J. Org. Chem. **1998,** *63,* 4671−4678 **4671**

Hydride Affinities of Arylcarbenium Ions and Iminium Ions in Dimethyl Sulfoxide and Acetonitrile

Xian-Man Zhang,* Joseph W. Bruno,* and Emmeline Enyinnaya

Chemistry Department, Wesleyan University, Middletown, Connecticut 06459

Received January 22, 1998

Gibbs free energies for scission of C−H bonds leading to carbanion and proton (mode *a*), radical pair (mode *b*), and carbenium ion and hydride (mode *c*) have been determined for a series of acidic C−H bonds in ca. 45 weak acids. This involved the use of the equilibrium acidities (or homolytic bond dissociation enthalpies), redox potentials in DMSO or MeCN solution, and the appropriate thermodynamic cycles in the two solvents. The introduction of electron-donating groups generally results in small-to-negligible effects on ΔG_{R-} values (mode *a* scission) but in a relatively large stabilizing influence on the ΔG_{R^+} values for heterolytic cleavage to hydride and carbenium ion (mode *c*). Electron-withdrawing groups exert large stabilizing effects on ΔG_{R^-}, but their effects on ΔG_{R^+} are dependent on the nature of the substituents. The heterolytic processes *a* are usually favored in solution due to the strong solvation of the proton. Homolytic scission (mode *b*) is usually more favorable than the corresponding heterolytic process *c*, but they can be comparable when strong electron-donating groups such as dialkylamino are present. Indeed, heterolytic cleavage to hydride and carbenium ion was ca. 10 kcal/mol more favorable than homolytic cleavage for a series of highly stabilized 2-benzoyl-*N,N′*-dialkylperhydropyrimidines.

Introduction

Carbenium ions are key intermediates in important organic reactions such as E1 elimination, S_N1 substitution, and various rearrangements.[1] As such, correlation of carbenium ion thermodynamic stability with structure and substitution pattern has been the subject of considerable effort. The approach traditionally employed involves the determination of pK_{R^+}, and this method has been applied to a wide variety of stable triarylcarbenium salts and related stable carbenium ion salts.[2] The pK_{R^+} scale is based on the reaction of the carbenium ion of interest with water, a process leading to carbinol and proton (eq 1). The pK_{R^+} value is equal to the pH or the acidity function of the medium used when the concentration of the carbenium ion is equal to that of the carbinol (eq 3). In other words, the K_{R^+} value is defined as the equilibrium constant (eq 2) for carbinol formation (eq 1).

$$Ph_3C^+ + H_2O \rightleftharpoons Ph_3COH + H^+ \qquad \text{(eq.1)}$$

$$K_{R+} = \frac{[H^+]\,[Ph_3COH]}{[Ph_3C^+]} \qquad (2)$$

or

$$pK_{R+} = pH + \log\left(\frac{[Ph_3C^+]}{[Ph_3COH]}\right) \qquad (3)$$

More recently Arnett has used calorimetric studies to determine enthalpies of heterolysis for some carbon−carbon, carbon−hydrogen, and carbon−oxygen bonds; the use of redox potentials and the appropriate thermodynamic cycle also leads to a determination of the related homolysis enthalpies.[3] Additionally, Parker has utilized organic pK_a data and the realization that formation of the organic carbanion is related to carbenium ion formation by two redox events. The advantage of this latter approach is that there is a considerable body of data on organic pK_as; these may be used with the thermodynamic cycle shown in eqs 4−8 (Scheme 1) to determine ΔG_{R^+}, which is the free energy for C−H heterolysis to carbenium ion and hydride in solution.[4]

Despite detailed studies on kinetic and thermodynamic effects in hydride transfers,[5] it is clear that C−H heterolysis resulting in carbenium ions is not as well understood as is the formation of carbanions; this is clearly due to the fact that hydride transfer is encountered less frequently in organic systems than is proton transfer. However, hydride abstraction *is* a common reaction in organometallic chemistry.[6] Recently Bullock and co-workers reported a study of the kinetic hydridicity of a series of metal hydrides, and their rate studies

---

(1) (a) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34,* 1393−1405. (b) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985. (c) Isaacs, N. *Physical Organic Chemistry*, 2nd ed.; Longman Scientific: London, 1995; Chapter 10.

(2) (a) Freedman, H. H. In *Carbonium Ions*, Vol. IV; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1973; Chapter 28. (b) Okamoto, K.; Takeuchi, K.; Kitagawa, T. *Adv. Phys. Org. Chem.* **1995**, *30*, 173.

(3) (a) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Venimadhavan, S. *J. Am. Chem. Soc.* **1990**, *112,* 7346−7353. (b) Arnett, E. M.; Amarnath, K.; Harvery, N. G.; Cheng, J. P. *Science* **1990**, *247*, 423−430. (c) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 3522. (d) Arnett, E. M.; Flowers, R. A.; Ludwig, R. T.; Meekhof, A. E.; Walek, S. A. *J. Phys. Org. Chem.* **1997**, *10*, 499−513.

(4) (a) Cheng, J.-P.; Handoo, K. L.; Parker, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 2655−2660. See also: (b) Handoo, K. L.; Cheng, J.-P.; Parker, V. D. *J. Am. Chem. Soc.* **1993**, *115*, 5067−5072.

(5) (a) Kreevoy, M. M.; Ostovic, D.; Lee, I.-S. H.; Binder, D. A.; King, G. W. *J. Am. Chem. Soc.* **1988**, *110*, 524−530. (b) Lee, I.-S. H.; Jeoung, E. H.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1997**, *119*, 2722−2728 and references therein.

(6) (a) Sanders, A.; Cohen, L.; Geiring, W. P.; Kenedy, D.; Magatti, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 5430−5431. (b) Kiel, W. A.; Lin, G.-Y.; Gladysz, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3299−3301. (c) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648−4650. (d) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570−5572. (e) Hayes, J. C.; Jernakoff, P.; Miller, G. A.; Cooper, N. J. *Pure Appl. Chem.* **1984**, *56*, 25−33. (f) Asaro, M. F.; Bodner, G. S.; Gladysz, J. A.; Cooper, S. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1020−1024. (g) Guerchais, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1986**, 663−664. (h) Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 58−69. (i) Slack, D. A.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1974**, 701−702. (j) Laycock, D. E.;

S0022-3263(98)00120-0 CCC: $15.00

Scheme 1

$$\mathrm{R{-}H} \rightleftharpoons \mathrm{R}^- + \mathrm{H}^+ \qquad \mathrm{p}K_\mathrm{a} \tag{4}$$

$$\mathrm{R}^- \rightleftharpoons \mathrm{R}^\bullet + e^- \qquad \mathrm{FE_{ox}}(\mathrm{R}^-) \tag{5}$$

$$\mathrm{H}^+ + e^- \rightleftharpoons \mathrm{H}^\bullet \qquad \mathrm{FE_{re}}(\mathrm{H}^+) \tag{6}$$

$$\mathrm{R}^\bullet \rightleftharpoons \mathrm{R}^+ + e^- \qquad \mathrm{FE_{ox}}(\mathrm{R}^\bullet) \tag{7}$$

$$\mathrm{H}^\bullet + e^- \rightleftharpoons \mathrm{H}^- \qquad \mathrm{FE_{re}}(\mathrm{H}^\bullet) \tag{8}$$

$$\mathrm{R{-}H} \rightleftharpoons \mathrm{R}^+ + \mathrm{H}^- \qquad \Delta G_{\mathrm{R}^+} \tag{9}$$

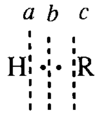
involved hydride transfer to triphenylcarbenium ion (eq 10);[7] however, attempts to determine thermodynamic

$$\mathrm{M{-}H} + \mathrm{Ph_3C^+} \rightleftharpoons \mathrm{M^+} + \mathrm{Ph_3CH} \tag{10}$$

hydridicities have been less common.[8] For that reason, we have been interested in developing additional quantitative information on the thermodynamics of hydride transfer. Also, we note that thermodynamic studies (acidity and bond enthalpy determinations) on organometallic compounds are often carried out in acetonitrile solution.[9] The available $\mathrm{p}K_{\mathrm{R}^+}$ data refer to reactions involving hydroxide transfer in aqueous solution,[2] and it is not clear how these data are related to ΔG_{R^+} in organic solvents. In this paper we will use a new thermodynamic cycle based on gas-phase C−H bond dissociation enthalpy (BDE) to determine ΔG_{R^+} data for a series of compounds, including many stable, isolable carbenium ion systems of use to the synthetic chemist; some of the available data are from $\mathrm{p}K_\mathrm{a}$ studies in DMSO solution, so we will also compare DMSO and MeCN data for hydride transfer.

Results and Discussion

Any covalent H−R bond has three different bond cleavage modes, which are denoted as *a*, *b*, and *c*. Mode a is heterolysis to proton and carbanion and is a process for which considerable data exist. The thermodynamic data are usually expressed in terms of $\mathrm{p}K_\mathrm{a}$, and the solution Gibbs free energy difference (ΔG_{R^-}) for the process in eq 11 is equal to 1.37 $\mathrm{p}K_\mathrm{a}$ (kcal/mol). There are many different ways to determine the equilibrium acidities ($\mathrm{p}K_\mathrm{a}$s) in different solvents,[10] but the most extensive acidity scale established for organic weak acids was developed in dimethyl sulfoxide (DMSO) solution by Bordwell and co-workers.[11] The DMSO equilibrium acidities are virtually free from ion pair effects, since DMSO is a very polar solvent and highly effective at solvating protons.



$$\mathrm{H{-}R} \xrightleftharpoons{\Delta G_{\mathrm{R}^-}} \mathrm{H}^+ + \mathrm{R}^- \tag{11}$$

Gibbs Free Energies ($\Delta G_{\mathrm{R}^\bullet}$) of Radicals. Bond cleavage mode *b* is quantified by the homolytic bond dissociation enthalpy (BDE). The direct measurement of the BDE is often difficult, if not impossible, since most radicals are very reactive intermediates. The BDEs of the acidic C−H bonds have, however, been determined by a combination (eq 16) of the equilibrium acidities and the oxidation potentials of the conjugate anions, both of which were measured in DMSO solution.[12] Equation 16 was originally derived from the thermodynamic cycle shown in Scheme 2, which is the solution counterpart of the gas-phase acidity thermodynamic cycle.[13] Bordwell and co-workers have emphasized that their empirical BDEs are gas-phase BDEs, even though both equilibrium acidity and oxidation potential measurements were carried out in DMSO solution;[12b,16] this is based on the notion that the entropy of solvation for $\mathrm{R}^\bullet$ and RH (which differ only by one H atom) should be similar and cancel, which is supported by available thermodynamic data.[14] The constant C has been determined to have the value 73.3 kcal/mol in DMSO[12b,15] and 59.5 kcal/mol in MeCN[9d,12b,15] when the oxidation potential of the conjugate base is referred to the ferrocene/ferrocenium couple; this term covers thermodynamic contributions arising from hydrogen atom formation, solvation free energies, hydrogen atom transfer energies, and the $T\Delta S°$ term. The BDEs determined from eq 16 have been shown to be consistent with the best available literature values to within ±2 kcal/mol.[16]

To use these gas-phase BDE data for the determination of solution quantities ($\Delta G_{\mathrm{R}^\bullet}$ or ΔG_{R^+}), it is necessary to determine the entropy change associated with solvation. The entropy of the hydrogen atom is 27.4 cal/mol·K in the gas phase,[17] and it was estimated to be 11 cal/mol·K in acetonitrile and DMSO solutions.[18] Therefore, the Gibbs free energy ($\Delta G_{\mathrm{R}^\bullet}$) for the homolytic cleavage of the H−R bond *in solution* can be calculated from the $\mathrm{BDE_{HR}}$

Hartgarink, J.; Baird, M. C. *J. Org. Chem.* **1980**, *45*, 291−299. (k) Bly, R. S.; Silverman, G. S.; Hossain, M. M.; Bly, R. K. *Organometallics* **1984**, *3*, 642−644. (l) Hneihen, A. S.; Fermin, M. C.; Maas, J. J.; Bruno, J. W. *J. Organomet. Chem.* **1992**, *429*, C33−C37.

(7) Cheng, T.-Y.; Bullock, R. M. *Organometallics* **1995**, *14*, 4031−4034.

(8) (a) Xu, A. N.; Studebaker, D. B.; Westmoreland, T. D. *Organometallics* **1996**, *15*, 4888−4890. (b) Ceccon, A.; Giacometti, G.; Venzo, A.; Paolucci, D.; Benozzi, D. *J. Organomet. Chem.* **1980**, *185*, 231−239. (c) Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1984**, *106*, 2554−2558. (d) Nietlispach, D.; Bakhmutov, V. I.; Berke, H. *J. Am. Chem. Soc.* **1993**, *115*, 9191−9195.

(9) (a) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257−2263. (b) Krisjansdottir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983−1987. (c) Krisjansdottir, S. S.; Norton, J. R. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH: New York, 1992; Chapter 9. (d) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711−6718. (e) Tilset, M. *J. Am. Chem. Soc.* **1992**, *114*, 2740−2741. (f) Skagestad, V.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 5077−5083. (g) Smith, K.-T.; Romming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681−8689.

(10) Izutsu, K. *Acid−Base Dissociation Constants in Dipolar Aprotic Solvents*, IUPAC Chemical Data Series, No. 35; Blackwell Scientific Publications: Oxford, 1990.

(11) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(12) (a) Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229. (b) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X.-M. *J. Am. Chem. Soc.* **1991**, *113*, 9790−9795.

(13) Janousek, B. K.; Reed, K. T.; Brauman, J. I. *J. Am. Chem. Soc.* **1980,** *102*, 3125.

(14) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

(15) Wayner, D. D. M.; Lusztyk, E.; Page, D.; Ingold, K. U.; Mulder, P.; Laarhoven, L. J. J.; Aldrich, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 8737.

(16) Bordwell, F. G.; Zhang, X.-M. *Acc. Chem. Res.* **1993**, *26*, 510.

Scheme 2

$$\text{R-H} \rightleftharpoons \text{R}^- + \text{H}^+ \qquad \text{p}K_a \qquad (12)$$

$$\text{R}^- \rightleftharpoons \text{R}^\bullet + e^- \qquad FE_{ox}(\text{R}^-) \qquad (13)$$

$$\text{H}^+ + e^- \rightleftharpoons \text{H}^\bullet \qquad C \qquad (14)$$

$$\text{R-H} \rightleftharpoons \text{R}^\bullet + \text{H}^\bullet \qquad \text{BDE}_{\text{HR}} \qquad (15)$$

$$\text{BDE}_{\text{HR}} = 1.37\ \text{p}K_a + 23.1\ E_{ox}(\text{R-}) + C \qquad (16)$$

in the gas phase by subtracting the $T\Delta S$ term for the hydrogen atom (eq 17). Since the entropy difference of hydrogen atom between gas phase and solution is 16.4 cal/mol·K for DMSO and acetonitrile,[18] the $T\Delta S$ term is calculated to be 4.9 kcal/mol at 298 K. Thus eq 17 illustrates the method used to determine solution $\Delta G_{\text{R}^\bullet}$ values.

$$\Delta G_{\text{R}\cdot} = \text{BDE}_{\text{HR}} - T\Delta S = \text{BDE}_{\text{HR}} - 4.9\ \text{kcal/mol} \qquad (17)$$

Gibbs Free Energy (ΔG_{R^+}) of Carbenium Ions. The direct determination of the Gibbs free energy (ΔG_{R^+}) for heterolytic bond cleavage by mode *c* (eq 21) would also be impractical, since both carbenium ion and hydride are very reactive species. However, we use the thermodynamic cycle shown in Scheme 3 to determine the solution Gibbs free energy for the process. It should be noted that this approach is fundamentally similar to that used by Parker (eqs 4−8),[4] since eqs 4−6 in that cycle constitute the thermodynamic cycle for the determination of bond dissociation enthalpies. The advantage of beginning with BDEs for the determination of ΔG_{R^+} is that the BDEs are gas-phase quantities which may be readily converted to solution ΔG_{R^+} values with the appropriate $T\Delta S$ term (eq 17), *provided* the oxidation potentials (eqs 19, 20) are determined in the solvent of interest. This means that pK_a need only be determined in one solvent; again we note that we are assuming equal solvation energies for $\text{R}^\bullet$ and RH. This assumption was used in the original determination of BDEs from solution data; this approach is acceptable for C−H acids, although it may be compromised by hydrogen-bonding effects in O−H acids.[3,15]

The incorporation of electrochemical potentials in thermodynamic cycles normally requires that the potentials be referred to the standard normal hydrogen electrode (NHE); however, in Scheme 3 we are interested in the *difference* in potentials $E°(\text{R}^\bullet/\text{R}^+) - E°(\text{H}^\bullet/\text{H}^-)$. Thus the choice of reference is arbitrary, so long as it is consistent for eqs 19 and 20; we have chosen to refer the redox potentials to the ferrocene/ferrocenium couple because this has been used in many previous determinations of BDE from pK_a. Parker has estimated the reduction potentials of the hydrogen atom vs NHE in acetonitrile and DMSO solutions,[19] and we have adjusted these to the ferrocene/ferrocenium (Fc/Fc$^+$) couple using his data.[19] The reduction potentials of hydrogen atom, together with the related literature information is summarized in Table 1. The expression used for the calculation of ΔG_{R^+} is given in eq 22, in which $E_{\text{re}}(\text{H}^\bullet)$ is the hydrogen atom reduction potential vs Fc/Fc$^+$ in the appropriate solvent (Table 1).

Scheme 3

$$\text{R-H} \rightleftharpoons \text{R}^\bullet + \text{H}^\bullet \qquad \Delta G_{\text{R}\cdot} \qquad (18)$$

$$\text{R}^\bullet - e^- \rightleftharpoons \text{R}^+ \qquad FE_{ox}(\text{R}^\cdot) \qquad (19)$$

$$\text{H}^\bullet + e^- \rightleftharpoons \text{H}^- \qquad -FE_{re}(\text{H}^\cdot) \qquad (20)$$

$$\text{R-H} \rightleftharpoons \text{R}^+ + \text{H}^- \qquad \Delta G_{\text{R}^+} \qquad (21)$$

$$\Delta G_{\text{R}+} = \Delta G_{\text{R}\cdot} + 23.1\ E_{ox}(\text{R}^\cdot) - 23.1\ E_{re}(\text{H}^\cdot) \qquad (22)$$

Table 1. Reduction Potentials of Hydrogen Atom in Acetonitrile and Dimethyl Sulfoxide

solvent	$E_{\text{re}}(\text{H}^\bullet)$ vs NHE,[a] V	$E_{\text{re}}(\text{H}^\bullet)$ vs Fc/Fc$^+$, V
acetonitrile	−0.60	−1.128[b]
dimethyl sulfoxide	−0.55	−1.087[c]

[a] Taken from ref 4b. [b] The NHE in acetonitrile is reported to be −0.528 V vs Fc/Fc$^+$ couple (ref 4b). [c] The NHE in dimethyl sulfoxide is reported to be −0.537 V vs Fc/Fc$^+$ (ref 4b).

Gibbs Free Energies of Anions, Radicals, and Cations in DMSO and MeCN. The Gibbs free energies (ΔG_{R^-}, $\Delta G_{\text{R}^\bullet}$, and ΔG_{R^+}) in DMSO solution were obtained for anions, radicals and cations derived from toluene, four xanthenes, four fluorenes, and nine triphenylmethanes, and the results are summarized in Table 2. Similar data for 12 9-dialkylaminofluorenes are summarized in Table 3. Table 4 contains thermodynamic data for two 2-benzoyl-*N*,*N*′-dialkylperhydropyrimidines and two α,α-bis(cycloalkylamino)acetophenones. Finally, Table 5 contains MeCN solution data for a variety of triarylmethane derivatives and four cyano-substituted compounds. The determination of BDE with eq 16 requires the equilibrium acidities and the oxidation potentials of the conjugate anions. The pK_a of triphenylmethane was determined to be 30.6,[11] which is close to the upper limit of the DMSO acidity scale. It is difficult, if not impossible, to determine the equilibrium acidities in DMSO solution for the triphenylmethanes with electron-donating groups, and so the BDE values for these triphenylmethanes could not be determined with eq 16 and the related DMSO solution data. However, the BDEs of triphenylmethane and derivatives with a *p*-phenyl, a *p*-thiomethoxy, or a *p*-methoxy substituent (entries 41, 43, 45, Table 5) show C−H BDEs of 80.5 ± 0.5 kcal/mol.[20] Parker et al.[4a] estimated that the pK_a value of $(p\text{-Me}_2\text{NC}_6\text{H}_4)_3\text{CH}$ in DMSO is 39.4, based on Breslow's results.[21] The oxidation potential of the corresponding carbanion was measured in DMSO to be −2.047 V (vs Fc/Fc$^+$),[4a] which leads to the determination of the BDE as 80.0 kcal/mol. Arnett has reported data for a series of triphenylmethane derivatives, including **39** and **47**; these exhibit BDEs of 79.2 and 78.1 kcal/mol.[3d] In addition, a number of 2-substituted or 2,7-disubstituted fluorenes exhibit constant BDEs (79.5 ± 1 kcal/mol) for the acidic C−H bonds,[16] regardless the electron-withdrawing or -donating substituents; the equilibrium acidities of fluorenes with electron-donating groups are readily measured in DMSO

---

[17] Lide, D. R. *CRC Handbook of Chemistry and Physics*, 76th ed.; Boca Raton, FL, 1995; pp 5−15.

[18] Brunner, E. *J. Chem. Eng. Data* **1985**, *30*, 269.

[19] Parker, V. D. *J. Am. Chem. Soc.* **1992**, *114*, 7458−7462.

[20] Bordwell, F. G.; Cheng, J.-P.; Satish, A. V. Twyman, C. L. *J. Org. Chem.* **1992**, *57*, 6542.

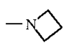
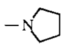
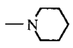
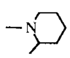
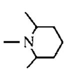
[21] Breslow, R.; Chu, W. *J. Am. Chem. Soc.* **1973**, *95*, 411−418.

Table 2. Free Energies for C−H Bond Homolysis, Deprotonation, and Hydride Loss in Dimethyl Sulfoxide (DMSO) Solution

no.	precursor	ΔG_{R^-}[a]	$\Delta G_{R^\bullet}$[e]	$E_{re(R^+)}$[f]	ΔG_{R^+}[g]	pK_{R^+}[h]
1	toluene	58.9	82.8	0.220	113.0	−23.8
2	xanthene	41.1	70.8	−0.347	87.9	−0.85
3	9-cyanoxanthene	18.6	64.3	0.120	92.2	(−4.33)
4	9-phenylxanthene	38.2	71.5	−0.352	88.5	1.1
5	9-(*p*-MeOC$_6$H$_4$)xanthene	38.9	71.2	−0.410	86.8	(0.18)
6	fluorene	31.0	74.9	0.250	105.8	−16.6[i]
7	9-phenylfluorene	24.5	69.4	0.110	97.0	(−8.51)
8	9-(*o*-MeC$_6$H$_4$)fluorene	25.8	71.8	0.180	101.1	(−15.3)
9	9-mesitylfluorene	25.5	71.1	0.217	101.2	(−12.4)
10	Ph$_3$CH	41.9	76.2	−0.133	98.2	−6.5
11	*p*-PhCOC$_6$H$_4$CHPh$_2$	30.7[b]	73.8[b]	−0.181[b]	94.7	(−6.6)
12	*p*-NO$_2$C$_6$H$_4$CHPh$_2$	23.0[b]	73.3[b]	−0.063[b]	96.9	−9.3
13	(*p*-NO$_2$C$_6$H$_4$)$_3$CH	17.4[b]	74.6[b]	0.284[b]	106.3	−16.4
14	(*p*-Me$_2$NC$_6$H$_4$)$_3$CH	54.0[c]	75.3[c]	−1.109[c]	74.8	9.4
15	(4-ClC$_6$H$_4$)$_3$CH	37.0[c]	76.3[c]	−0.170[c]	97.5	−7.6
16	4-PhC$_6$H$_4$CHPh$_2$	40.3[b]	75.8[b]	−0.281[b]	94.4	(−6.77)
17	(*p*-HC$_6$F$_4$)$_3$CH	18.2[d]	82.8[d]	0.372[d]	116.5	(−21.5)
18	(*p*-BrC$_6$F$_4$)$_3$CH	15.3[d]	82.5[d]	0.311[d]	114.8	(−20.0)

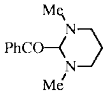
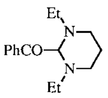
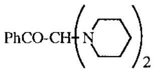
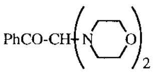
[a] Equilibrium acidities in kcal/mol (1.37 pK_a) taken from ref 33b unless otherwise indicated. [b] Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1992**, *114*, 9787−9792. [c] Reference 4a. [d] Zhang, X.-M.; Bordwell, F. G. Unpublished results. [e] Gibbs free energies in kcal/mol for homolytic cleavage determined by eq 17. The corresponding BDE values were taken from ref 34b, unless otherwise indicated. [f] Reduction potentials of the cations or the oxidation potentials of the radicals in volts; data from ref 34b unless specified otherwise. [g] Gibbs free energies in kcal/mol of heterolytic cleavage by mode c, calculated by eq 22. Estimated uncertaintes ±0.5 kcal/mol. [h] In aqueous acid.[2] Numbers in parentheses were estimated from Figure 1 and eq 24. [i] Experimental results taken from ref 2.

Table 3. Free Energies for Scission of the C−H Bonds of 9-(Dialkylamino)fluorenes (9-R^{1}R^{2}NFlH) in DMSO Solution

No	NR^{1}R^2	ΔG_{R^-}[c]	$\Delta G_{R^\bullet}$[d]	$E_{re(R^+)}$[e]	ΔG_{R^+}[f]	pK_{R^+}, (calc.)[g]
19	NMe$_2$	30.8	66.7	-0.928	70.4	14.4
20	NEt$_2$	29.3	65.9	-0.919	69.7	15.1
21	N(^{i}Pr)$_2$	28.5	68.4	-0.822	74.5	11.0
22	NMe(n-Bu)	30.3	67.5	-0.893	72.0	13.3
23	NMeBz[a]	30.1	67.9	-0.835	73.7	11.7
24		29.9	61.0	-0.930	64.6	19.3
25		30.4	64.9	-0.960	67.8	17.3
26		30.8	67.5	-0.831	73.4	12.1
27		29.3	66.8	-0.839	72.5	12.7
28		26.6	67.5	-0.825	73.6	12.0
29	NCy$_2$[b]	27.5	68.2	-0.770	73.5	10.0

[a] *N*-Methyl-*N*-benzylaminofluorene. [b] *N*,*N*-Dicyclohexylaminofluorene. [c] Equilibrium acidities in kcal/mol (1.37 pK_a) taken from ref 33b. [d] Gibbs free energies in kcal/mol for homolytic cleavage determined by eq 17. The corresponding BDE values were taken from ref 33b. [e] Reversible oxidation potentials of the radicals in volts vs Fc/Fc$^+$. Data taken from ref 34b. [f] Gibbs free energies in kcal/mol of heterolytic cleavage by mode c, calculated by eq 22. Estimated uncertainties ±0.5 kcal/mol. [g] In aqueous acid.[2] All values were estimated from Figure 1 and eq 24.

Table 4. Free Energies for C−H Bond Scission of 2-Benzoyl-*N*,*N*′-dialkylperhydropyrimidine and α,α-Bis(cycloalkylamino)acetophenones in Dimethyl Sulfoxide (DMSO)

No	Precursor	ΔG_{R^-}[a]	$\Delta G_{R^\bullet}$[b]	$E_{re(R^+)}$[c]	ΔG_{R^+}[d]	pK_{R^+}[e]
30		38.2	68.1	-1.451	59.7	23.6
31		37.0	66.9	-1.490	57.6	25.3
32		35.1	68.9	-1.203	66.2	17.8
33		33.4	70.6	-1.080	70.8	14.4

[a] Equilibrium acidities in kcal/mol (1.37 pK_a) taken from ref 33b. [b] Gibbs free energies in kcal/mol for homolytic cleavage determined by eq 17. The corresponding BDE values taken from ref 34b. [c] Reversible oxidation potentials of the radicals in volts vs Fc/Fc$^+$. Data taken from ref 34b unless otherwise indicated. [d] Gibbs free energies in kcal/mol of heterolytic cleavage by mode c, calculated by eq 22. Estimated uncertainties ±0.5 kcal/mol. [e] In aqueous acid.[2] All values estimated from Figure 1.

solution.[22] Clearly, then, the BDEs for a series of structurally similar compounds are thus often insensitive to the electronics of remote substituents;[23] we have therefore used a C−H BDE of 80 kcal/mol for the remaining triphenylmethane derivatives in Table 5. The relative reduction potentials of a series of triphenylmethyl cations have been determined in acetonitrile solution,[2a] and we have determined that the reduction potential of triphenylmethylcarbenium tetrafluorborate is −0.141V vs the Fc/Fc$^+$ couple in acetonitrile. The resulting ΔG_{R^+} values for these triphenylmethanes are summarized in Table 5, along with the reduction potentials and the BDEs.

Correlation of ΔG_{R^+} with pK_{R^+} for Carbenium Ions. As a confirmation of the method employed here,

---

(22) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979.

(23) Angelici has also shown this to be true for metal hydrides with a variety of phosphine co-ligands: Wang, D.; Angelici, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 935−942.

Table 5. Homolytic Bond Dissociation Enthalpies and Free Energies for C−H Bond Scission in Acetonitrile Solution

no.	precursor	BDE_{C-H}[a]	$E_{re(R^+)}$[f]	ΔG_{R^+}[g]	pK_{R^+}[h]
34	$PhCH_2CN$	82.2[b]	0.785[b]	120.5	(−29.0)
35	*p*-$MeOC_6H_4CH_2CN$	80.9[b]	0.195[b]	105.6	(−16.3)
36	*p*-$NCC_6H_4CH_2CN$	83.0[b]	1.125[b]	129.2	(−36.7)
37	*p*-$NCC_6H_4CH_2Ph$	81.9[b]	0.210[b]	107.0	(−17.5)
38	Ph_3CH	81.0[c]	−0.141	99.1	−6.6
39	*p*-$FC_6H_4CHPh_2$	79.2[d]	−0.147	98.0	−6.42
40	*m*-$CH_3OC_6H_4CHPh_2$	80	−0.163	97.6	(−6.1)
41	*p*-$C_6H_5C_6H_4CHPh_2$	80.6[c]	−0.176	97.9	(−6.3)
42	*p*-$CH_3C_6H_4CHPh_2$	80	−0.227	96.1	−5.4
43	*p*-$CH_3SC_6H_4CHPh_2$	80.9[c]	−0.296	95.4	−5.1
44	(*p*-$CH_3C_6H_4)_3CH$	80	−0.344	93.4	−3.56
45	*p*-$CH_3OC_6H_4CHPh_2$	80.9[c]	−0.360	93.9	−3.3
46	(*p*-$CH_3OC_6H_4)_2CHPh$	80	−0.522	89.3	−1.0
47	(*p*-$CH_3OC_6H_4)_3CH$	78.1[d]	−0.659	86.1	0.82
48	*p*-$Me_2NC_6H_4CHPh_2$	80	−0.801	82.9	3.6
49	(*p*-$Me_2NC_6H_4)_3CH$	80.0[e]	−1.178	74.2	9.36

[a] Homolytic bond dissociation energies in kcal/mol, estimated unless otherwise indicated. [b] Data from ref 34b. [c] Bordwell, F. G.; Cheng, J.-P.; Satish, A. V.; Twyman, C. L. *J. Org. Chem.* **1992**, *57*, 6542. [d] Reference 3d. [e] Reference 4a. [f] The reduction potentials of the triphenylmethyl cations (V), vs Fc/Fc$^+$, as measured in acetonitrile. Data taken from ref 2a, unless indicated otherwise. [g] In kcal/mol. Estimated uncertainties ±0.5 kcal/mol. [h] In aqueous acid.[2] Numbers in parentheses were estimated from Figure 1 and eq 23.

we sought to compare the DMSO ΔG_{R^+} values with those obtained in the previous studies by Arnett[3d] and Parker.[4] Fortunately, eight of the compounds in Table 2 were also determined in Parker's study (numbers 2, 4, 6, 7, 10, and 14−16) and five were reported in Arnett's work (numbers 2, 4, 10, 16, and 14), so we sought to check the correlation of these sets with our values. A plot of our ΔG_{R^+} data vs those of Parker[4] exhibits a slope of 1.00 ± 0.07, a zero intercept (actually, 1 ± 6), and $r = 0.985$; all of the overlapping eight compounds showed agreement in ΔG_{R^+} to within ±3 kcal/mol. A similar comparison with Arnett's data gave a slope of 0.9 ± 0.2, an intercept of 5 ± 19, and $r = 0.93$. Arnett's data were derived from measurements of the enthalpy of reaction between $B(CN)_3H^-$ and carbenium ion (ΔH_h), with which it is necessary to assume that entropy terms cancel; Arnett has noted that differences in solvent (sulfolane vs DMSO) and reaction standard state (in hydride addition vs proton removal) may lead to unanticipated entropic contributions,[3d] and this could be the origin of the scatter in the data comparison.

A similar strategy has been used to compare ΔG_{R^+} data obtained in DMSO and MeCN. If we plot ΔG_{R^+} for the compounds studied here vs their pK_{R^+} values (known for 10 of the compounds in Table 2 and 10 of those in Table 5), an excellent fit results for each set of data (Figure 1, r(DMSO) = 0.988, r(MeCN) = 0.994); the relevant conversions (from the least-squares fits) are given in eqs 23 and 24. Arnett has shown that a similar correlation

$$\Delta G_{R^+}(\text{MeCN}) = -1.53pK_{R^+} + 88.2 \text{ kcal/mol} \tag{23}$$

$$\Delta G_{R^+}(\text{DMSO}) = -1.09pK_{R^+} + 87.5 \text{ kcal/mol} \tag{24}$$

exists for his ΔH_h data and that the fit is particularly good for triphenylmethyl derivatives ($r = 0.989$ for a series of eleven derivatives).[3d] Thus pK_{R^+} serves to anchor the ΔG_{R^+} scales in the two solvents, and eqs 23 and 24 could be used to determine the equation relating these scales. In practice, however, in the normal range for stable carbenium ions (ΔG_{R^+} ca. 70−100 kcal/mol), the difference for a given compound is usually less than the uncertainty in the experimental results (ca. 0.5−1 kcal/mol). Indeed triphenylcarbenium and crystal violet have been studied in both solvents (entries 10, 14, 38, and 49), and in both cases the DMSO and MeCN ΔG_{R^+} values agree to within 1 kcal/mol. It is worth noting that DMSO and MeCN pK_a values typically differ by ca. 9−11 p*K* units, or ca. 12−16 kcal/mol.[2,24] This has been attributed to the difference in solvation of the proton, which contributes significantly; mass spectrometry studies show that proton binding of the first gas-phase water (yielding H_3O^+) is exothermic by ca. 165 kcal/mol[25] and coordination of the second water molecule liberates an additional 36 kcal/mol.[26] Similar processes may be expected in solution, and DMSO is more effective in solvating the proton than is MeCN; this leads to the lower p*K* values in DMSO (vs MeCN). The solvation of hydride is much less exothermic than is solvation of the proton; the energy of the former has been shown to be similar to that for most organic anions, and this explains the comparable ΔG_{R^+} values seen in the two solvents.[27]

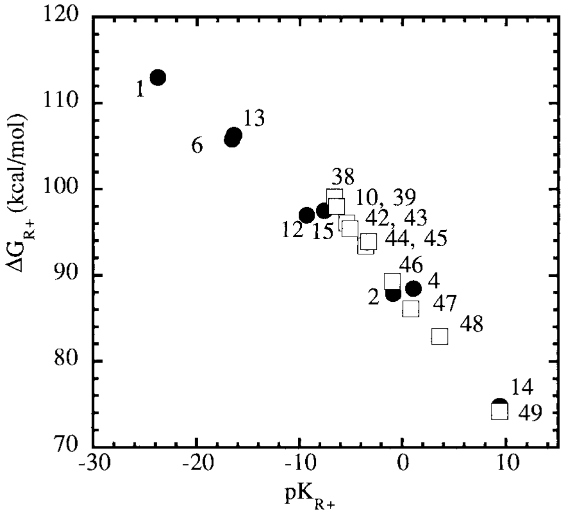


Figure 1. Plot of ΔG_{R^+} vs pK_{R+} for compounds in Tables 2 and 5. Data are for studies done in DMSO (●) or MeCN (□).

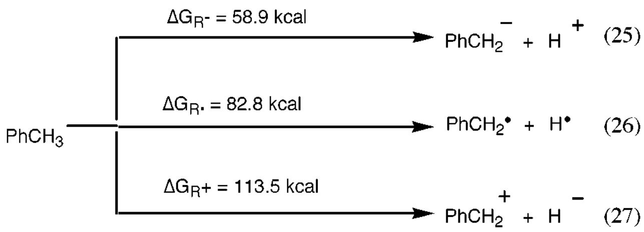
---

(24) Fermin, M. C.; Thiyagarajan, B.; Bruno, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 974−979.

(25) Munson, M. S. B. *J. Am. Chem. Soc.* **1965**, *87*, 2332.

(26) Kebark, P.; Searles, S. K.; Zolla, A.; Scarborough, J.; Arshadi, M. *J. Am. Chem. Soc.* **1967**, *89*, 6393.

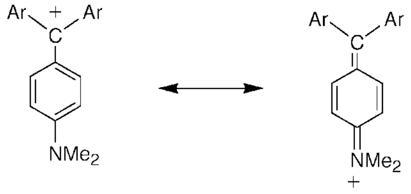
Scheme 4



The correlation of ΔG_{R^+} with pK_{R^+} allows us to address another consideration. All of the thermodynamic cycles discussed herein involve redox potentials determined with cyclic voltammetry. The rigorous determination of thermodynamic potentials requires reversible voltammetric waves, but some of the species described herein give rise to irreversible reductions and/or oxidations. In these cases we have used peak potentials, and this practice has been shown previously to lead to negligible errors in the calculated thermodynamic quantities.[28] Fortunately, all of the compounds contained in Tables 3 and 4 exhibited reversible redox behavior, so the potentials cited are true thermodynamic potentials. In addition, many of the para-substituted trityl derivatives also exhibit reversible reduction of the carbenium ion; the fact that these compounds *and* those exhibiting irreversible redox behavior fit the same plot of ΔG_{R^+} vs pK_{R^+} suggests that the use of peak potentials does not constitute a significant source of error.

Gibbs Free Energies for the Formation of Anions, Radicals, and Carbenium Ions. The free energies for the benzylic C−H bond scission by the three different cleavage modes (DMSO solution) are summarized in Scheme 4. It is known that homolytic cleavage is the thermodynamically favorable process in the gas phase.[16] Examination of Table 2 and Scheme 4 shows that heterolytic cleavage by mode *a* is the most favorable process in DMSO solution; the ΔG_{R^-} value of toluene is 24 kcal/mol less than the $\Delta G_{R\cdot}$ value, and about 54 kcal/mol lower than the heterolytic cleavage to hydride (mode *c*). The low energy for mode a scission in solution is clearly associated with the strong solvation of the proton; this order is generally seen, but we will note below some interesting energetic comparisons.

The heterolysis energies reported in Tables 2−5 show clear evidence for the influence of substituents in all classes of compounds studied. As expected, introduction of electron-donating groups has the opposite effects on ΔG_{R^-} and ΔG_{R^+} values; examination of entries 34 and 35 (Table 5) shows that introduction of a *p*-methoxy group into $PhCH_2CN$ increases the ΔG_{R^-} by 2.6 kcal/mol but decreases the ΔG_{R^+} value by 14.6 kcal/mol. Electron-withdrawing groups, however, can operate via a combination of inductive and resonance effects. Both will stabilize the carbanions, and examination of Table 2 shows that the introduction of electron-withdrawing groups decreases the ΔG_{R^-} values; hence, for the series of triarylmethyl anions the introduction of para substituents benzoyl (entry 11, 30.7 kcal/mol) or nitro (entry 12, 23.0 kcal/mol) diminishes ΔG_{R^-} relative to that of trityl (entry 10, 41.9 kcal/mol), while the presence of three donor Me_2N groups (entry 14, 54.0 kcal/mol) results in a higher ΔG_{R^-} value. Conversely, electron-withdrawing substituents destabilize carbenium ions by inductive effects but may stabilize them via resonance effects. The ΔG_{R^+} values for $(HC_6F_4)_3CH$ (entry 17) and $(p\text{-}BrC_6F_4)_3CH$ (entry 18) are 18.3 and 16.6 kcal/mol higher than that of triphenylmethane since the inductive effects of fluorophenyl substituents are dominant.[29] For the nitro and benzoyl groups, resonance effects are more important; these substituents do not increase ΔG_{R^+} values but result in small decreases of 1.3 and 3.5 kcal/mol, respectively, relative to trityl. The most dramatic result is that the introduction of a 4-dimethylamino group into each of the phenyl rings of triphenylmethane stabilizes the carbenium ion (via the iminium resonance contributor shown) to the extent that heterolysis to hydride and carbenium ion (ΔG_{R^+} = 75 kcal/mol) is comparable in energy to homolytic bond cleavage ($\Delta G_{R\cdot}$ = 75.3 kcal/mol) in DMSO.



Gibbs Free Energies of the Anions, Radicals, and Cations Derived from 9-Substituted Fluorenes. Examination of entries 2 and 6 of Table 2 shows that the ΔG_{R^-} value of fluorene is 10 kcal/mol less than that of xanthene, while the ΔG_{R^+} value of fluorene is 18 kcal/mol higher than that of xanthene. Clearly, the significant stabilization of fluorenide anion is associated with its 14 π-electron aromatic character, and the destabilization of 9-fluorenyl cation is associated with its 12 π-electron antiaromatic character.[30] Introduction of a phenyl group in the 9-position of fluorene has a significant influence on the stabilities of the corresponding anion, radical, and cation, all of which are more stable than are the unsubstituted derivatives. These results suggest that the phenyl substituents on the 9-phenylfluorenyl anion, radical, and cation are situated so as to delocalize the negative charge, unpaired electron, or positive charge into the phenyl ring. Note, however, that this favorable disposition of the 9-phenyl substituent can be disrupted by the introduction of one or two methyl groups into its ortho positions; this should increase the steric interaction with the C-1 and C-8 hydrogen atoms on the fluorene rings, force the 9-phenyl substituent to twist relative to the fluorenyl ring, and thus increase the values of ΔG_{R^-}, $\Delta G_{R\cdot}$, and ΔG_{R^+} values relative to those of 9-phenylfluorene. Indeed, 9-(*o*-MeC_6H_4)fluorene (entry 8) and 9-mesitylfluorene (entry 9) show ΔG_{R^-}, $\Delta G_{R\cdot}$, and ΔG_{R^+} values that are all higher than those of 9-phenylfluorene; the effects on ΔG_{R^-} and $\Delta G_{R\cdot}$ are small, but the effects on ΔG_{R^+} are more pronounced. Related effects have been documented previously.[31]

---

(27) (a) Parker, V. D. *Acta Chem. Scand.* **1992**, *46*, 1133−1138. (b) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109−6114.

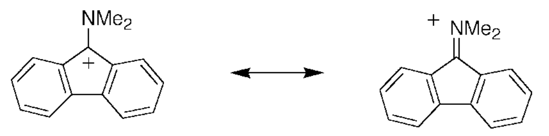
(28) Zhang, X.-M.; Fry, A. J.; Bordwell, F. G. *J. Org. Chem.* **1996**, *61*, 4101−4106.

(29) (a) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195. (b) Bordwell, F. G.; Zhang, X.-M.; Filler, R. *J. Org. Chem.* **1993**, *58*, 6067−6071.

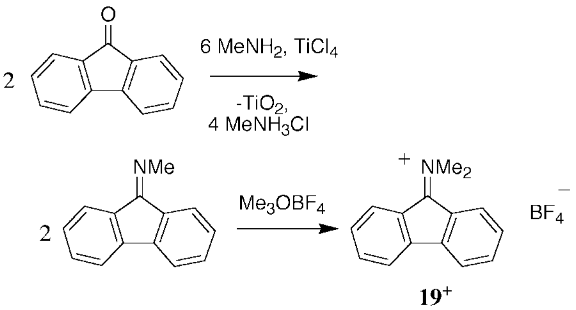
(30) Allen, A. D.; Sumonja, M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 2371−2375.

(31) (a) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929−2935. (b) McKinley, S. V.; Rakshys, J. W., Jr.; Young, A. E.; Freedman, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 4715−4724.

The data in Table 3 show that introduction of various 9-dialkylamino groups into fluorene has a small-to-negligible stabilizing influence on the corresponding carbanions; these effects become more significant as the size of the alkyl group increases. This may be attributed to polarizability effects, since the polarizability effect is proportional to the size of substituent.[32] Examination of the fourth column of Table 3 shows that introduction of the 9-dialkylamino group stabilizes the corresponding carbenium ions by 30−40 kcal/mol, and the ΔG_{R^+} values for these 9-dialkylaminofluorenes are ca. 20−30 kcal/mol less than that of the commonly used triphenylmethyl carbenium ion (Table 2). This stabilization can be attributed to the amino groups, and the 9-dialkylaminofluorenyl carbenium ion is best considered to be an iminium ion; although iminium ions can be susceptible to hydrolysis, the recent isolation (and crystallographic characterization) of a series of iminium ion salts from 50% aqueous acetone shows that hydrolysis does not preclude their preparation and isolation.[33] The stabilities of these 9-dialkylaminofluorenyl cations was also suggested by the observation that voltammetric oxidation of the 9-aminofluorenyl anion exhibited reversible waves for both the anion-to-radical and radical-to-cation oxidations.[34] The stabilization due to these 9-dialkylamino groups also brings the ΔG_{R^+} value close to the corresponding $\Delta G_{\mathrm{R}^\bullet}$ values, so heterolytic cleavage of the C−H bond to carbenium ion and hydride in solution is comparable in energy (within 2−6 kcal/mol) to homolytic cleavage. We have used the relationships given in eqs 23 and 24 to calculate $\mathrm{p}K_{\mathrm{R}^+}$ values for these iminium ions; the aforementioned susceptibility toward hydrolysis would presumably preclude the direct measurement of these.



As part of our goal to prepare and characterize stable hydride acceptors, we have synthesized the dimethyliminium derivative of fluorenone. This was done via the sequence shown in eq 28,[35] which led to the isolation of the tetrafluoroborate salt as a yellow-orange solid (derived from compound **19** in Table 3). Voltammetric studies in MeCN indicated that salt $\mathbf{19}^+\mathrm{BF}_4^-$ exhibited a reversible reduction to the radical at −0.896 V (vs Fc/Fc$^+$), indicating that compound **19** has $\Delta G_{\mathrm{R}^+} = 72.0$ kcal/mol in MeCN. This compares well with the value (70.4 kcal/mol) determined for **19** in DMSO solution (Table 3), consistent with the notion that MeCN vs DMSO solvation effects are small for hydride transfer.

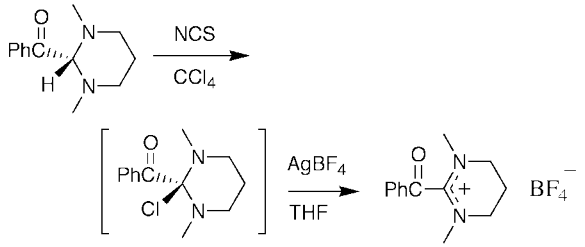


(28)

$\mathbf{19}^+$

Anions, Radicals, and Cations Derived from α,α-Bis(cycloalkylamino)acetophenones and 2-Benzoyl-*N,N*′-dialkylperhydropyrimidines. Examination of entries 30 and 31 of Table 4 shows that the ΔG_{R^-} values of 2-benzoyl-*N,N*′-dialkylperhydropyrimidines are about 3−4 kcal/mol higher than that of acetophenone,[36] and the $\Delta G_{\mathrm{R}^\bullet}$ values are about 20−21 kcal/mol less than that of acetophenone ($\Delta G_{\mathrm{R}^-} = 33.8$ kcal/mol, $\Delta G_{\mathrm{R}^\bullet} = 88$ kcal/mol).[36] It is worth noting that the ΔG_{R^+} values of 2-benzoyl-*N,N*′-dialkylperhydropyrimidines are also about 10−15 kcal/mol less than those of 9-dialkylaminofluorenes. Interestingly, they are even ca. 10 kcal/mol less than the corresponding $\Delta G_{\mathrm{R}^\bullet}$ values, indicating that heterolytic cleavage of the C−H bond by mode *c* is favored by ca. 10 kcal/mol relative to homolytic C−H cleavage in DMSO solution. Although the ΔG_{R^-} and $\Delta G_{\mathrm{R}^\bullet}$ values of α,α-bis(cycloalkylamino)acetophenones (entries 32, 33) are close to those of the 2-benzoyl-*N,N*′-dialkylperhydropyrimidines (entries 30, 31), the ΔG_{R^+} values of the former are about 10 kcal/mol higher than those of the latter. The difference is presumably caused by the steric interaction of two six-membered rings in the α,α-bis(cycloalkylamino)acetophenones, which will prevent the carbenium ion from becoming coplanar with the two nitrogen atoms.

We have synthesized the cationic pyrimidine derivative $\mathbf{30}^+\mathrm{BF}_4^-$ from the neutral precursor by way of a sequence (eq 29) involving chlorination (*N*-chlorosuccinimide, $\mathrm{CH}_2\mathrm{Cl}_2$) and treatment with AgBF_4 in THF; the desired salt was precipitated as a colorless solid. This method proved superior to an alternative one involving direct hydride transfer to $\mathrm{Ph}_3\mathrm{CBF}_4$; although this reaction led to some $\mathbf{30}^+\mathrm{BF}_4^-$, the product was invariably contaminated with acid-derived impurities. In addition, we observed formation of a paramagnetic violet side product which is presumed to arise from competing electron-transfer pathways. We have not isolated and purified the chloride intermediate, which is represented as a covalent species in eq 29. The compound may ionize in polar media, and its NMR spectrum in $\mathrm{CD}_3\mathrm{CN}$ is similar to that of $\mathbf{30}^+\mathrm{BF}_4^-$.



(29)

$\mathbf{30}^+$ BF$_4^-$

Conclusions. Described herein is the use of a thermodynamic cycle designed to allow the use of gas-phase BDEs for the calculation of the free energies of proton,

---

[32] Bordwell, F. G.; Zhang, X.-M. *J. Am. Chem. Soc.* **1994**, *116*, 973−976.

[33] (a) Knop, O.; Cameron, T. S.; Bakshi, P. K.; Kwiatkowski, W.; Choi, S. C.; Adhikesavalu, D. *Can. J. Chem.* **1993**, *71*, 1495−1523. (b) Westerwelle, U.; Keuper, R.; Risch, N. *J. Org. Chem.* **1995**, *60*, 2263−2266.

[34] (a) Bordwell, F. G.; Cheng, J.-P.; Seyedrezai, S. E.; Wilson, C. A. *J. Am. Chem. Soc.* **1988**, *110*, 8178. (b) Zhang, X.-M.; Bordwell, F. G. *J. Org. Chem.* **1992**, *57*, 4163−4168.

[35] Meng, Q.; Thibblin, A. *J. Am. Chem. Soc.* **1997**, *119*, 1224−1229.

[36] Bordwell, F. G.; Harrelson, J. A., Jr.; Zhang, X.-M. *J. Org. Chem.* **1991**, *56*, 4448−4450.

hydrogen atom, or hydride transfer for a wide variety of organic substrates. The transfer from gas phase to solution phase involves the assumption that the solvation energies for substrate RH and its radical analogue $R^\bullet$ are similar; a related assumption was originally used to convert DMSO pK_a data into gas-phase BDEs.[16] Thus the use of BDEs for the determination of ΔGs in DMSO is thermodynamically precise, since this process cancels the original assumption. We have also provided evidence to support the contention that the effects arising from transfer from the gas phase to acetonitrile solution are small; while the solvation energies in DMSO and MeCN are not equivalent, the transfer involves the difference of two small differences in solvation energy (the actual quantity is $(\Delta G_{DMSO}(RH) - \Delta G_{DMSO}(R^\bullet)) - (\Delta G_{MeCN}(R^\bullet) - \Delta G_{MeCN}(RH))$, in which all of the ΔGs refer to solvation energies). The utility of this approach is that it allows one to use DMSO pK_a data for the calculation of ΔG_{R^-}, $\Delta G_{R^\bullet}$, and ΔG_{R^+} in either DMSO or acetontrile (or presumably, any other solvent for which voltammetric data are available). This is important since all of the substrates in Table 5 are weaker acids than is MeCN; therefore MeCN pK_a data are unavailable. Moreover, the solution ΔG data are of importance to the synthetic chemist and for furthering our understanding of the energetics of solution-phase reaction thermodynamics. Since various salts $Ar_3C^+BF_4^-$ are synthetically accessible,[37] the results described herein (and elsewhere[3,4]) provide access to hydride acceptors with ΔG_{R^+} ranging from ca. 60 to 98 kcal/mol. We have begun using these data in the study of organometallic thermodynamics, and these results will be the subject of forthcoming publications.

Experimental Section

The equilibrium acidities were determined by the overlapping indicator titration method described previously;[38] the data have been published and can be found in the references given in Tables 2−4. Redox potentials were determined with a EG&G Versastat computer-interfaced potentiostat, with platinum disk working electrode, platinum wire counter electrode, and Ag/AgI or Ag/$AgNO_3$ reference electrode; all potentials are referenced to the ferrocene/ferrocenium couple. Fluorenone methylimine was prepared from fluorenone, methylamine, and titanium(IV) chloride according to the method of Thibblin.[35] The 2-benzoyl-*N*,*N*-dimethylperhydropyrimidine was prepared by condensing glyoxal and 1,3-bis(methylamino)propane and crystallized from 2-propanol.[34b] Salts of the cations described below were handled under a nitrogen atmosphere using standard Schlenk line techniques. Methylene chloride was distilled from P_2O_5 under nitrogen. THF was distilled from sodium benzophenone ketyl under nitrogen.

Synthesis of $19^+BF_4^-$. In a nitrogen glovebox, 0.44 g (2.27 mmol) of fluorenone methylimine and 0.67 g (4.55 mmol) of trimethyloxonium tetrafluoroborate (Aldrich) were weighed into a flask with a gas inlet. Using a nitrogen purge, 30 mL of dry, degassed methylene chloride was added via syringe. The solution was stirred for ca. 2 h, during which time it developed an orange color and precipitated an orange solid. Half of the solvent was removed in vacuo, and the resulting solution was cooled to 0 °C. The resulting orange solid was collected by filtration and dried in vacuo; yield 0.30 g (45%). ^1H NMR (CD_3CN): 7.97 (d, 2H), 7.74 (m, 2H), 7.67 (m, 2H), 7.43 (m, 2H), 4.09 ppm (s, 6H). ^{13}C NMR (CD_3CN): 137.9, 135.8, 132.1, 130.3, 129.8, 124.2, 122.5, 50.4. IR (Nujol): 1676 (m), 1644 (m), 1594 (m), 1040 cm^{-1} (s, br, BF_4). High-resolution MS: calcd for $[C_{15}H_{14}N]^+$, 208.112625; found, 208.112500.

Synthesis of $30^+BF_4^-$. Crystalline 2-benzoyl-*N*,*N*-dimethylperhydropyrimidine (**30**) (0.44 g, 2.0 mmol) and *N*-chlorosuccinimide (0.50 g, 4.0 mmol) were weighed into a gas inlet flask and degassed. Using a nitrogen purge, 30 mL of methylene chloride was added via syringe. The resulting yellow solution was stirred overnight at ambient temperature. The solvent was removed in vacuo. The oily residue was taken up in 20 mL of THF, and 0.5 g (2.7 mmol) of $AgBF_4$ was added with a nitrogen-charged addition tube. The resulting solution was stirred overnight, during which time it yielded a colorless precipitate of AgCl; this was removed by filtration. The oily residue was extracted with CH_2Cl_2, and a colorless solid was precipitated by cooling a CH_2Cl_2−hexane solution. Yield: 0.22 g (36%). ^1H NMR (CD_3CN): 8.18 (m, 2H), 7.95 (m, 1H), 7.75 (m, 2H), 3.72 and 3.59 (broad mult, 4H), 3.07 (s, 6H), 2.34 and 2.22 (broad mult, 2H). ^{13}C NMR (CD_3CN): 185.8, 157.8, 138.2, 132.2, 130.4, and 118.0, 47.8, 41.2, and 19.2 ppm. IR (Nujol): 1693 (s), 1596 (m), 1066 (br, s, BF_4). High-resolution MS: calcd for $[C_{13}H_{17}N_2O]^+$, 217.134088; found, 217.134100.

Acknowledgment. We thank the National Science Foundation for financial support and Mr. Matt Law for skilled experimental assistance. High-resolution mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois, supported in part by a grant from the National Institute of General Medical Sciences. The 70-SE-4F mass spectrometer was purchased in part with funds from the National Institute of General Medical Sciences (GM 27029).

JO980120D

---

[37] (a) Olah, G. A.; Svoboda, J. J.; Olah, J. A. *Synthesis* **1972**, 544. (b) McKinley, S. V.; Rakshys, J. W., Jr.; Young, A. E.; Freedman, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 4715−4724.

[38] Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. D.; Drucker, G. E.; Margolin, Z.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006−7014.