m, arom H). The yellow cation (mp 188–193 °C dec was shown to be 99% pure by NMR. The pK_{R^+} value of this carbocation was determined to be −5.49 (±0.06) by monitoring the changes of the cation's absorption with the changes of the acid concentration of the solvents, according to the method of Arnett and Bushick.[63]

2,4,6-Triphenylpyrylium tetrafluoroborate was obtained from Alfa Corp., recrystallized from 1,2-dichloroethane, and dried in a vacuum oven at 80 °C for 4 h; yellow needles; mp 248–250 °C (lit.[64] mp 251–257 °C).

Perinaphthene was prepared following the procedure of Bondjouk and Johnson.[65] The product, a pale yellow compound (99% 1*H*-phenalene with 3% saturated analogue and no other impurities) has to be dried in a vacuum oven and kept in the drybox.

NMR spectrum (300 MHz, $CDCl_3$): δ 4.16 (s, 1-H), 6.04 (dt, 2-H), 6.59 (dt, 9-H), 6.97 (dd, 3-H), 7.24 (m, 4-H), 7.31 (d, 8-H), 7.36 (dd, 5-H), 7.52 (dd, 7-H), 7.56 (dd, 6-H).



1*H*-phenalene (mp 84–85 °C)

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(49) Anet, F. A.; Bavin, P. M. G. *Can. J. Chem.* **1956**, *34*, 991.

(50) Bavin, P. M. G. *Can. J. Chem.* **1960**, *38*, 1917.

(51) Matthews, 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.

(52) Wislicenus, W.; Russ, K. *Ber. Dtsch. Chem. Ges.* **1910**, 2719.

(53) Von Holbro, T.; Tagmann, E. *Helv. Chim. Acta* **1950**, *33*, 2181.

(54) Murphy, W. S.; Hauser, C. R. *J. Org. Chem.* **1966**, *31*, 85.

(55) Bordwell, F. G.; Clemens, A. H. *J. Org. Chem.* **1982**, *47*, 2510.

(56) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.

(57) Martinmaa, J. In *The Chemistry of Nonaqueous Solvents*; Lagowski, J. J., Ed.; Academic Press: New York, 1976.

(58) Schilling, S. L. Ph.D. Thesis, Duke University, 1984.

(59) Dauben, H. J., Jr.; Honen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442.

(60) Closs, G. L.; Bell, W. A.; Heyn, H.; Dev, V. *J. Am. Chem. Soc.* **1968**, *90*, 173.

(61) Davis, M. A.; Winthrop, S. O.; Thomas, R. A.; *J. Med. Chem.* **1964**, *7*, 88.

(62) Strietwieser, A., Jr.; Hammons, J. H.; Ciuffarin, E.; Brauman, J. I. *J. Am. Chem. Soc.* **1967**, *89*, 59.

(63) Arnett, E. M.; Bushick, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1564.

(64) Dimroth, K.; Reichardt, C.; Vogel, K. *Organic Syntheses*; Baumgarten, H. E., Ed.; John Wiley & Sons: New York, 1973; Collect. Vol. V, p 1135.

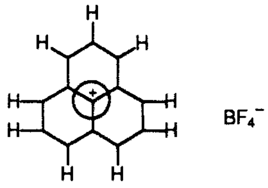
(65) Bondjouk, P.; Johnson, P. D. *J. Org. Chem.* **1978**, *43*, 3979.

Table I. E Values (V) for Carbanions in Sulfolane/3-Methylsulfolane (5%) Solvent

anion	E_{ox}^{b}	$E_{1/2}$	technique and conditions^{a}
2,7-dibromo-9-carbomethoxy fluorenide	−0.233 (−0.243)	−0.286	SHACV (a), Pt electrode, 18/108° ac amplitude 80 mV; frequency 35 Hz
9-cyanofluorenide	−0.453 (−0.424)	−0.481	SHACV (a), Pt electrode, 14/104° ac amplitude 80 mV; frequency 30 Hz
9-carbomethoxyfluorenide	−0.501 (−0.492)	−0.555	SHACV (a), Pt electrode, 22/112° ac amplitude 80 mV; frequency 40 Hz
9-(phenylsulfonyl)fluorenide	−0.291 (−0.309)	−0.392	E_{ox} obtained by CV, glassy carbon electorde; $E_{1/2}$ obtained by SHACV (b), Pt electrode, 22/112° ac amplitude 120 mV; frequency 40 Hz
2-bromo-9-(phenylthio)fluorenide	−0.693 (−0.720)	−0.732	SHACV (a), Pt electrode, 20/110° ac amplitude 130 mV; frequency 50 Hz
9-(phenylthio)fluorenide	−0.848	−0.882	SHACV (b), Pt electrode, 30/120° ac amplitude 95 mV; frequency 50 Hz
9-phenylfluorenide	−1.033 (−1.028)	−1.101	SHACV (a), Pt electrode, 12/102° ac amplitude 105 mV; frequency 25 Hz
fluorenide	−1.072 (−1.120)	−1.123	SHACV (b), Pt electrode, 16/106° ac amplitude 100 mV; frequency 40 Hz
4,4′-dinitrodiphenylmethyl	−0.576	−0.642	SHACV (b), Pt electrode, 22/112° ac amplitude 80 mV; frequency 40 Hz

^{a}All E_{ox} values obtained by CV at a scan rate of 25 mV/s under an Ar blanket. SHACV scan rates indicated as (a) 5 mV/s and (b) 10 mV/s. All values reported vs ferrocenium/ferrocene $E_{1/2}$ values as obtained under identical conditions. All solutions are 1.5 mM in anion concentration. All values obtained at 25 °C using Ag/AgNO$_3$ reference electrode and Pt wire auxiliary electrode. Counterion is K$^+$. Error for scan rates ranging from 25 to 100 mV/s = ±25 mV. ^{b}Values in parentheses are irreversible E_{ox} in DMSO measured by CV in Bordwell's laboratories.[62]

Perinaphthenium tetrafluoroborate was obtained from 1*H*-phenalene by hydride transfer with trityl tetrafluoroborate in CH$_2$Cl$_2$ at −10 °C under argon. The solution was cooled to −78 °C for 20 min and filtered at −78 °C under argon. A dark yellow powder, which became dark green after some time, was warmed to 0 °C and then transferred to the drybox. All the carbocation salts were dried under vacuum and transferred to an argon-filled drybox: mp (in a sealed tube) 115–124 °C dec; NMR, two peaks in the aromatic region, ratio 1/2 (H1/H).



perinaphthenium or phenalenium tetrafluoroborate

Generation of Anions. The anion precursor (0.04–0.06 g) was dissolved in 40 mL of degassed 5% 3-methylsulfolane/95% sulfolane, and then an excess amount (0.02–0.04 g) of KH was added to it. All of the operations for preparing the anion solutions were done in an argon-filled oxygen-free Vacuum Atmospheres drybox. The mixture was stirred for about 30–60 min at room temperature. After a high enough anion concentration was obtained (visualized by the anion color), the solution mixture was filtered directly into the reaction vessel of the calorimeter.

Calorimetry. Heats of reaction (ΔH_{rxn}) of the carbocations with the various anions in the sulfolane mixture were measured with a Tronac 450 titration calorimeter at 25 °C. The operation of the calorimeter was checked periodically by measuring the heat of neutralization of an aqueous solution of sodium hydroxide with a standard aqueous HCl solution.

The solutions of the carbocations (0.08–0.1 M) were prepared inside the argon-filled drybox with an analytical balance and volumetric flask. Before each calorimetric run, the calibrated motor-driven buret, filled with carbocation solution, and the reaction vessel, containing about 40 mL of carbanion solution, were connected to the calorimeter insert assembly. A dry argon atmosphere was maintained at the top of the reaction vessel to protect the carbanion solution/solvent from air. The operation of the Tronac 450 titration calorimeter has been described elsewhere.[66] All ΔH_{rxn} measurements were conducted in the isoperibolic mode at 25 °C. Each reported ΔH_{rxn} is the average of at least four and usually six or more enthalpy measurements with the same stock solution of carbocations. Reproducibility of the ΔH_{rxn} results was verified by using different samples of the carbocations and several carbanion solutions prepared on different days over a period of several months.

Product Analysis. Products were analyzed by HPLC, NMR, and elemental analysis after isolation.[18]

Electrochemical Measurements. The sources of the substrates used in electrochemical measurements and their purifications were given in the previous section.

All solvent distillations were performed in an all-glass apparatus that was oven-dried and flushed with argon before use.

The sulfolane solution of 0.1 M supporting electrolyte was made from the above solvent and triply recrystallized (1/5 ethanol/ether) tetrabutylammonium tetrafluoroborate (Aldrich). The Bu$_4$NBF$_4$ salt was vacuum-dried at 60 °C for 24 h before use.

The electrochemical measurements were performed by using a BAS-100A electrochemical analyzer equipped with a three-electrode assembly. The platinum or gold working electrode (BAS) was polished with BAS polishing diamond suspension and rinsed with ethanol before each run. The glassy-carbon working electrode (BAS) was polished with BAS polishing alumina and rinsed before use. The counter electrode was a platinum wire (BAS). The silver/silver nitrate reference electrode was made by inserting a silver wire (o.d. = 1 mm; Aldrich; 99.99+%) into 0.1 M solution of AgNO$_3$, which was isolated from the electrolyte solution by a fritted-glass bridge (VYCOR membrane). The solvent for the silver nitrate solution was dependent on the actual solvent used in the electrochemical measurement. The ferrocenium/ferrocene redox couple served as the internal standard for all measurements, and its $E_{1/2}$ value was checked against the reference electrode before and after the measurements. When required, a three-electrode airtight cell was used; in other circumstances, a BAS-supplied electrical cell was used for the measurements. The preparation of carbanion and carbocation solutions and the detailed experimental conditions for individual compounds are given below.

Preparation of Carbanion Solutions. The sample of carbon acid (enough for making 10 mL of a 1.5 mM solution) was weighed into the electrical cell inside a drybox. The cell was transferred quickly to the BAS cell stand and flushed with highly purified argon for 3 min or more. Ten milliliters of the 0.1 M supporting electrolyte solution was then added to the cell via a Hamilton airtight syringe, and the solution was flushed with argon for 1 min. A quantity of potassium dimsyl solution sufficient to generate 1.5 mM solution of anion was added to the cell. The electrochemical measurement was taken immediately after preparation of the anion solution.

Preparation of Carbocation Solution. A sample of carbenium tetrafluoroborate sufficient for preparing 10 mL of a 1.5 mM solution was weighed into the cell inside a drybox and transferred to the cell stand where it was blanketed with highly pure argon for a few minutes. Ten milliliters of the supporting electrolyte solution was added to the cell via an airtight syringe. The electrochemical measurement was taken immediately afterwards.

Methods and Conditions for Determining $E_{1/2}$. The techniques and conditions used to determine $E_{1/2}$ for individual carbocations and carbanions in sulfolane solvent systems are given in Tables I and II. In general, the error in CV measurements for scan rates of 25–100 mV/s was ±25 mV. Errors in SHACV measurements for scan rates of 5–10 mV/s were ±30 mV in sulfolane solvent.

Data Analysis. The error in ΔH_{homo} was determined by propagation of error (in both the electrochemical and calorimetric data) through the equation $\Delta H_{homo} = \Delta H_{het} + \Delta G_{ET}$. In addition, the small error in the redox potentials arising from entropic considerations is included. At a 95% confidence limit, the error in the reported values of ΔH_{homo} ranges between 3.0 and 3.5 kcal/mol.

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(66) (a) Arnett, E. M.; Chawla, B.; Bell, L.; Taagepera, M.; Hehre, W. J.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5729. (b) Arnett, E. M.; Chawla, B. *J. Am. Chem. Soc.* **1978**, *100*, 217. (c) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1976**, *98*, 1468.

Table II. E Values (V) for Carbocations in Sulfolane/3-Methylsulfolane (5%) Solvent

cation	E_{red}	$E_{1/2}{}^{b}$	technique and conditions for obtaining $E_{1/2}{}^{a}$
trimethylcyclopropenylium	−1.505	−1.375 (−1.60)	SHACV, Pt electrode, 54/144° ac amplitude 135 mV; frequency 50 Hz
triphenylcyclopropenylium	−1.289	−1.304 (−1.16)	SHACV, Pt electrode, 50/140° ac amplitude 120 mV; frequency 40 Hz
trityl	reversible by CV	−0.133 (−0.20)	CV, glassy carbon electrode
9-phenylxanthylium	reversible by CV	−0.352	CV, glassy carbon electrode
xanthylium	−0.335	−0.347	SHACV, Pt electrode, 48/138° ac amplitude 120 mV; frequency 25 Hz
triphenylpyrylium	reversible by CV	−0.770	CV, glassy carbon electrode
perinaphthenium	reversible by CV	−0.013	CV, glassy carbon electrode
tropylium	−0.620	−0.622 (−0.62)	SHACV, Pt electrode, 40/130° ac amplitude 70 mV; frequency 50 Hz
9,9-dimethyl-10-phenyl-9,10-dihydroanthracenium	reversible by CV	−0.133	CV, glassy carbon electrode
4,4′-dimethoxydiphenylmethyl	−0.446	−0.450	SHACV, Pt electrode, 90/180° ac amplitude 120 mV; frequency 40 Hz

[a] All E_{red} values obtained by CV at a scan rate of 25 mV/s under an Ar blanket. SHACV scan rate is 5 mV/s. All values reported vs ferrocenium/ferrocene $E_{1/2}$ values as obtained under identical conditions. All solutions are 1.5 mM in cation concentration. All values obtained at 25 °C using Ag/AgNO$_3$ reference electrode and Pt wire auxiliary electrode. Counterion is BF$_4^-$. Error for scan rates ranging from 25 to 100 mV/s = ±25 mV. [b] Values in parentheses are reversible $E_{1/2}$ measured in DMSO in Breslow's laboratories.[68]

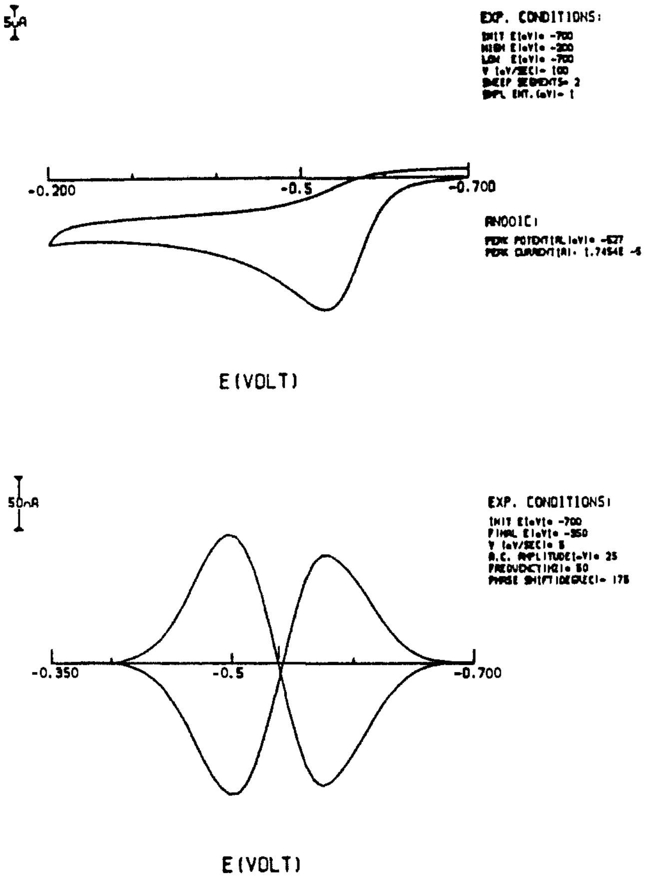

Figure 1. Irreversible cyclic voltammogram (CV, top) and reversible second-harmonic ac voltammogram (SHACV, bottom) for the oxidation of 9-COOMeFl$^-$ in acetonitrile. Identical data are obtained in DMSO and sulfolane/3-methylsulfolane (5%).

Results

An important requirement for the validity of this research is that the redox potentials obtained by cyclic voltammetry be reversible. There was good reason to question whether this condition could be met on the basis of preliminary studies with the simple BAS-CV-1B equipment. Accordingly, a more advanced BAS-100 electrochemical unit that would be capable of the SHACV technique was used. Figure 1 demonstrates the power of this method for obtaining $E_{1/2}$ for oxidation of the 9-carbomethoxyfluorenide anion. Clearly the simple cyclic voltammograms are anything but reversible, whereas the SHACV trace is beautifully symmetrical with a sharply delineated $E_{1/2}$ value of −0.555 ± 0.01.

Table III. Redox Potentials for Ions in the 25–80 °C Temperature Range (V) in Sulfolane Solvent Mixture

ion	25 °C	40 °C	60 °C	80 °C
ferrocene[a]	−0.201	−0.201	−0.201	−0.205
9-phenylxanthylium[a]	−0.387	−0.386	−0.385	−0.378
9,9-dimethyl-10-phenyl-9,10-dihydroanthracenium[a]	−0.133	−0.129	−0.137	−0.137
triphenylpyrilium[a]	−0.770	−0.755	−0.760	−0.756
perinaphthenium[a]	−0.013	−0.015	−0.028	−0.030
trityl[b]	reversible by CV	−0.110	−0.113	−0.109
9-carbomethoxyfluorenide[a]	−0.555	−0.540	−0.535	−0.530

[a] $E_{1/2}$ values obtained by CV and/or SHACV. [b] Irreversible E_{ox} values obtained by CV. All values referenced vs ferrocene/ferrocenium redox couple using glassy carbon working electrode, Ag/AgNO$_3$ reference electrode, Pt auxiliary electrode. Scan rate at 25 °C is 25 mV/s; at 40–80 °C scan rate is 100 mV/s. Solvent is sulfolane/3-methylsulfolane (5%). SD = ±25 mV.

The $E_{1/2}$ values obtained for cations and anions in sulfolane/3-methylsulfolane solution and the necessary experimental conditions are given in Tables I and II. The oxidation potentials of the anions listed on Table I include our own measurements determined by SHAC voltammetry in sulfolane and the published values of Bordwell and his students using the simple BAS equipment and DMSO solvent.[67] Clearly, there is excellent correspondence between their values obtained under irreversible conditions and the more experimentally sophisticated SHACV values for reversible oxidation in sulfolane solvent mixture. Table II compares the $E_{1/2}$ values for the reduction of the resonance-stabilized cations obtained by us in the sulfolane solvent system and those obtained by Breslow et al. in DMSO.[68] Within experimental error, these values are in close agreement. In addition, measurements for each carbanion were obtained in dimethyl sulfoxide and acetonitrile; identical $E_{1/2}$ values (within experimental error) were obtained in all three solvent systems.

Table III tabulates data for the temperature dependence of redox potentials of several cations and anions in sulfolane/3-methylsulfolane solvent. This demonstrates that $\Delta S_{\mathrm{redox}} \approx 0$ within experimental error for these systems.

Tables IV–IX present all of the data that we have obtained to date for ten carbocations interacting with seven substituted fluorenide anions as their potassium salts in sulfolane/3-methylsulfolane (5%) at 25 °C. Tables X and XI use data from ref 13 with four para-substituted phenylmalononitrile anions, which are considerably less basic than any of the fluorenyl anions reported in this paper. The arylmalononitrile anion data were obtained

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(67) (a) Bausch, M. J. Ph.D. Thesis, Northwestern University, 1985. (b) Cheng, J.-P. Ph.D. Thesis, Northwestern University, 1987.

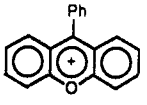
(68) Breslow, R.; Chu, W. *J. Am. Chem. Soc.* **1973**, *95*, 411.

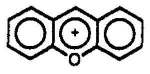
Table IV. Heats of Heterolysis and Homolysis, CRP, AOP's, and Free Energies of Electron Transfer (kcal/mol) for Reaction of Trityl Cation with Fluorenides in Sulfolane/3-Methylsulfolane (5%) at 25 °C

	trityl[a]					
anion	pK_a	$E_{1/2}$(ox),[b] V	AOP	ΔH_{hct}[c]	ΔG_{ET}	ΔH_{homo}[d]
9-PhFl⁻	17.9	−1.101	−0.87	35.51 ± 0.56	−22.32	13.18
9-PhSFl⁻	15.4	−0.882	0.76	33.61 ± 0.34	−17.27	16.34
2-Br-9-PhSFl⁻	13.2	−0.732	1.20	29.41 ± 0.52	−13.81	15.60
9-PhSO$_2$Fl⁻	11.55	−0.392	6.78	28.35 ± 0.59	−5.97	22.38
9-COOMeFl⁻	10.35	−0.555	2.83	25.81 ± 0.42	−9.73	16.08
9-CNFl⁻	8.30	−0.481	0.28	24.62 ± 0.62	−8.02	16.60
2,7-Br$_2$-9-CO$_2$MeFl⁻	6.52	−0.286	2.34	19.76 ± 0.85	−3.53	16.23

[a] pK_{R^+} = −6.63, CRP = 28.88. [b] Reversible $E_{1/2}$ of oxidation from anion to radical measured in sulfolane/3-methylsulfolane at 25 °C by cyclic voltammetry or second-harmonic ac voltammetry. SD = ±0.025 V. [c] ΔH_{hct} measured in a calorimeter at 25 °C using $\Delta H_{hct} = -\Delta H_{rxn}$. [d] Calculated from the equation $\Delta H_{homo} = \Delta H_{het} + \Delta G_{ET}$, where $\Delta G_{ET} = 23.06[E_{1/2}(C^-) - E_{1/2}(C^+)]$; SD = ±3.5 kcal/mol.

Table V. Heats of Heterolysis and Homolysis, CRP's, and Free Energies of Electron Trnasfer (kcal/mol) for Reaction of 9-Phenylxanthylium and Xanthylium Cations with Fluorenides in Sulfolane/3-Methylsulfolane (5%) at 25 °C

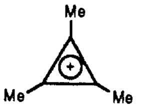


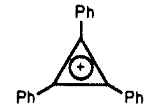


	9-phenylxanthylium[a]			xanthylium[b]		
anion	ΔH_{het}	ΔG_{ET}	ΔH_{homo}	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
9-PhFl⁻						
9-PhSFl⁻	29.21 ± 0.42	−12.22	16.99	33.03 ± 1.64	−12.34	20.69
2-Br-9-PhSFl⁻	23.84 ± 0.49	−8.76	15.08	30.13 ± 1.12	−8.88	21.25
9-COOMeFl⁻	22.35 ± 0.86	−4.68	17.67	27.33 ± 0.79	−4.80	22.53
9-CNFl⁻	20.51 ± 0.28	−2.97	17.54			
2,7-Br$_2$-9-CO$_2$MeFl⁻	17.44 ± 0.43	1.52	18.96	24.62 ± 1.02	1.41	26.03

[a] pK_{R^+} = 1.1, CRP = 30.47. [b] pK_{R^+} = −0.85, CRP = 35.33.

Table VI. Heats of Heterolysis and Homolysis, CRP's, and Free Energies of Electron Transfer (kcal/mol) for Reaction of Trimethylcyclopropenylium and Triphenylcyclopropenylium Cations with Fluorenides in Sulfolane/3-Methylsulfolane (5%) at 25 °C

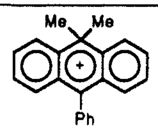


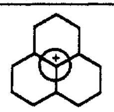


	trimethylcyclopropenylium[a]			triphenylcyclopropenylium[b]		
anion	ΔH_{het}	ΔG_{ET}	ΔH_{homo}	ΔH_{hct}	ΔG_{ET}	ΔH_{homo}
9-PhFl⁻				29.34 ± 0.28	4.68	34.02
9-PhSFl⁻	25.21 ± 0.37	11.37	36.58	27.49 ± 0.18	9.73	37.22
2-Br-9-PhSFl⁻	22.63 ± 0.38	14.82	37.46	25.40 ± 0.50	13.19	38.59
9-PhSO$_2$Fl⁻				22.23 ± 0.36	21.03	43.26
9-COOMeFl⁻	16.54 ± 0.16	18.91	35.45	20.62 ± 0.12	17.27	37.89
9-CNFl⁻				19.56 ± 0.30	18.98	38.54
2,7-Br$_2$-9-CO$_2$MeFl⁻	11.46 ± 0.47	25.11	36.57	16.22 ± 0.10	23.48	39.70

[a] pK_{R^+} = 7.4, CRP = 48.25. [b] pK_{R^+} = 3.1, CRP = 50.13.

Table VII. Heats of Heterolysis and Homolysis, CRP's, and Free Energies of Electron Transfer (kcal/mol) for Reaction of 9,9-Dimethyl-10-phenyl-9,10-dihydroanthracenium and Perinaphthenium Cations with Fluorenides in Sulfolane/3-Methylsulfolane (5%) at 25 °C





	9,9-dimethyl-10-phenyl-9,10-dihydroanthracenium[a]			perinaphthenium[b]		
anion	ΔH_{hct}	ΔG_{ET}	ΔH_{homo}	ΔH_{hct}	ΔG_{ET}	ΔH_{homo}
9-PhFl⁻						
9-PhSFl⁻	31.77 ± 0.62	−17.27	14.50	33.83 ± 0.45	−20.04	13.79
2-Br-9-PhSFl⁻	29.18 ± 0.35	−13.81	15.37	30.39 ± 0.42	−16.58	13.81
9-COOMeFl⁻	26.22 ± 0.54	−9.73	16.49	25.03 ± 0.20	−12.50	12.53
9-CNFl⁻						
2,7-Br$_2$-9-CO$_2$MeFl⁻	20.76 ± 1.78	−3.53	17.23	18.26 ± 0.54	−6.30	11.96

[a] pK_{R^+} = −5.49, CRP = 29.29. [b] pK_{R^+} = unknown, CRP = 25.33.

in acetonitrile rather than sulfolane. The following data are presented:

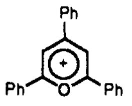
(a) The pK_{R^+} of the cation (the primary criterion for its stability as obtained from published reports) and its reduction potential are listed.

(b) The carbinol reduction potential (see discussion) for each cation C_c^+ is defined as

$$\mathrm{CRP} = -1.37\mathrm{p}K_{R^+} - 23.06E_{red}(C_c^+) \qquad (6)$$

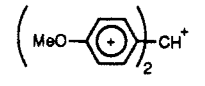
(c) The pK_a value for ionization of the parent fluorene com-

Table VIII. Heats of Heterolysis and Homolysis, CRP's, and Free Energies of Electron Transfer (kcal/mol) for Reaction of 2,4,6-Triphenylpyrylium and Tropylium Cations with Fluorenides in Sulfolane/3-Methylsulfolane (5%) at 25 °C

	 2, 4, 6-triphenylpyrylium[a]			 tropylium[b]		
anion	$\Delta H_{\rm het}$	$\Delta G_{\rm ET}$	$\Delta H_{\rm homo}$	$\Delta H_{\rm het}$	$\Delta G_{\rm ET}$	$\Delta H_{\rm homo}$
9-PhFl$^-$	21.73 ± 0.40	-7.63	14.10	33.84 ± 0.32	-11.05	22.79
9-PhSFl$^-$	18.02 ± 0.45	-2.58	15.44	30.52 ± 0.45	-6.00	24.52
2-Br-9-PhSFl$^-$	15.55 ± 0.17	0.88	16.43	28.59 ± 0.12	-2.54	26.05
9-PhSO$_2$Fl$^-$				27.17 ± 0.54	5.30	32.47
9-COOMeFl$^-$	9.03 ± 0.30	4.96	13.99	24.89 ± 0.53	1.55	26.44
9-CNFl$^-$				22.52 ± 0.22	3.25	25.77
2,7-Br$_2$-9-CO$_2$MeFl$^-$				19.45 ± 0.11	7.75	27.20

[a] pK_{R^+} = unknown, CRP = 26.79. [b] pK_{R^+} = 4.7, CRP = 39.23.

Table IX. Heats of Heterolysis and Homolysis, CRP's, and Free Energies of Electron Transfer (kcal/mol) for Reaction of 4,4'-Dimethoxydiphenylmethyl Cation with Fluorenides in Sulfolane/3-Methylsulfolane (5%) at 25 °C

	 4,4'-dimethoxydiphenylmethyl[a]		
anion	$\Delta H_{\rm het}$	$\Delta G_{\rm ET}$	$\Delta H_{\rm homo}$
9-PhFl$^-$	40.62 ± 0.84	-15.01	25.61
9-PhSFl$^-$	35.99 ± 0.60	-9.96	26.03
2-Br-9-PhSFl$^-$	29.77 ± 0.71	-6.50	23.27
9-COOMeFl$^-$	27.26 ± 0.67	-2.42	24.84
2,7-Br$_2$-9-CO$_2$MeFl$^-$	20.89 ± 0.55	3.78	24.67

[a] pK_{R^+} = -5.65, CRP = 37.64.

pound in DMSO at 25 °C, measured either by Professor Bordwell's group or by our own, is given for each anion listed (Table IV).

(d) The acid oxidation potential[44] is defined for each anion C_a^- as

$$\text{AOP} = 1.37\text{p}K_a + 23.06E_{ox}(C_a^-) \qquad (7)$$

(e) Heats of heterolysis include the latest updated values obtained by calorimetry in our laboratory. A number of new values have been obtained from the heats of reaction with the sign changed for the reaction of various anions with the cations indicated at the top of each table. To the best of our knowledge, this is the most complete set of directly measured thermodynamic data for heterolysis of carbon–carbon bonds in solution that is presently available anywhere.

(f) Free energies of electron transfer are derived for each carbocation–carbanion combination by multiplying the difference of their redox potentials by 23.06, the factor used for converting volts to kilocalories per mole.

(g) Finally, the enthalpies of homolysis obtained from $\Delta H_{\rm het}$'s and $\Delta G_{\rm ET}$'s are listed as shown in eq 5 with the basic assumption that $\Delta S_{\rm ET}$ is negligible for this series of ions.

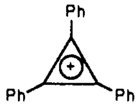
All values for $\Delta H_{\rm het}$, $\Delta G_{\rm ET}$, $\Delta H_{\rm homo}$, AOP, and CRP are expressed in kilocalories per mole at 25 °C.

Discussion

Validity of the Method. Our approach for determining enthalpies of homolysis from enthalpies of heterolysis through the measurement of the redox potentials of the carbocations and carbanions is subject to reasonable skepticism. The first question is whether the redox potentials that were determined by cyclic voltammetry are reliable, reversible values. This problem was faced by Bordwell et al.,[44] whose measurements were based on conventional cyclic voltammetry. They have presented several persuasive, but not conclusive, arguments for why their measurements derived from irreversible voltammograms are close approximations to the reversible oxidation values for many of the carbanions investigated in the present study. We have attacked the problem by employing an alternative technique, second-harmonic ac voltammetry, which allows a closer approach to the reversible electrode potential for highly unstable ion-radical processes. In our hands the method has apparently been successful for every carbocation and carbanion in this study, although its actual application frequently requires considerable effort and patience in order to obtain the symmetrical SHAC voltammograms.

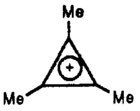
Table I compares E_{ox} values for a variety of anions as obtained by us using ordinary cyclic voltammetry and the $E_{1/2}$ as obtained by the SHACV method. The agreement between the two sets of results provides comforting support for both methods. A totally independent source of support is the excellent agreement obtained by Bordwell[44,67] using a cycle essentially identical with ours to reproduce homolytic bond dissociation energies for a variety of carbon–hydrogen bonds whose BDE's had been measured previously by a variety of methods. Table II compares the E_{ox} and

Table X. Heats of Heterolysis and Homolysis, AOP's, CRP, and Free Energies of Electron Transfer (kcal/mol) for Reactions of Para-Substituted Phenylmalononitrile Anions with Triphenylcyclopropenylium Cation in Acetonitrile[a] at 25 °C

				 triphenylcyclopropenylium[b]		
anion	pK_a	$E_{1/2}$, V	AOP	$\Delta H_{\rm het}$	$\Delta G_{\rm ET}$	$\Delta H_{\rm homo}$
p-ClPhMN	3.14	-0.128	1.35	11.3 ± 0.3	23.34	34.64
p-HPhMN	4.24	-0.166	1.98	12.2 ± 0.3	22.46	34.66
p-MePhMN	4.85	-0.331	-0.99	13.4 ± 0.3	18.66	32.06
p-MeOPhMN	5.68	-0.374	-0.84	14.0 ± 0.3	17.66	31.66

[a] All data are taken from ref 3. [b] $E_{1/2}$ measured using SHACV vs gold electrode at -40 °C in acetonitrile on BAS 100-A. $E_{1/2}$ = -1.14 V, CRP = $\Delta H_{\rm cmf} + 23.06E_{1/2}$ = 46.91.

Table XI. Heats of Heterolysis and Homolysis, AOP's, CRP and Free Energies of Electron Transfer (kcal/mol) for Reactions of Para-Substituted Phenylmalononitrile Anions with Trimethylcyclopropenylium Cation in Acetonitrile[a] at 25 °C



trimethylcyclopropenylium[b]

anion	pK_a	$E_{1/2}$, V	AOP	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
p-ClPhMN	3.14	−0.128	1.35	7.34 ± 0.3	31.29	38.63
p-HPhMN	4.24	−0.166	1.98	8.63 ± 0.3	30.42	39.05
p-MePhMN	4.85	−0.331	−0.99	9.57 ± 0.3	26.61	36.18
p-MeOPhMN	5.68	−0.374	−0.84	10.91 ± 0.3	25.62	36.53

[a] All data are taken from ref 3. [b] $E_{1/2}$ measured using SHACV vs platinum electrode at 25 °C in acetonitrile on BAS 100-A. $E_{1/2} = -1.485$ V, CRP = $\Delta H_{cmf} + 23.06E_{1/2} = 50.78$.

$E_{1/2}$ values for the reduction of a variety of cations to the radical and the $E_{1/2}$ values for some of these as obtained by others.[7,68,69] We conclude that the agreement between our values and those measured by other workers and by other methods provides strong support for the use of both ordinary CV and SHACV for the study of the ions reported here, although it would be unwise to make a general claim for the validity of the methods.

Some years ago Taft, Jensen, and McKeever[70-72] measured the potentials of half-cells of triarylcarbenium ion salts against a silver electrode to determine their reduction potentials against their corresponding free radicals under nearly equilibrium conditions in acetonitrile at 25 °C. Corresponding measurements were made with the triarylmethyl carbanions in equilibrium with their radicals. Figure 2 presents a plot of Jensen's reduction potentials *versus* corresponding values obtained for the same ions with the use of cyclic voltammetry and polarography.[69,73] The agreement between these three completely independent techniques lends credibility to them all and to the reversibility of the electrode processes.

Entropy Problem. A fundamental question that arises over the use of redox potentials for the determination of ΔH_{homo} from ΔH_{het} is the mingling of free energy terms (E_{ox} and E_{red}) with enthalpy terms as we have done here. There is no fundamental reason why the entropy changes for the redox processes should be insignificant, although wide experience suggests that ΔS_{redox} might be proportional to ΔG_{redox} and ΔH_{redox}, at least for each family of cation–anion combinations. However, there is good reason to believe for the systems discussed here that free energy and enthalpy terms may be combined with impunity for several reasons:

(1) A series of reactions between resonance-stabilized substituted cyclopropenium ions and para-substituted phenylmalononitrile anions were studied close to equilibrium where ΔG°_{het}, ΔH°_{het}, and ΔS°_{het} could all be determined directly by the variation of equilibrium constants over a temperature range and by calorimetry. For all of these systems a particularly striking fact was the very small ΔS°_{het} values, which made $\Delta G^\circ_{het} \approx \Delta H^\circ_{het}$.[13] For that series of compounds, it clearly makes no difference whether the free energy or enthalpy terms are combined with the redox potentials; ΔG°_{homo} will be obtained. Most of the cases reported here, however, are very far from equilibrium, and there is no guarantee that $\Delta G^\circ_{het} \approx \Delta H^\circ_{het}$, although the two sets of properties might very reasonably be proportional to each other. Accordingly, it must be demonstrated experimentally that the free energies and enthalpies of the redox processes are essentially equivalent, or their differences must be determined.

ΔS°_{redox} may be determined from the temperature coefficient of the redox potentials, where $(\partial \Delta G^\circ_{redox}/\partial T) = -\Delta S^\circ_{redox}$. Table III presents several determinations demonstrating clearly that the entropy changes for the redox processes of these ions produce a negligible error in our *overall estimation* of ΔH_{homo}. In other cases $T\Delta S_{redox}$ may be required to convert ΔG_{ET} to ΔH_{ET}.

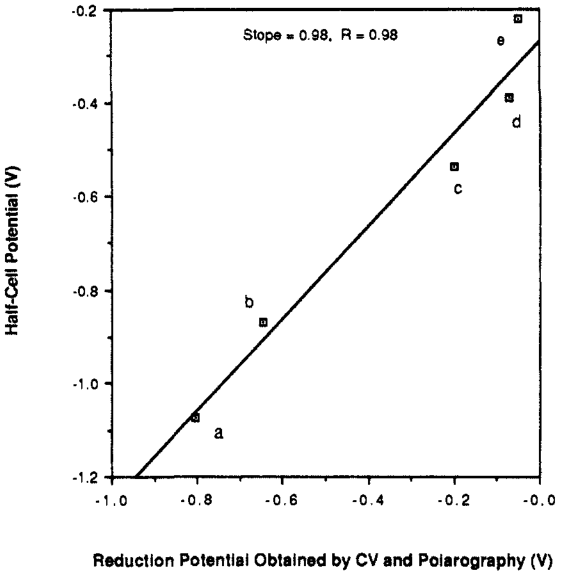


Figure 2. Plot of the half-cell potential for the reaction $Ar_3C^+ + Ag \rightleftharpoons {}^1/_2(Ar_3C)_2 + Ag^+$[72] vs the reduction potentials of substituted trityl cations[69,73] in acetonitrile at 25 °C: (a) 4,4′,4″-tris(*N*,*N*-dimethylamino)trityl, (b) 4,4′-bis(*N*,*N*-dimethylamino)trityl, (c) 4,4′,4″-tri-*p*-methoxytrityl, (d) 4,4′,4″-trimethyltrityl, (e) 4-methoxytrityl.

(2) Bordwell, Bausch, Cheng, and Harrelson[44] were able to substantiate their method, which is very similar to ours, by checking their derived BDE values for C–H bonds against a variety of published values that had been measured directly. The paucity of such measured results for C–C bond dissociation energies limits our ability to make such comparisons. However, Stein's estimate of less than 15 kcal/mol for the trityl–trityl bond in hexaphenylethane[24] corresponds well with our estimated ΔH_{homo} of 13 kcal/mol for the trityl–9-phenylfluorenyl bond.

Benson's method of group equivalents[39] may also be applied as a rough estimate for determining BDE values for C–C, although, conversely, the experiments reported here may be considered as a reasonable test of that method. For example, the heat of homolysis of the tropylium–thiophenol C–S bond was found experimentally by us to be 24.57 ± 3 kcal/mol, while the value calculated from Benson's additivity approach is 30.38 ± 4 kcal/mol.

Unfortunately, there is little prospect for testing our approach to heterolysis enthalpies for the sterically hindered symmetrical aliphatic systems, the ΔH_{homo}'s of which have been studied by Rüchardt[36] and Griller.[37,38] The relevant carbocations would probably rearrange under stable ion conditions[74] and, even if they

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(69) Volz, H.; Lotsch, W. *Tetrahedron Lett.* **1969**, 2275.

(70) Taft, R. W.; McKeever, L. D. *J. Am. Chem. Soc.* **1966**, *88*, 4544.

(71) Jensen, E. D.; Taft, R. W. *J. Am. Chem. Soc.* **1964**, *86*, 116.

(72) (a) Jensen, E. D. Doctoral Dissertation, The Pennsylvania State University, 1964. (b) McKeever, L. D. Doctoral Dissertation, University of California—Irvine, 1966.

(73) Nemcova, I.; Nemec, I. *J. Electroanal. Chem. Interfacial Electrochem.* **1971**, *30*, 506.

(74) Olah, G. A.; Olah, J. A. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1970; p 715.

did not, would suffer elimination rather than a bond-forming coordination reaction if brought into direct contact with their very reactive carbanion counterparts.[75] Also, there is at present no reliable method for preparation of the free carbanions in solution. Perhaps the corresponding carbenium redox potentials could be obtained,[7,10,76] but the technique developed here is limited to resonance-stabilized systems for which the heats of coordination can be measured by reaction calorimetry.

Extrathermodynamic Correlations of the Properties Measured. Tables IV–IX give the complete set of data determined so far for ΔH_{het}, $\Delta G°_{\text{ET}}$, and the derived ΔH_{homo}'s for ten carbocations and seven carbanions with the pK_{R^+}, pK_a, $E_{1/2\,\text{ox}}$, and $E_{1/2\,\text{red}}$ for the various ions and the AOP's and CRP's of the radicals. The pK_a's are free energy terms for heterolysis of C–H bonds, all of which have been measured and tabulated by Bordwell or ourselves. The pK_{R^+} values were determined by the usual indicator method in aqueous sulfuric acid solutions and either are literature values or were determined here. $E_{1/2\,\text{ox}}$ and $E_{1/2\,\text{red}}$ were determined by CV and SHACV methods and combined to produce $\Delta G°_{\text{ET}}$ (i.e., $\Delta G°_{\text{ET}} = 23.06[E_{\text{ox}}(\text{C}_a^-) - E_{\text{red}}(\text{C}_c^+)]$).

A number of these properties have important features in common. pK_a, pK_{R^+}, ΔH_{het}, and the redox potentials all involve the conversion of a charged species in solution to a neutral species or vice versa. Correspondingly, solvation energies and dielectric constants should have a significant effect on these processes (we have demonstrated previously an excellent correlation of $\Delta G°_{\text{ET}}$ versus $1/D$ as demanded by the Born equation).[13] In contrast, ΔH_{homo} involves the conversion of a neutral molecular species to a pair of uncharged radicals and would be expected to show negligible solvation effects of the type that totally dominate the heterolysis properties. Beyond this, ΔH_{homo} will be influenced primarily by the factors that stabilize resonance-stabilized radicals. These are much less familiar than those that apply to resonance-stabilized carbocations and carbanions.

Heats of Heterolysis and the "Master Equation". In previous publications[14,18,19] we have demonstrated that the heats of heterolysis for bond rupture to yield resonance-stabilized carbocations and carbanions can be correlated with surprisingly high precision using a very simple principle, i.e., that ΔH_{het} is related directly to the stabilities of the resulting carbocations and the carbanions. Our original master equation[14] used pK_{R^+} values for the carbocations as their measure of stability:

$$\Delta H_{\text{het}} = apK_a + bpK_{R^+} + \text{constant} \tag{8}$$

However, this may be improved considerably either by using delocalization energies from molecular orbital calculations[77] or, better, by scaling these stabilities for all carbocations in terms of their heats of reaction with 9-carbomethoxyfluorenide anion (ΔH_{cmf}).[18,19] The reason for the improvement probably lies in the fact that pK_{R^+} is a free energy term determined from equilibrium constants for the fission of the carbon–oxygen bond of the carbinol precursors of the cations in aqueous sulfuric acid. Not surprisingly, some of the factors that go into the breaking of a C–O bond under these conditions render them unsuitable models for the breaking of a C–C bond in sulfolane solution. Figure 3 displays the original correlation using all of the data in Tables IV–XI with pK_{R^+} as the stability criterion. Figure 4 gives the corresponding plot using ΔH_{cmf} for carbanion–cation combinations. Considering the structural diversity of the carbocations and the mingling of acetonitrile and sulfolane data, the correlation is remarkably good.

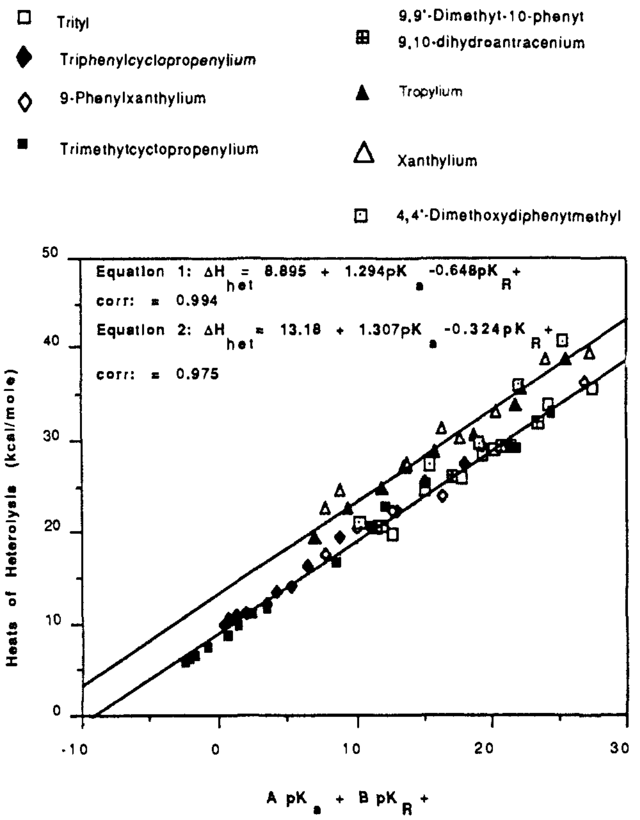

Figure 3. Correlations of heats of heterolysis for C–C bonds with master equations.

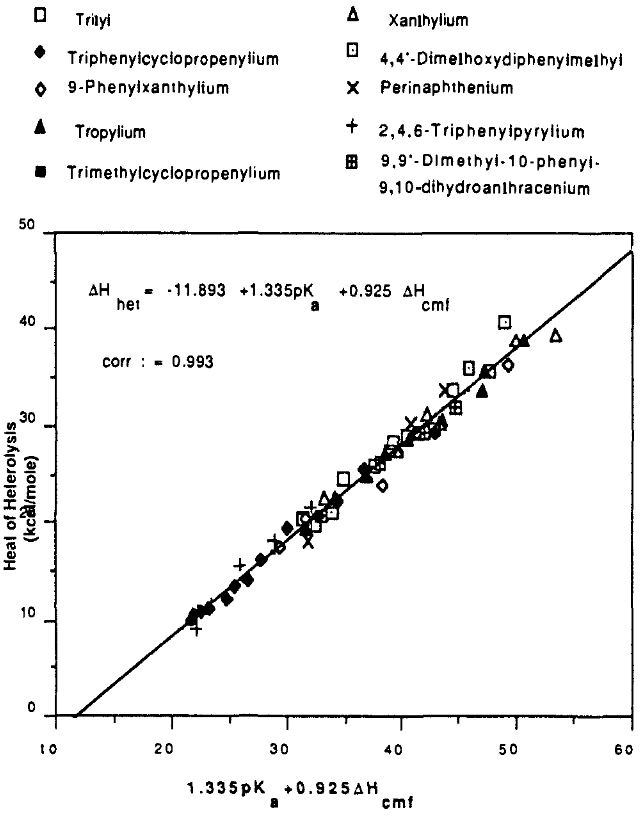

Figure 4. Correlation of heats of heterolysis for C–C bonds with modified master equation.

This correlation and others we have developed for C–O, C–N, and C–S bonds[19] indicate that ΔH_{het} can be estimated with good precision from pK_a values[78] and appropriate carbocation stabilization energies for reaction of an enormous variety of resonance-stabilized cations and anions. Extension to bonds producing less stable ions is not appropriate at this point except in the gas phase.[46]

The relationships between the processes that are correlated by eq 8 may be analyzed by the following formulas.

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(75) For example: the *tert*-butyl carbanion would doubtless deprotonate a *tert*-butyl carbocation rather than form 2,2,3,3-tetramethylbutane.

(76) Wasielewski, M. R.; Breslow, R. *J. Am. Chem. Soc.* **1976**, *98*, 4222.

(77) Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*; John Wiley & Sons: New York, 1961; p 365.

(78) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456, and private communications.

$$C_a\text{-H (DMSO)} \rightarrow C_a^- \text{ (DMSO)} + H^+ \text{ (DMSO) } pK_a \quad (9)$$

$$C_c\text{-OH } (H_2O) \rightarrow C_c^+ \text{ } (H_2O) + {}^-OH \text{ } (H_2O) \quad pK_{R^+} \quad (10)$$

$$C_a\text{-H (DMSO)} + C_c\text{-OH } (H_2O) \rightarrow C_a^- \text{ (DMSO)} + C_c^+ \text{ } (H_2O) + H^+ \text{ (DMSO)} + {}^-OH \text{ } (H_2O) \quad (11)$$

The terms on the right hand side of eq 11 may be converted into free energy terms, obtained at standard states of high dilution in DMSO (for the generation of the carbanion) and water (for generation of the carbenium ion), simply by multiplication by 1.37 (the familiar conversion factor, 2.303RT at 25 °C). If free energies for heterolysis of C_a–H bonds in DMSO and of C_c–OH bonds in water were correlated perfectly with heterolysis of C_a–C_c bonds, which produce the same carbenium ions and carbanions in sulfolane, eq 8 could be written

$$\Delta H_{het} = 1.37pK_a - 1.37pK_{R^+} + \text{constant} \quad (12)$$

In fact, the coefficient for pK_a actually is close to 1.3 for several modifications of eq 8, all of which involve replacement of pK_{R^+} by other properties that describe the stabilities of the carbocations.[18,19] Not surprisingly, this implies that the free energy of heterolysis for a C_a–H bond in DMSO is a good model for making the same carbanion by C_a–C_c cleavage in sulfolane, but the free energy of heterolysis of the C_c–OH bond in water is a rather poor one for making the carbenium ion. However, it is an important fact that all of the various master equations, which are variants of eq 8, have correlation coefficients that are better than 0.99. This means that although the free energies and entropies of transfer for C_a–H and C_a^- from DMSO to sulfolane and of C_c–OH and C_a^+ from water to sulfolane are undoubtedly large, they must remain in proportion to ΔH_{het} as the structures of C_a^- and C_c^+ are varied. The surprising quality of these correlations suggests that ΔH_{het}'s for many systems not examined by us should be interpolated with good precision from a wide variety of stability parameters for resonance-stabilized anions and carbenium ions.

Other Correlations of ΔH_{het}. Previous reports[14,18,19] have noted excellent correlations between heats of reaction of carbocations with carbanions and their pK_a's. Since $\Delta H_{het} = -\Delta H_{rxn}$ and pK_a is proportional to the free energy of ionization, this correlation confirms that structural effects on the reactivities of carbanions against protons in solution are reflected proportionately in their interactions with resonance-stabilized carbocations. As happens so often (especially in nonaqueous systems), there is a good extrathermodynamic correlation between enthalpy and free energy changes of related processes. Figure 5 provides an updated example of such a correlation with the trityl- and triphenylcyclopropenium cation (TPCP) with the series of fluorenide anions listed in Tables IV–IX.

Figure 6 relates the ΔH_{het} for trityl and TPCP cations with the series of fluorenide carbanions and the corresponding oxidation potentials of the carbanions. Others have also noted correlations between $E_{1/2}$ values and pK_a's, which in turn we have shown to correlate with ΔH_{het}.[78] In both cases the process involves the conversion of a charged species to a neutral one or vice versa, and it is reasonable to expect that ion stabilization and solvation energies are the major factors. One may also consider that the energy for the transfer of one electron from the anion to the electrode is correlated with the transfer of two electrons to a proton or to a carbocation. Figures 7 and 8 show further plots of the pK_{R^+} and $E_{1/2}$ for 10 carbocations with their ΔH_{het} with 9-carbomethoxyfluorenide anion. The much greater scatter in Figures 7 and 8 compared to 4 and 5 is presumably the result of the much larger structural variation of the cations compared to the anions.

Electron-Transfer Energies. Electron transfer is a matter of great current interest[79] especially as it relates to the mechanisms of reaction between nucleophiles and electrophiles.[80,81] Here we compare ΔH_{het} with ΔG_{ET}. ΔH_{het} refers to the energy required to convert a neutral molecule into a pair of ions, while ΔG_{ET} is the energy released when the ions are converted into their respective (neutral) free radicals. Figure 9 shows correlations for these electrostatically analogous processes. These values obtained from the $E_{1/2}$ for oxidation of the carbanion and reduction of the carbocation reflect the relative stabilization of the radical pairs versus the corresponding ion pairs. We are unaware of any comparable published data and draw attention to the trends in Tables IV–IX. A negative sign for ΔG_{ET} implies spontaneous electron transfer from the carbanions to the cations, which in turn parallels directly the diminishing heats of reaction ($\Delta H_{rxn} = -\Delta H_{het}$) for coordination of the cations with the anions. The most spontaneous (least endergonic) reactions correspond to the most exothermic ΔH_{rxn}. The actual magnitude of ΔH_{het} or ΔG_{ET} for any given anion is entirely dependent upon the cation with which it reacts, although all ΔH_{het} values are endothermic; ΔG_{ET} varies

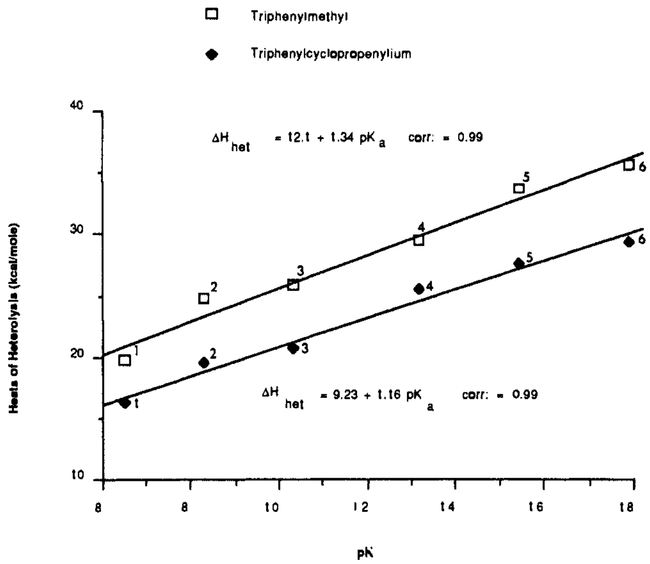

Figure 5. Plots of heats of heterolysis with pK_a of two cations: (1) 2,7-dibromo-9-carbomethoxyfluorenide, (2) 9-cyanofluorenide, (3) 9-carbomethoxyfluorenide, (4) 2-bromo-9-(phenylthio)fluorenide, (5) 9-(phenylthio)fluorenide, (6) 9-phenylfluorenide.

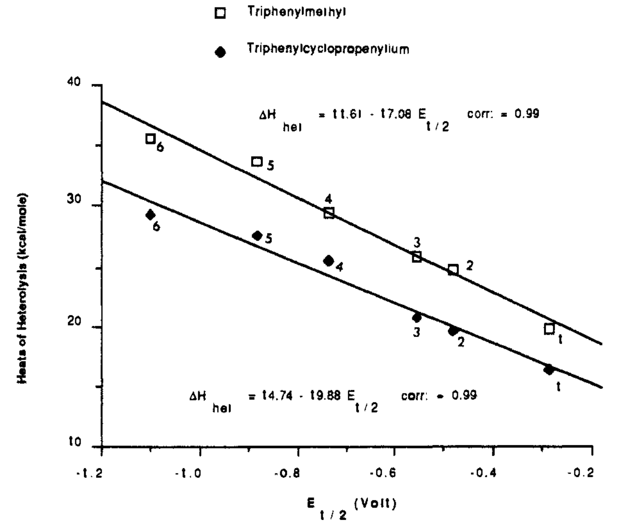

Figure 6. Plots of heats of heterolysis with oxidation potentials of fluorenide anions for two cations: (1) 2,7-dibromo-9-carbomethoxyfluorenide, (2) 9-cyanofluorenide, (3) 9-carbomethoxyfluorenide, (4) 2-bromo-9-(phenylthio)fluorenide, (5) 9-(phenylthio)fluorenide, (6) 9-phenylfluorenide.

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(79) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Reactivity and Structure Concepts in Organic Chemistry, Vol. 23; Hafner, K., Rees, C. W., Trost, B. M., Lehn, J.-M., Schleyer, P. v. R., Zahradnik, R., Eds.; Springer-Vorlag: Berlin, 1987.

(80) Shaik, S. S. *Isr. J. Chem.* **1985**, *26*, 367.

(81) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212.

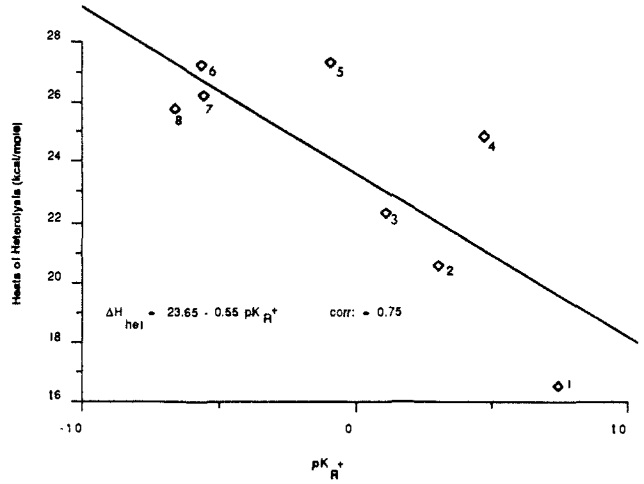

Figure 7. Plot of heats of heterolysis of 9-carbomethoxyfluorenide anion with the pK_{R^+} of the cations: (1) trimethylcyclopropenylium, (2) triphenylcyclopropenylium, (3) 9-phenylxanthylium, (4) tropylium, (5) xanthylium, (6) 4,4′-dimethoxydiphenylmethyl, (7) 9,9-dimethyl-10-phenyl-9,10-dihydroanthracenium, (8) trityl.

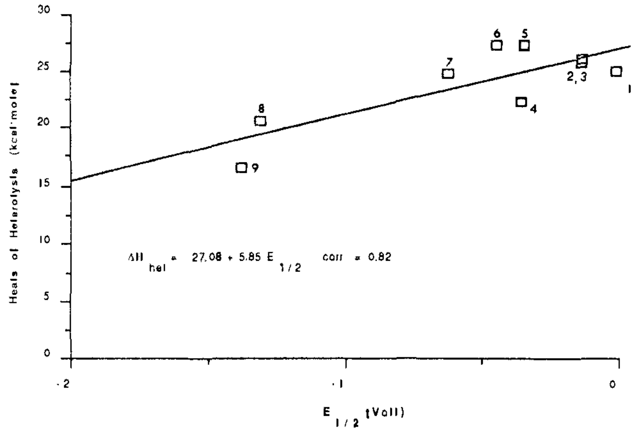

Figure 8. Plot of heats of heterolysis of 9-carbomethoxyfluorenide anion with the reduction potentials of the cations: (1) perinaphthenium, (2) trityl, (3) 9,9-dimethyl-10-phenyl-9,10-dihydroanthracenium, (4) 9-phenylxanthylium, (5) xanthylium, (6) 4,4′-dimethoxydiphenylmethyl, (7) tropylium, (8) triphenylcyclopropenylium, (9) trimethylcyclopropenylium.

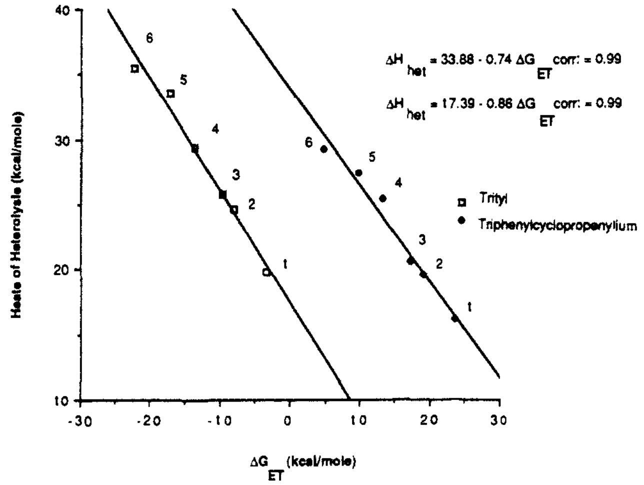

Figure 9. Heats of heterolysis vs ΔG_{ET}: (1) 2,7-dibromo-9-carbomethoxyfluorenide, (2) 9-cyanofluorenide, (3) 9-carbomethoxyfluorenide, (4) 2-bromo-9-(phenylthio)fluorenide, (5) 9-(phenylthio)fluorenide, (6) 9-phenylfluorenide.

over a wide range from exergonic to endergonic.

It is important to recognize that the individual electrode processes actually involve transfer to or from a standard ferrocene/ferrocenium couple rather than direct electron transfer between the cation and the anion. However, ΔG_{ET} refers to direct electron transfer between the radicals and ions and is *independent of the reference cell used to determine the half-cell potentials* of the cations and anions. In all cases ΔG_{ET} is more sensitive to structural variation of the anion than is ΔH_{het}.

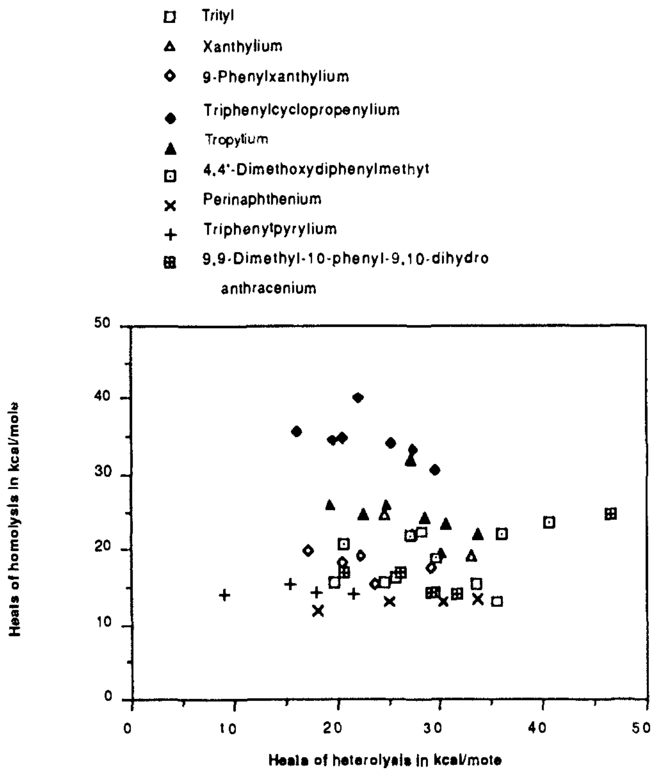

Figure 10. Plot of heats of heterolysis vs heats of homolysis for seven fluorenide anions with nine cations.

We have shown that ΔH_{het} correlates fairly well (but not very well) with the pK_{R^+} of the carbenium ion and also that both properties correlate fairly well with the corresponding reduction potentials. In turn, these proportionalities support, and are supported by, the classic electrochemical studies of Taft, Jensen, and McKeever,[70-72] which provided the first truly independent evidence that pK_{R^+} values obtained by the acidity function method represent bona fide free energy increments for carbenium ion stabilization.

Heats of Homolysis. Homolysis energies are obtained by summing ΔH_{het} with ΔG_{ET} (assuming $\Delta S_{\text{ET}} \approx 0$). To the best of our knowledge, the ΔH_{homo} values in Tables IV–XI are without precedent and deserve examination from several points of view. In contrast to ΔH_{het} values, which cover a range of 15–20 kcal/mol, ΔH_{homo} values for most of our series cover a range of only 3–4 kcal/mol, usually in a direction opposite to the trend for ΔH_{het}. The relative stabilities of delocalized radicals or those with remote functional groups are determined primarily by the number of resonance forms of the polycyclic aromatic species, rather than by the polar effects of their substituents.[24] However, most of the anions reported here carry functional groups close to the center of charge. The best model for the homolysis of these compounds (Tables IV–XI) is the BDE's for cleavage of the corresponding C–H bonds from Bordwell and Bausch.[44,78,82] Good correlations between ΔH_{homo} and BDE are obtained for each family of cation–anion reaction, but there is no general relationship. Bordwell has given preliminary discussions of the radical stabilization effects of various groups, but clearly this important topic is still in the early stages of development. Neumann, Uzick, and

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(82) ΔG_{ET} and ΔH_{homo} values are anomalous for the 9-PhSO$_2$Fl$^-$ anion in all tables where it is shown, and we emphasize that the data for this ion are as reproducible as for the others. For discussion of the contribution of the phenylsulfonyl group to anion and radical stabilities, see: Bordwell, F. G.; et al. *J. Phys. Org. Chem.* **1988**, *1*, 225.

Zarkadis[83] have recently reviewed earlier comparisons of radical stabilizations and used ESR study of trityl radical equilibration as a means of evaluation. Within the columns in each table, ΔH_{homo} becomes gradually more endothermic as ΔH_{het} becomes less endothermic, but the variation in ΔH_{homo} is insignificant compared to that of ΔH_{het} within the error propagated by our method.[82]

Examination of Figure 10 and of the tables leads to the interesting conclusion that *there is no general relationship between* ΔH_{het} *and* ΔH_{homo}. The latter are remarkably insensitive to structural variation in the anions but vary wildly as the cation is changed. This is a forceful demonstration of the sharp difference between factors that stabilize resonance-stabilized radicals as compared to carbocations and carbanions.

Radical Stability Factors: Acidity Oxidation Potentials and Carbinol Reduction Potentials. Bordwell and Bausch[44b] proposed using the AOP = $pK_a + E_{ox}$ for anions to evaluate the effects of structural change on their radicals.

$$C_a\text{-}H \rightarrow C_a^- + H^+ \qquad pK_a \tag{9}$$

$$C_a^- \rightarrow C_a^{\bullet} + e^- \qquad E_{ox}(C_a^-) \tag{13}$$

$$C_a\text{-}H \rightarrow C_a^{\bullet} + H^{\bullet} \qquad \text{AOP} \tag{14}$$

Comparison of AOP's for a series of related carbon acids, C_a–H, provides the relative bond dissociation energies for the C–H bonds, which, in turn, compare the stabilities of their radicals relative to their respective acid precursors. We may now extend this type of analysis to the other half of the homolysis problem for C_a–C_c bonds in which a series of $C_c^{\bullet}$ radicals are formed rather than just a hydrogen atom. We define the carbinol reduction potential as the homolytic bond energy for the C–OH bond in a carbinol.

$$C_c\text{-}OH \rightarrow C_c^+ + OH^- \qquad pK_{R^+} \tag{15}$$

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

$$C_c^+ + e^- \rightarrow C_c^{\bullet} \qquad -E_{red}(C_c^+) \tag{17}$$

$$C_c\text{-}OH \rightarrow C_c^{\bullet} + {}^{\bullet}OH \qquad \text{CRP} \tag{18}$$

By analogy to Bordwell's treatment, since $E_{ox}(OH^-)$ is constant for the series of $C_c^{\bullet}$ radicals, their CRP's are a measure of their stabilities relative to each other and to their carbinol precursors. *CRP's are relative* C_c*–OH bond dissociation energies.* Unlike the AOP's of Bordwell and Bausch, which were all measured in DMSO, the CRP's derived in this paper combine pK_{R^+}'s measured in aqueous H_2SO_4 solutions with $E_{ox}(C_c^+)$ measured in sulfolane/3-methylsulfolane. However, since the same complexities apply to all CRP's reported here, considerable cancellation of proportional solvation factors may be expected. Thus, AOP's and CRP's provide two independent means for determining relative radical stabilization factors and should give the same number for the same structural factor.

Equation 8 and its variants provide extrathermodynamic correlation equations for relating ΔH_{het}'s to pK_{R^+}'s and pK_a's for generation of their component ions. In a similar manner, ΔH_{homo}'s can be related to estimates of the stabilities of their component radicals through their AOP's and CRP's. The value of these master equation correlations is that they provide two independent means for estimating the heterolysis and homolysis energies in solution for the cleavage of bonds that produce either resonance-stabilized radicals or carbenium ions and carbanions. Following Scheme I, eq 5, substituting from eq 8, and multiplying pK_a and pK_{R^+} by 1.37 to convert them to free energy terms in kilocalories per mole

$$\Delta H_{homo} = a(1.37pK_a) - b(1.37pK_{R^+}) + a(23.06E_{ox}(C_a^-)) - b(23.06E_{red}(C_c^+)) \tag{19}$$

which, by comparison with eqs 6 and 7, gives

$$\Delta H_{homo} = a\text{AOP} + b\text{CRP} \tag{20}$$

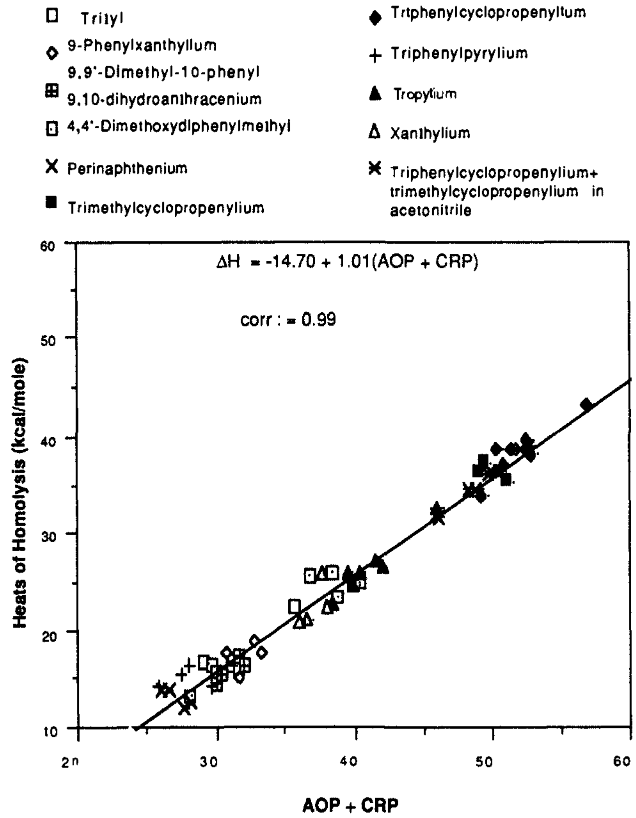

Figure 11. Plot of heats of homolysis vs AOP + CRP for 10 carbocations with the fluorenide anions and for triphenyl- and trimethylcyclopropenylium cations with the phenylmalononitriles.

This relates, quite reasonably, the energy required to cleave the C_a–C_c bonds to $C_a^{\bullet}$ and $C_c^{\bullet}$ to the corresponding cleavages of C_a–H and C_c–OH bonds. Figure 11 tests this relationship (using $\Delta H_{cmf} \approx -1.37pK_{R^+}$) and shows an excellent correlation despite the quite different conditions under which some of the components were determined.

It is important to use the correct signs with pK_{R^+} and $E_{red}(C_c^+)$. The heat of homolysis must become increasingly positive as the radicals become increasingly unstable. On the other hand, pK_{R^+} becomes increasingly negative as the carbenium ions become increasingly unstable and the reduction potentials of C_c^+ also do. Therefore, both pK_{R^+} and $E_{red}(C_c^+)$ should carry negative signs if they are to reflect their correct effects on ΔH_{homo}. This is not a problem for AOP since the signs and magnitudes of pK_a and $E_{ox}(C_c^-)$ are in the same direction as AOP.

Conclusions

By combining calorimetric heterolysis enthalpies with electron-transfer energies derived from redox potentials, we have determined homolysis energies for carbon–carbon bonds, which yield resonance-stabilized free radicals upon cleavage. Reasonable correlations are found between ΔH_{het}, pK_a, pK_{R^+}, $E_{1/2\,ox}$, $E_{1/2\,red}$, and ΔG_{ET}. Factors, such as solvation, which stabilize the ions, clearly play a dominating role in these correlations. Different patterns are observed for correlations with the derived ΔH_{homo}'s for which the trends are often quite puzzling.

The carbinol reduction potential is defined as the relative bond dissociation energy for C–OH bonds in carbinol precursors of resonance-stabilized carbenium ions. CRP's are analogous to the acid oxidation potentials of Bordwell and Bausch. ΔH_{homo}'s are related to CRP's and AOP's and provide alternative stability measures for resonance-stabilized radicals.

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[83] Neumann, W. P.; Uzick, W.; Zarkadis, A. K. *J. Am. Chem. Soc.* **1986**, *108*, 3762.