

with the experimental  $\log k_{\text{obsd}}$  values. Application of the test to reactions with  $\text{Ph}_2\text{CHCl}$ , which gives  $\text{S}_{\text{N}}2$  kinetics and products with no evidence of radical-type products, gave linear Marcus-type plots and  $\log k_{\text{SET}}$  values corresponding to the experimental  $\log k_{\text{obsd}}$  values. It was concluded that the " $\text{S}_{\text{N}}2$  reactions" of 9- $\text{R}_2\text{N-Fl}^-$  ions with  $\text{Ph}_2\text{CHCl}$  are occurring by a radical pair mechanism. This approach promises to be of general use for elucidating the role of SET in reactions of families of anions with electrophiles.

**Concluding Remarks.** The  $\text{Me}_2\text{SO}$  acidity scale, for which about 300 representative values are given in Table II, furnishes (a) quantitative acidity data that can

(60) Ebersson, L. *Acta Chem. Scand. Ser. B* 1982, B36, 533-546; 1984, B38, 439-459. Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: New York, 1978.

(61) Lund, H.; Kristensen, L. H. *Acta Chem. Scand. Ser. B* 1979, B33, 495-498. Lund, T.; Lund, H. *Acta Chem. Scand., Ser. B* 1986, B40, 470-485.

(62) Pross, T. *Acc. Chem. Res.* 1985, 18, 212-219.

be related to intrinsic gas-phase data to provide information on solvation effects and (b) quantitative basicity data that can be related to reactivity data by means of Brønsted, Hammett, and Marcus equations. Combination of the  $\text{p}K_{\text{a}}$  data with electrochemical data can provide estimates of (a) relative radical stabilities, (b) homolytic bond dissociation energies of H-A acids, (c) radical cation acidities, and (d) the acidities of radicals.

*The experimental results presented and referred to in this paper were obtained during the past 15 years by the students whose names appear in the references. Special thanks goes to W. S. Matthews, who modified the Steiner method, reducing the time necessary for each titration and at the same time making it more precise. The author wishes to express his sincere appreciation to these research associates and wishes to thank the National Science Foundation and Petroleum Research Fund for financial support during this period. Discussions with Prof. R. W. Taft were most helpful in preparing the manuscript. We are grateful to Crown Zellerbach Corp. and more recently to Gaylor Chemical Corp. for generous gifts of dimethyl sulfoxide.*

## Structural and Solvent Effects Evaluated from Acidities Measured in Dimethyl Sulfoxide and in the Gas Phase<sup>1</sup>

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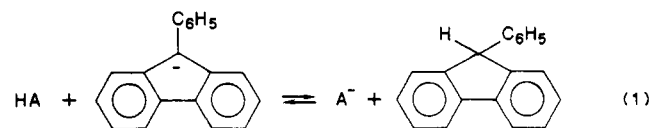
The preceding paper gives extensive data for equilibrium acidities in dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ ) and makes comparisons with corresponding results in other condensed-phase media.<sup>2</sup> In the present paper the results of 76 selected gas-phase acidities<sup>3</sup> are compared with corresponding results in  $\text{Me}_2\text{SO}$  as a means of separating inherent effects of molecular structure on acidities from solvent effects. Simplified concepts are presented on relationships between solvent effects and structure. Broad applicability of the results and concepts is shown.

Table I gives comparisons of gas-phase and  $\text{Me}_2\text{SO}$  acidities, expressed by  $1.364\Delta\text{p}K_{\text{a}} = -\Delta G^\circ$  values in

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Frederick G. Bordwell is Professor Emeritus at Northwestern University. (For a biography summarizing his earlier research activities, see *Acc. Chem. Res.* 1972, 5, 374). In the period 1970-1980 the Bordwell research group established acidity scales in  $\text{Me}_2\text{SO}$  and *N*-methyl-2-pyrrolidone solvents using a method adapted from one developed by E. C. Steiner at Dow Chemical Co. Since 1980 the research focus has shifted to the application of the data in the  $\text{Me}_2\text{SO}$  scale to problems in physical organic chemistry, the results of which are summarized in the preceding Account in this issue.

kcal/mol (hereafter abbreviated as kcal) for the proton-transfer equilibria (eq 1) of 76 typical acids HA with



9-phenylfluorenyl ion (9- $\text{PhFl}^-$ ). The acids have been selected to illustrate important kinds of structural and solvent effects. Positive values of  $-\Delta G^\circ$  indicate greater acidity (lower  $\text{p}K_{\text{a}}$ ) for HA than for 9-phenylfluorene (9- $\text{PhFlH}$ ) and vice versa. The acidities from  $\text{NH}_4^+$  to  $\text{CH}_4$  cover a range of 211 kcal in the gas phase and 74 kcal in  $\text{Me}_2\text{SO}$  solution. The values in the table are arranged in order of increasing  $\text{Me}_2\text{SO}$  medium effects, as defined by  $\Delta G^\circ_{(\text{g})} - \Delta G^\circ_{(\text{s})} = \delta_s \Delta G^\circ$  (where  $s = \text{Me}_2\text{SO}$ ), which cover a range of 160 kcal or 117  $\text{p}K_{\text{a}}$  units.

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(2) Bordwell, F. G. *Acc. Chem. Res.*, preceding paper, in this issue.

(3) All neutral-acid  $-\Delta G^\circ_{(\text{g})}$  values are from the gas-phase acidity scale of Prof. J. E. Bartmess (available by request in care of the Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600). The unpublished results of Drs. F. Anvia, A. D. Headley, J. F. Gal, I. Koppel, M. Mishima, R. W. Taft, and S. Ueki have been incorporated into this scale, which is anchored to the most reliable absolute thermodynamic acidities. The gas-phase acidities for the three positively charged acids in Table I are from ref 4 with correction to a proton affinity of  $\text{NH}_3$  of 204.0 kcal/mol. All  $-\Delta G^\circ_{(\text{s})}$  values are from  $\text{p}K_{\text{a}}$ 's cited in ref 2.

Table I  
Inherent Structural Effects on Acidities Relative to 9-Phenylfluorene ( $-\Delta G^\circ_{(g)}$  Values) and Accompanying Condensed-Phase Solvent Effects of Dimethyl Sulfoxide ( $\delta_s \Delta G^\circ$  Values)<sup>a</sup>

HA	$\delta_s \Delta G^\circ$	$-\Delta G^\circ_{(g)}$	$-\Delta G^\circ_{(s)}$	HA	$\delta_s \Delta G^\circ$	$-\Delta G^\circ_{(g)}$	$-\Delta G^\circ_{(s)}$
1. NH <sub>4</sub> <sup>+</sup>	-126.0	137.5	11.5	39. CNCH <sub>2</sub> CO <sub>2</sub> Et	5.0	1.9	6.9
2. C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>	-111.2	130.6	19.4	40. indene	6.0	-9.1	-3.1
3. C <sub>6</sub> H <sub>5</sub> NH <sup>+</sup>	-100.0	119.8	19.8	41. HBr	6.1	17.3	23.4
4. octafluorofluorene	-8.6	18.2	9.6	42. C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	6.2	-23.6	-17.4
5. <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OH	-5.0	14.6	9.6	43. imidazole	6.3	-7.3	-1.0
6. <i>p</i> -CNC <sub>6</sub> H <sub>4</sub> OH	-3.9	10.2	6.3	44. <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	6.5	-9.8	-3.3
7. <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	-3.3	-0.7	-4.0	45. <i>o</i> -FC <sub>6</sub> H <sub>4</sub> OH	6.6	-3.5	3.1
8. <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	-2.3	14.4	12.1	46. C <sub>6</sub> H <sub>5</sub> OH	6.6	-6.8	-0.2
9. C <sub>6</sub> H <sub>5</sub> CH(CN) <sub>2</sub>	-2.2	20.8	18.6	47. <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH	6.7	-7.2	-0.5
10. CF <sub>3</sub> CONHC <sub>6</sub> H <sub>5</sub>	-2.0	9.1	7.1	48. 2-aminopyridine	6.7	-20.1	-13.4
11. (CF <sub>3</sub> ) <sub>3</sub> COH	-1.8	11.5	9.7	49. C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H	6.8	2.5	9.3
12. (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NH	-1.3	-8.3	-9.6	50. (CH <sub>3</sub> CO) <sub>2</sub> CH <sub>2</sub>	7.3	-1.2	6.1
13. carbazole	-0.9	-1.9	-2.8	51. CH <sub>3</sub> SOCH <sub>3</sub>	7.4	-30.9	-23.5
14. 9- <i>tert</i> -butylfluorene	-0.8	-8.1	-8.9	52. pyrazole	8.1	-10.9	-2.8
15. <i>o</i> -CNC <sub>6</sub> H <sub>4</sub> OH	-0.6	8.4	7.8	53. pyrrole	8.4	-15.4	-7.0
16. fluoradene	-0.5	10.6	10.1	54. C <sub>6</sub> H <sub>5</sub> SH	8.7	1.7	10.4
17. 1,3-diphenylindene	-0.2	6.7	6.5	55. CH <sub>3</sub> (CO <sub>2</sub> Et) <sub>2</sub>	8.8	-6.8	2.0
18. triphenylmethane	-0.1	-17.3	-17.4	56. HONO	9.2	5.0	14.2
19. 2,5-diphenylcyclopentadiene	-0.1	5.0	4.9	57. CH <sub>3</sub> CONH <sub>2</sub>	9.2	-19.6	-10.4
20. 9-phenylfluorene <sup>b</sup>	(0.0)	(0.0)	(0.0)	58. C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	9.7	-19.0	-9.3
21. <i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH	0.0	3.1	3.1	59. CH <sub>3</sub> CN	11.4	-29.7	-18.3
22. CH <sub>3</sub> CONHC <sub>6</sub> H <sub>5</sub>	0.1	-5.1	-5.0	60. CF <sub>3</sub> CH <sub>2</sub> OH	11.9	-18.6	-6.7
23. <i>t</i> -BuCH(CO <sub>2</sub> Et) <sub>2</sub>	0.1	-9.0	-8.9	61. cyclopentadiene	12.0	-12.2	-0.2
24. 9-neopentylfluorene	0.4	-3.7	-3.3	62. C <sub>2</sub> H <sub>5</sub> C≡CH	12.5	-27.4	-14.9
25. CF <sub>3</sub> CO <sub>2</sub> H	0.4	19.2	19.6	63. <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH	13.0	-32.5	-19.5
26. 9-isopropylfluorene	0.7	-8.0	-7.3	64. <i>n</i> -C <sub>4</sub> H <sub>9</sub> SH	13.1	-11.9	1.2
27. Cl <sub>2</sub> CHCO <sub>2</sub> H	1.1	14.7	15.8	65. CH <sub>3</sub> CO <sub>2</sub> H	13.7	-5.6	8.1
28. fluorene	2.0	-8.5	-6.5	66. HCl	14.4	7.5	21.9
29. CF <sub>3</sub> CONH <sub>2</sub>	2.2	-1.2	1.0	67. CH <sub>3</sub> COCH <sub>3</sub>	14.6	-26.4	-11.8
30. indole	2.3	-6.4	-4.1	68. H <sub>2</sub> S <sup>c</sup>	15.0	-9.3	5.7
31. 4-aminopyridine	2.5	-14.3	-11.8	69. HCN	15.1	-8.3	6.8
32. CH <sub>2</sub> (CN) <sub>2</sub>	2.5	6.6	9.1	70. CH <sub>3</sub> NO <sub>2</sub>	15.1	-14.2	0.9
33. diphenylmethane	2.8	-22.7	-19.9	71. C <sub>2</sub> H <sub>5</sub> OH	19.0	-35.3	-16.3
34. C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CN	3.1	-8.6	-5.5	72. CH <sub>4</sub>	~22	-73.0	~-51
35. 3-aminopyridine	3.3	-17.8	-14.5	73. CH <sub>3</sub> OH	23.3	-38.5	-15.2
36. C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	3.9	-38.2	-34.3	74. NH <sub>3</sub>	~29	-60.6	~-32
37. <i>p</i> -FC <sub>6</sub> H <sub>4</sub> OH	4.1	-4.4	-0.3	75. H <sub>2</sub> O	30.1	-48.6	-18.5
38. CH <sub>3</sub> SO <sub>2</sub> CH <sub>3</sub>	4.6	-22.7	-18.1	76. HF	~34	-30.2	~-4

<sup>a</sup> Positive values denote acidifying effect, in kcal/mol. <sup>b</sup> The acidity of 9-phenylfluorene is 335.5 kcal/mol in the gas phase<sup>8</sup> and 24.5 kcal/mol in Me<sub>2</sub>SO solution.<sup>2</sup> <sup>c</sup> Based on pK<sub>HA</sub> = 12.2 estimated from Arnett, E. M.; Small, L. E. *J. Am. Chem. Soc.* 1977, 99, 808-816.

For a neutral acid HA, the size of the medium effect provides a measure of the ability of the Me<sub>2</sub>SO solvent to stabilize the anion A<sup>-</sup> relative to the 9-PhFl<sup>-</sup> ion, minus the ability of the Me<sub>2</sub>SO solvent to stabilize HA relative to 9-PhFlH. Comparisons of the corresponding  $-\Delta G^\circ_{(g)}$  and  $\delta_s \Delta G^\circ$  values for reaction 1 differentiate between those effects of molecular structure on acidity that are intrinsic (given by  $-\Delta G^\circ_{(g)}$  values in Table I, or by their differences) and those effects that are due to Me<sub>2</sub>SO solvation (given by the corresponding  $\delta_s \Delta G^\circ$  values in Table I). It is clear from the results in Table I that the structural effects on  $\delta_s \Delta G^\circ$  values have no apparent relationship to the corresponding effects on  $-\Delta G^\circ_{(g)}$  and  $-\Delta G^\circ_{(s)}$  values. Even the signs may differ between the three sets of results. There is very poor linear correlation ( $R^2 = 0.498$  for the 76 acids of Table I;  $R^2 = 0.818$  if the NH<sup>+</sup> acids are omitted) for  $-\Delta G^\circ_{(g)}$  vs  $-\Delta G^\circ_{(s)}$ . For  $\delta_s \Delta G^\circ$  vs  $-\Delta G^\circ_{(g)}$  there is a very crude reverse trend ( $R^2 = 0.504$  with the NH<sup>+</sup> acids omitted). This result can be attributed to varying tendencies within families of acids for anion solvation to increase as inherent acidity decreases.

In the following sections we examine the effects on  $\delta_s \Delta G^\circ$ ,  $-\Delta G^\circ_{(g)}$ , and  $-\Delta G^\circ_{(s)}$  values of the following kinds of changes in acid or anion structures: (a) the charge on HA, (b) the nature of the atom at the acidic site, (c) the extent of charge dispersal or charge localization in A<sup>-</sup>, (d) the presence of adjacent lone pair-lone pair repulsions in A<sup>-</sup>, (e) phenyl substitution at the acidic

site, (f) ring closures, (g) benzo fusions, (h) the presence of dipolar substituents at the acidic site and at remote sites, and (i) steric hindrance. Before starting these discussions, we remind the reader of the following points. If the solvation energy of A<sup>-</sup> is greater than that for 9-PhFl<sup>-</sup>, the proton-transfer equilibrium of reaction 1 will tend to shift to the right in Me<sub>2</sub>SO compared to the gas phase, but if the solvation energy of HA is greater than for 9-PhFl, the shift will tend toward the left. 9-Phenylfluorene has been selected as the standard of comparison because (a) its solvation is relatively small and (b) the solvation energy of 9-PhFl<sup>-</sup> is relatively small compared to the solvation energy of most anions (A<sup>-</sup>). As a result, since the A<sup>-</sup> solvation energies will nearly always be greater than those of their conjugate acids (HA), the equilibrium shift caused by Me<sub>2</sub>SO solvation will be dominated by (b), and a net shift to the right will occur so that  $\delta_s \Delta G^\circ \geq 0$  is frequently found (positive values in Table I). The NH<sup>+</sup> and certain dipolar substituted acid results are unusual in this regard and give negative values in Table I.

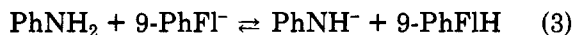
**Effects of a Positive Charge.** The presence of the positive charges in NH<sub>4</sub><sup>+</sup> and PhNH<sub>3</sub><sup>+</sup> acids increases their intrinsic acidities compared to that of their conjugate-base acids (NH<sub>3</sub> and PhNH<sub>2</sub>) by 198 and 154 kcal, respectively, in accord with the expected huge inherent effects of a positive charge.<sup>4</sup> Corresponding

(4) Taft, R. W. *Prog. Phys. Org. Chem.* 1983, 14, 247.

large, but not huge, effects of the positive charge are observed on the  $\text{Me}_2\text{SO}$  acidity differences, i.e.,  $\sim 44$  kcal for  $\text{NH}_4^+$  compared to  $\text{NH}_3$  and 37 kcal for  $\text{PhNH}_3^+$  compared to  $\text{PhNH}_2$ , respectively. The enormous  $\text{Me}_2\text{SO}$  solvent effects on the acidities of positively charged acids compared to the neutral acids (eq 2 and 3), which lead to the large negative  $\delta_s \Delta G^\circ$  values in Table I, are a consequence of the much larger cation than anion or neutral HA solvation energies.



$$-\Delta G^\circ_{(g)} = 131 \text{ kcal}; -\Delta G^\circ_{(s)} = 19 \text{ kcal}$$



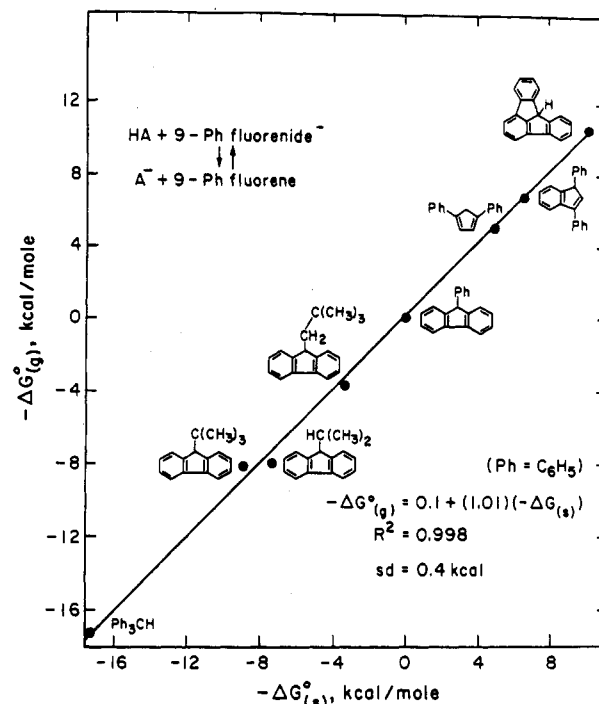
$$-\Delta G^\circ_{(g)} = -24 \text{ kcal}; -\Delta G^\circ_{(s)} = -17 \text{ kcal}$$

Nevertheless, other structural features are also of significance. For example, the values of  $\delta_s \Delta G^\circ$  in Table I for  $\text{NH}_4^+$ ,  $\text{C}_6\text{H}_5\text{NH}_3^+$ , and  $\text{C}_5\text{H}_5\text{NH}^+$  decrease in magnitude significantly in the order  $-126.0$ ,  $-111.2$ , and  $-100.0$  kcal, respectively. As the number of hydrogen-bond donor  $\text{NH}^+$ 's decrease in the cation and its size increases, the solvation energy decreases ( $\text{Me}_2\text{SO}$  is a strong H-bond acceptor), shifting equilibrium 1 to the right. From the standpoint of solvent effects, we emphasize that the acidity differences relative to 9-PhFlH between  $\text{PhNH}_3^+$  and  $\text{PhNH}_2$  are leveled from 154 to 37 kcal on going between gas and  $\text{Me}_2\text{SO}$  phases (eq 2 and 3), and this is a typical order of magnitude result for positively charged acids.

**Effects of the Atom at the Acidic Site.** Gas-phase acidities (as shown by the  $-\Delta G^\circ_{(g)}$  values of Table I) increase markedly along the series  $\text{CH}_4$  ( $-73.0$ )  $<$   $\text{NH}_3$  ( $-60.6$ )  $<$   $\text{OH}_2$  ( $-48.6$ )  $<$   $\text{HF}$  ( $-30.2$ )  $<$   $\text{H}_2\text{S}$  ( $-9.3$ )  $<$   $\text{HCl}$  ( $7.5$ )  $<$   $\text{HBr}$  ( $17.3$ ), reflecting two periodic trends. First, for elements within a given period, acidity increases as the group number and element electronegativity increase. Second, for elements in a given group, acidity increases with increasing group number.

In  $\text{Me}_2\text{SO}$ , the increasing acidity increments ( $-\Delta \Delta G^\circ_{(s)}$  values relative to  $\text{CH}_4$ ) along the series  $\text{CH}_4 < \text{NH}_3 < \text{OH}_2 < \text{HF}$  are significantly greater than the corresponding gas-phase (intrinsic)  $-\Delta \Delta G^\circ_{(g)}$  values, i.e.,  $0 < 19 < 32 < 55$  kcal compared to  $0 < 12.4 < 24.4 < 42.8$  kcal, respectively. This follows from the fact that the intrinsic acid order is augmented in  $\text{Me}_2\text{SO}$  by the effects of increasing  $\text{A}^-$  solvation energies that result from decreases in ion size and from the increasing relief of lone pair-lone pair intraionic repulsions on solvation.<sup>8</sup> In contrast, along the series  $\text{HF} < \text{HCl} < \text{HBr}$  or  $\text{H}_2\text{O} < \text{H}_2\text{S}$ , the size of the anion increases substantially, and charge localization and lone pair-lone pair repulsion decrease. (Note the substantial decreasing  $\delta_s \Delta G^\circ$  values.) The result is that the effects of anion solvation oppose the intrinsic acidity order. Thus, relative to HF, the  $-\Delta \Delta G^\circ_{(s)}$  acidity increments of the HF, HCl, HBr series are (0), 18, and 19 kcal and those for the  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$  series are (0) and 24.2 kcal, whereas the  $-\Delta \Delta G^\circ_{(g)}$  acidity increments are much larger (0, 37.7, and 47.5 kcal and 0.0 and 39.3 kcal for the first and second series, respectively).

The intrinsic CH acidities increase markedly with increasing valence state electronegativity of carbon, as expected from increasing stabilization of  $\text{A}^-$ . Along the series  $\text{CH}_3\text{CH}_3 < \text{CH}_2=\text{CH}_2 < \text{HC}\equiv\text{CH}$  the gas-phase acidity increments,  $-\Delta \Delta G^\circ_{(g)}$  values with statistical



**Figure 1.** Proton-transfer equilibria 1 for hydrocarbons (HA) giving highly charge dispersed carbanions ( $\text{A}^-$ ) in the gas phase vs dimethyl sulfoxide at 298 K. Ordinate,  $-\Delta G^\circ_{(g)}$  (kcal/mol); abscissa,  $-\Delta G^\circ_{(s)}$  (kcal/mol). For these hydrocarbons,  $\delta_s \Delta G^\circ = \Delta G^\circ_{(g)} - \Delta G^\circ_{(s)} \cong 0$  in Table I.

corrections, are  $(0) < 14.3 < 44.6$  kcal, respectively. No  $\delta_s \Delta G^\circ$  values are available for this series due to the low acidities of these hydrocarbons in  $\text{Me}_2\text{SO}$ . The large gas-phase acidity increments for this CH series are remarkable when compared with those given above along the series  $\text{CH}_4 < \text{NH}_3 < \text{OH}_2 < \text{HF}$ . Although there are much greater electronegativity increments for this latter series, the gas-phase acidity increments are smaller because of increasing lone pair-lone pair repulsions in the charge-localized  $\text{A}^-$ 's of this series.

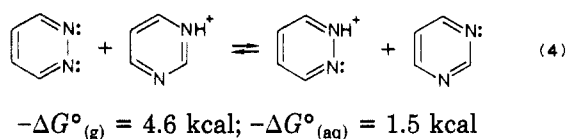
**Effects of Charge Dispersal vs Charge Localization in  $\text{A}^-$ .** In Figure 1,  $-\Delta G^\circ_{(g)}$  values are plotted vs corresponding  $-\Delta G^\circ_{(s)}$  values for the eight acids of Table I that give the most highly charge-dispersed (CD) carbanions with no heteroatoms, i.e., fluoradene, 1,3-diphenylindene, 2,5-diphenylcyclopentadiene, 9-phenylfluorene, 9-neopentylfluorene, 9-isopropylfluorene, 9-*tert*-butylfluorene, and triphenylmethane. A linear relationship of unit slope results, covering a range of ca. 28 kcal in acidities (the least-squares equation is  $-\Delta G^\circ_{(g)} = 0.1 + 1.01(-\Delta G^\circ_{(s)})$ ,  $R^2 = 0.998$ ,  $\text{sd} = 0.4$  kcal). Since the change from the gas phase to  $\text{Me}_2\text{SO}$  solution causes an enormous increase in absolute acidity, it is remarkable that the differences in acidities of these hydrocarbons remain the same in  $\text{Me}_2\text{SO}$  as in the gas phase. This must mean that the solvation energies for these CD carbanions remain essentially constant throughout the series. In other words, the free energies of transfer,  $\Delta G^\circ_{\text{t}}^{\text{g}\rightarrow\text{s}}$ , of these CD carbanions between the gas and  $\text{Me}_2\text{SO}$  phases are nearly the same, differing only in small effects arising from creating different-sized molecular cavities in  $\text{Me}_2\text{SO}$ . From known values<sup>5</sup> of  $\Delta G^\circ_{\text{t}}^{\text{g}\rightarrow\text{s}}$  for charge-

(5) Marcus, Y. *J. Chem. Soc., Faraday Trans. 1* 1987, 83, 2985. Marcus, Y.; Kamlet, M. J.; Taft, R. W. *J. Phys. Chem.*, in press.

localized anions, e.g.,  $\text{Br}^-$  and  $\text{CH}_3\text{CO}_2^-$ , the  $\delta_s\Delta G^\circ$  values of Table I, and estimates of the hydrogen-bonding solvation energies between  $\text{Me}_2\text{SO}$  and the conjugate acids,  $\text{HBr}$  and  $\text{CH}_3\text{CO}_2\text{H}$ , etc.,<sup>6</sup> we place the values (with uncertainties of  $\pm 5$ ) of  $\Delta G^\circ_{\text{t}^{\text{g}\rightarrow\text{s}}}$  for all of the highly CD carbanions at  $\sim 50$  kcal.

Charge localization and lone pair-lone pair repulsions are frequently associated either with anions of small volume or with the presence in the anion of a significant amount of charge on a single strongly electronegative atom with more than one lone pair (or with adjacent atoms of this kind).<sup>8</sup> As charge localization is increased at a solvent-accessible position of the anion, the interaction with the positive end of the  $\text{Me}_2\text{SO}$  dipole increases, anion solvation increases, and reaction 1 is shifted to the right, increasing the apparent solution acidity of HA and the values of  $\delta_s\Delta G^\circ$  and  $\Delta G^\circ_{\text{t}^{\text{g}\rightarrow\text{s}}}$ . Values of  $\Delta G^\circ_{\text{t}^{\text{g}\rightarrow\text{s}}}$  for many of the anions of Table I are accordingly greater than 50 kcal, increasing with charge localization but not necessarily with decreasing inherent acidity ( $-\Delta G^\circ_{(\text{g})}$  values of Table I). This point is illustrated by the following typical values of  $\Delta G^\circ_{\text{t}^{\text{g}\rightarrow\text{s}}}$  (obtained as indicated above for the value of 50 kcal for the highly CD carbanions):  $\sim 64$  kcal (for  $\text{C}_6\text{H}_5\text{O}^-$ ,  $\text{C}_6\text{H}_5\text{S}^-$ , cyclopentadienide, phenylacetylide, and  $\text{Br}^-$ ),  $\sim 70$  kcal (for  $\text{CH}_3\text{CO}_2^-$ ,  $\text{CN}^-$ ,  $\text{CH}_2\text{NO}_2^-$ , and  $\text{HS}^-$ ),  $\sim 75$  kcal (for  $\text{Cl}^-$ ),  $\sim 78$  kcal (for  $^-\text{OCH}_3$ ), and  $\sim 86$  kcal (for  $^-\text{OH}$ ). The value of  $\delta_s\Delta G^\circ = 14.4$  kcal for  $\text{HCl}$  and the  $\Delta G^\circ_{\text{t}^{\text{g}\rightarrow\text{s}}} \cong 75$  kcal for  $\text{Cl}^-$  seem quite consistent with the gas-phase single-molecule attachment energy of  $\text{Me}_2\text{SO}$  to  $\text{Cl}^-$  of 18.6 kcal.<sup>7</sup>

**Lone Pair-Lone Pair Repulsions between Adjacent Atoms.** Lone pair-lone pair repulsions between adjacent atoms have significant effects on acidities. There is relief of this repulsion in a gaseous anion by protonation and in solution by solvation.<sup>8</sup> These effects can be illustrated by the fact that proton-transfer equilibria, such as that in eq 4, lie well to the right.<sup>8</sup> A



shift in the opposite direction for eq 4 is expected by virtue of the significantly larger 2-aza than 3-aza "electron-withdrawing" substituent effect. The  $-\Delta G^\circ$  values observed are explained by the dominant effect of the adjacent atom lone pair-lone pair repulsion in pyridazine, which is relieved by protonation.<sup>8</sup> The equilibrium shift to the right is smaller in aqueous solution since there is greater solvation of the lone pairs of pyridazine than pyrimidine, thus reducing the lone

(6) Based upon  $\log K_{\text{formation}}$  equilibrium constants for 1:1 complexes between acid and  $\text{Me}_2\text{SO}$  in  $\text{CCl}_4$ , 25 °C that are estimated from the relationship  $\log K_f (\text{M}^{-1}) = -1.09 + 7.35 \alpha_2^{\text{H}} \beta_2^{\text{H}}$ ; Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Taft, R. W.; Morris, J. J.; Taylor, P. J.; Laurence, C.; Berthelot, M.; Doherty, R. M.; Kamlet, M. J.; Abboud, J.-L. *M. J. Am. Chem. Soc.* 1988, 110, 000. The  $\alpha_2^{\text{H}}$  parameter is a scaled hydrogen-bond donor strength parameter for acids in their monomeric form, and the  $\beta_2^{\text{H}}$  parameter is a scaled hydrogen-bond acceptor parameter for bases in their monomeric form. This equation describes over 1300 literature values of  $\log K_f$  for any acid-base pair to an average deviation of 0.09.

(7) Maguera, T. F.; Caldwell, G.; Sunner, J.; Ikuta, S.; Kebarle, P. J. *Am. Chem. Soc.* 1986, 108, 6140.

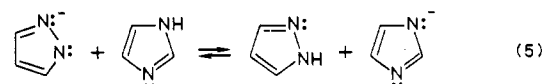
(8) Taft, R. W.; Anvia, F.; Taagepera, M.; Catalán, J.; Elguéro, J. J. *Am. Chem. Soc.* 1986, 108, 3237.

**Table II**  
Acidifying Effects of Phenyl Substitution for Hydrogen

acid pair	$-\Delta\Delta G^\circ_{(\text{g})}^{\text{a}}$	$-\Delta\Delta G^\circ_{(\text{s})}^{\text{b}}$	$\Delta\delta_s\Delta G^\circ^{\text{c}}$
1. PhOH/OH <sub>2</sub>	41.8	18.3	-23.5
2. PhNH <sub>2</sub> /NH <sub>3</sub>	37.0	~15	-22
3. PhCH <sub>3</sub> /CH <sub>4</sub>	34.8	~17	-18
4. PhCH <sub>2</sub> CN/CH <sub>3</sub> CN	21.1	12.8	-8.3
5. Ph <sub>2</sub> CH <sub>2</sub> /PhCH <sub>3</sub>	15.5	14.4	-1.1
6. Ph <sub>2</sub> NH/PhNH <sub>2</sub>	15.3	7.8	-7.5
7. PhCH(CN) <sub>2</sub> /CH <sub>2</sub> (CN) <sub>2</sub>	14.2	9.5	-4.7
8. PhSH/SH <sub>2</sub>	11.0	4.7	-6.3
9. 9-PhFlH/FlH <sub>2</sub> <sup>b</sup>	8.5	6.5	-2.0
10. Ph <sub>3</sub> CH/Ph <sub>2</sub> CH <sub>2</sub>	5.4	2.5	-2.9
11. PhC≡CH/HC≡CH	6.0		
12. PhCO <sub>2</sub> H/HCO <sub>2</sub> H	5.4		

<sup>a</sup> $-\Delta\Delta G^\circ_{(\text{g})} = -\Delta G^\circ_{(\text{g})}(\text{PhY}) + \Delta G^\circ_{(\text{g})}(\text{HY})$ , in kcal. <sup>b</sup> $-\Delta\Delta G^\circ_{(\text{s})} = -\Delta G^\circ_{(\text{s})}(\text{PhY}) + \Delta G^\circ_{(\text{s})}(\text{HY})$ , in kcal. <sup>c</sup> $\Delta\delta_s\Delta G^\circ = -\Delta\Delta G^\circ_{(\text{s})} + \Delta\Delta G^\circ_{(\text{g})}$ .

pair-lone pair repulsion effect. The relative acidities of pyrazole and imidazole in  $\text{Me}_2\text{SO}$  are similarly affected as shown by the smaller value of  $-\Delta G^\circ_{(\text{s})}$  than of  $-\Delta G^\circ_{(\text{g})}$  for eq 5:



$$-\Delta G^\circ_{(\text{g})} = 3.6$$
 kcal;  $-\Delta G^\circ_{(\text{s})} = 1.8$  kcal

Because of the dominant effect of relief of the adjacent atom lone pair-lone pair repulsion in its conjugate-base anion,<sup>8</sup> pyrazole has a 1.8 kcal larger value of  $\delta_s\Delta G^\circ$  in Table I than does imidazole. Likewise, the values of  $\delta_s\Delta G^\circ$  are 4.2 kcal greater for 2-aminopyridine than that for 4-aminopyridine,<sup>9</sup> 2.5 kcal greater for *o*-fluorophenol than that for *p*-fluorophenol, and 3.3 kcal greater for *o*-cyanophenol than that for *p*-cyanophenol. In the cases of the aminopyridines and the cyanophenols these effects on  $\delta_s\Delta G^\circ$  are large enough and in the correct direction to reverse the observed relative acidities in the gas and  $\text{Me}_2\text{SO}$  phases.

Where the data are available,  $\delta_s\Delta G^\circ$  values for the solvent water are generally found to be 2-4 times greater than corresponding values in  $\text{Me}_2\text{SO}$ .<sup>4</sup> Thus,  $\delta_s\Delta G^\circ$  values (obtained as in Table I) may be used as a semiquantitative predictor of solvent effects of water on acidities.

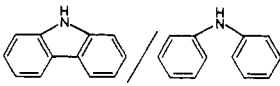
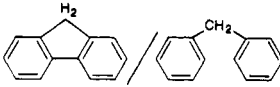
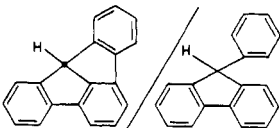
**Phenyl Substituent Effects.** The presence of a phenyl (Ph) substituent in place of H at an acidic site can stabilize a conjugate anion by  $\pi$ -electron-acceptor delocalization (R effect), by charge-induced dipole polarization (P effect), and by a dipolar field/inductive effect (F effect).<sup>10</sup>

These three kinds of Ph substituent interactions are greater in the anion than the molecular acid, and thus each of them increases acidity. However, the increase in stabilization on proton dissociation that results from Ph substitution varies widely with the acid structure. For example, the R effect on acidity increases in the sequence  $\text{PhOH} < \text{PhNH}_2 < \text{PhCH}_3$  as the change in charge delocalization into Ph increases on proton dissociation. However, with increasing delocalization of the anionic charge into Ph, the F and P substituent

(9) Taft, R. W.; Anvia, F.; Walsh, S., unpublished results.

(10) (a) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* 1987, 16, 1. (b) Taft, R. W.; Abboud, J.-L. M.; Anvia, F.; Berthelot, M.; Fujio, M.; Gal, J. F.; Headley, A. D.; Henderson, W. G.; Koppel, I.; Quian, J. H.; Mishima, M.; Taagepera, M.; Ueji, S. *J. Am. Chem. Soc.* 1988, 110, 1797.

Table III  
Inherent Acidifying Effects of Aromaticity and Coplanarity

acid pair	$-\delta\Delta G^\circ_{(g)}$	$-\delta\Delta G^\circ_{(s)}$
	6.4	6.8
	14.2	13.4
	10.6	10.1

effects of Ph are increasingly reduced.<sup>10</sup> The result is in conventional terms an unexpected one. The observed gas-phase Ph acidity effect (Table II) increases in the order  $\text{PhCH}_3$  (34.8) <  $\text{PhNH}_2$  (37.0) <  $\text{PhOH}$  (41.8).

Table II lists 12 typical observed gas- and solution-phase Ph substituent effects, as  $-\delta\Delta G^\circ_{(g)}$  and  $-\delta\Delta G^\circ_{(s)}$ , respectively. Since all three kinds of Ph effects are reduced by solvation (in varying amounts depending upon structure), the observed acidity enhancements are much less in solution than in the gas phase (note the negative values of  $\delta_s\Delta G^\circ = -\delta\Delta G^\circ_{(s)} + \delta\Delta G^\circ_{(g)}$  given in Table II).

The inherent phenyl substituent effects,  $-\delta\Delta G^\circ_{(g)}$  values of Table II, contain interesting trends. The following decreasing effects of Ph substitution into the simple molecules are found:  $\text{H}_2\text{O}$  (41.8) >  $\text{NH}_3$  (37.0) >  $\text{CH}_4$  (34.8) >  $\text{H}_2\text{S}$  (11.0) >  $\text{HC}\equiv\text{CH}$  (6.0) >  $\text{HCO}_2\text{H}$  (5.4). This is a complex order that does not correspond to any single predominant effect. However, the observed order of acidity effects is accommodated (as noted above for the first three members of the above series) by varying combinations of the three kinds of Ph effects.

For successive substitutions,  $\pi$  delocalization into the Ph substituent is subject to leveling (or saturation) caused in part by steric inhibition of resonance in the anions. Thus, in the  $\text{CH}_4$  family the successive Ph substitution effects ( $\delta\Delta G^\circ_{(g)}$ ) are 34.8, 15.5, and 5.4 kcal and in the  $\text{NH}_3$  family, 37.0 and 15.3 kcal. The acidity enhancements of Ph substitution are also reduced by the presence of other substituents as shown by the  $-\delta\Delta G^\circ_{(g)}$  values for  $\text{PhCH}_2\text{CN}/\text{CH}_3\text{CN}$  (21.1),  $\text{PhCH}(\text{CN})_2/\text{CH}_2(\text{CN})_2$  (14.2), and 9-PhFIH/FIH<sub>2</sub> (8.5).

**Ring-Closure Effects.** When two hydrogen atoms are elided from diphenylamine, diphenylmethane, and 9-phenylfluorene so as to form carbazole, fluorene, and fluorene, respectively, the enforced coplanarity of the phenyl rings and aromaticity in the fluorene anion cause a marked increase in acidity (Table III). The effects are as large in  $\text{Me}_2\text{SO}$  as in the gas phase because the extensive charge dispersal in the anions of these acids places them in the group where the solvation energy is essentially constant at ca. 50 kcal. The introduction of cyclopentadienide-type aromaticity in the fluorene anion makes a more important contribution than the enforced coplanarity of the two benzene rings since acidity enhancement for carbazole relative to diphenylamine is only half as large as for fluorene relative to diphenylmethane. The enhanced acidity of

Table IV  
Dipolar Effects of Fluoro Substituents

acid pair	$-\delta\Delta G^\circ_{(g)}^a$	$-\delta\Delta G^\circ_{(s)}^a$	ratio <sup>b</sup>	$\delta_s\Delta G^\circ_{\text{ref}}^c$
$(\text{CF}_3)_3\text{COH}/(\text{CH}_3)_3\text{COH}$	44.0	29.2	1.51	13.0
octafluorofluorene/fluorene	26.7	16.1	1.66	2.0
$\text{CF}_3\text{CH}_2\text{OH}/\text{CH}_3\text{CH}_2\text{OH}$	16.7	9.6	1.74	19.0
$\text{CF}_3\text{CO}_2\text{H}/\text{CH}_3\text{CO}_2\text{H}$	24.8	11.5	2.16	13.7
$\text{CF}_3\text{CONH}_2/\text{CH}_3\text{CONH}_2$	18.4	11.4	1.61	9.2
$\text{CF}_3\text{CONHPh}/\text{CH}_3\text{CONHPh}$	14.2	12.1	1.17	0.1
$m\text{-CF}_3\text{C}_6\text{H}_4\text{OH}/m\text{-CH}_3\text{C}_6\text{H}_4\text{OH}$	10.3	3.6	2.86	6.7

<sup>a</sup>  $-\delta\Delta G^\circ = -\Delta G^\circ(\text{first member}) + \Delta G^\circ(\text{second member})$ . <sup>b</sup>  $-\delta\Delta G^\circ_{(g)}/-\delta\Delta G^\circ_{(s)}$ , the attenuation factor. <sup>c</sup>  $\delta_s\Delta G^\circ(\text{second member})$ .

fluorene relative to 9-PhFIH is at least in part a consequence of the enforced coplanarity (or nearly so) of all three benzene rings.

**Effects of Benzo Fusions.** In the gas phase there is a progressive increase in acidity as benzene rings are fused across one or two double bonds in either (a) the series pyrrole, indole, and carbazole ( $-\Delta G^\circ_{(g)} = -15.4, -6.4,$  and  $-1.9$  kcal, respectively) or (b) the series cyclopentadiene, indene, and fluorene ( $-\Delta G^\circ_{(g)} = -12.2, -9.1,$  and  $-8.5$  kcal, respectively). In  $\text{Me}_2\text{SO}$ , a similar progression occurs with benzo fusion for the nitrogen acids,  $-\Delta G^\circ_{(s)} = -7.0, -4.1,$  and  $-2.8$  kcal, respectively, but for carbon acids, there is a striking reversal of the gas-phase order ( $-\Delta G^\circ_{(s)} = -0.2, -3.1,$  and  $-6.5$  kcal, respectively). Examination of the  $\delta_s\Delta G^\circ$  values (Table I), in the nitrogen series (8.4, 2.3, and  $-0.9$  kcal) and the carbon series (12.0, 6.0, and 2.0 kcal) reveals in both series decreasing  $\text{Me}_2\text{SO}$  solvation with increasing anion size. Interestingly, each member of the carbon series has an approximately 4 kcal greater value of  $\delta_s\Delta G^\circ$  than for the corresponding member of the nitrogen family. The relatively large solvation energy and intense charge of the cyclopentadienide carbanion are evidently decreased by charge-dispersing effects of the aza nitrogen and the phenyl ring fusions, producing the above decreases in  $\delta_s\Delta G^\circ$  values.

**Field Effects and Their Attenuation by Solvation.** Table IV presents dipolar acidity effects for a number of fluoro substituents. These results are typical of the acidifying effects of replacing hydrogen by weakly solvated heteroatom substituents. The effects of substitution of F for H (as indicated) are given for the gas phase ( $-\delta\Delta G^\circ_{(g)}$  values) and for  $\text{Me}_2\text{SO}$  solution ( $-\delta\Delta G^\circ_{(s)}$  values). The latter values are always attenuated compared to the corresponding intrinsic values. The partial passage of the lines of force between dipole and charge through a dipolar solvent reduces the dipolar substituent effect. The ratio  $-\delta\Delta G^\circ_{(g)}/-\delta\Delta G^\circ_{(s)}$ , gives the solvent attenuation factor. This factor is seen in Table IV to vary in a complex manner from 1.2 to 2.9, depending upon the system and the manner of substitution. Two qualitative dependences of the attenuation factor will be noted. As the substitution site is removed from the deprotonation site, the attenuation factor increases as shown by the 1.74 value for  $\text{CF}_3\text{C}_6\text{H}_4\text{OH}$  compared to the value of 2.86 for  $m\text{-CF}_3\text{C}_6\text{H}_4\text{OH}$ . As the  $\delta_s\Delta G^\circ$  value for the unsubstituted acid decreases for a related series of acids, the attenuation factor also decreases. This behavior is seen along the series  $\text{CF}_3\text{CO}_2\text{H}$  (2.2) >  $\text{CF}_3\text{CONH}_2$  (1.6) >  $\text{CF}_3\text{CONHPh}$  (1.2). It should also be noted in Table I that when  $\delta_s\Delta G^\circ$  is very small for the parent acid (as for fluorene or acetanilide), then the corresponding heteroatom acid (such

Table V  
Acidifying Effects of the *p*-NO<sub>2</sub> Substituent

acid pair	$-\delta\Delta G^\circ_{(g)}$	$-\delta\Delta G^\circ_{(s)}$	ratio <sup>a</sup>	$\Delta\delta_s\Delta G^\circ$ <sup>b</sup>
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> /C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	28.4	31.0	0.9	2.6
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> /C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	22.9	13.4	1.7	-9.5
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OH/C <sub>6</sub> H <sub>5</sub> OH	21.4	9.8	2.2	-11.6
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H/C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H	11.9	2.8	4.3	-9.1

<sup>a</sup>  $-\delta\Delta G^\circ_{(g)}/-\delta\Delta G^\circ_{(s)}$ , the attenuation factor. <sup>b</sup>  $\Delta\delta_s\Delta G^\circ = -\delta\Delta G^\circ_{(s)} + \delta\Delta G^\circ_{(g)}$ , in kcal.

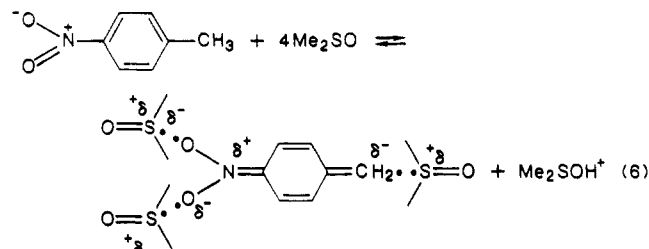
as octafluorofluorene or trifluoroacetanilide) has a significantly *negative* value of  $\delta_s\Delta G^\circ$ .

**Substituent Solvation-Assisted Resonance Effects.** If on acid dissociation the solvent not only solvates the anion center but also strongly solvates a dipolar substituent, the field and resonance effects of the solvated substituent become more complex.<sup>4</sup> The *p*-NO<sub>2</sub> substituent provides an example of substituent solvation-assisted resonance effects (SSAR). The SSAR effects are general for many substituents in a large variety of acid (and other) systems and contribute to reaction rates<sup>11</sup> and physical properties<sup>12</sup> as well as equilibrium acidities.<sup>10,13</sup> The relative magnitudes of SSAR effects increase in the following order: SOCH<sub>3</sub>, SO<sub>2</sub>R < CN < SO<sub>2</sub>CF<sub>3</sub> < RCO < NO<sub>2</sub> < NO. Quantitative treatments of SSAR effects are described in ref 10a and 12.

Values of  $\delta_s\Delta G^\circ$  from Table I (corrected for hydrogen bonding between Me<sub>2</sub>SO and the molecular acids) increase along the series C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub><sup>-</sup> (3.9) < C<sub>6</sub>H<sub>5</sub>NH<sup>-</sup> (6.7) < C<sub>6</sub>H<sub>5</sub>O<sup>-</sup> (9.8) < C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub><sup>-</sup> (10.3), as expected for increasing charge localization in the anionic center (decreasing  $\pi$  electronic charge delocalized into Ph). With the introduction of a *p*-NO<sub>2</sub> substituent  $\delta_s\Delta G^\circ$  values of this series take on a strangely mixed order: 6.5, -3.3, -5.0, -2.3, respectively. This behavior can be clarified by considering the *p*-NO<sub>2</sub> substituent acidifying effects,  $\delta\Delta G^\circ_{(g)}$  and  $\delta\Delta G^\circ_{(s)}$ , in each of the corresponding acids, as given in Table V.

Examination of Table V shows the acidifying effect of *p*-NO<sub>2</sub> in toluene acidities is 31.0 kcal in Me<sub>2</sub>SO but only 28.4 kcal in the gas phase—i.e., 2.6 kcal greater in solution! In the other acids of the series the *p*-NO<sub>2</sub> acidifying effects show conventional decreases in solution compared to the gas phase. In the benzoic acid series  $-\delta\Delta G^\circ_{(s)}$  is only 2.8 kcal compared to 11.9 kcal for  $-\delta\Delta G^\circ_{(g)}$ . The solvent effects of Me<sub>2</sub>SO on the *p*-NO<sub>2</sub> acidifying effects are shown in Table V as  $\Delta\delta_s\Delta G^\circ$  values. While the value of  $\Delta\delta_s\Delta G^\circ$  is 2.6 kcal in toluene, it is -9.5 kcal in aniline, the next in the series. The consequence of this large difference is that *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> is nearly as acidic in Me<sub>2</sub>SO as *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (Table I) whereas C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> is a stronger acid than C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> by 17 kcal. Clearly, the solvent attenuation factor for the *p*-NO<sub>2</sub> substituent is very different from that observed for a weakly solvated substituent, such as the *m*-CF<sub>3</sub> substituent in Table IV. Rather than the attenuation factor,  $-\delta\Delta G^\circ_{(g)}/-\delta\Delta G^\circ_{(s)}$ , remaining large, as it is in benzoic acid, the attenuation decreases rapidly and regularly through the series to a

value of 0.9 (for toluene). With increasing charge delocalization from the anion center across the para position to the NO<sub>2</sub> substituent, new solvation sites are created on the oxygens of this substituent. Given this condition, the solvent effect on the *p*-NO<sub>2</sub> acidifying effect should and does (Table V) increase in the order *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O<sup>-</sup> < *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sup>-</sup> < *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub><sup>-</sup>. A representation of the SSAR effect on the *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> acidity in Me<sub>2</sub>SO is given below.



**Steric Effects.** Gas-phase acidities are decreased through steric inhibition of resonance. For example,  $-\Delta G^\circ_{(g)}$  values decrease in the sequence CH<sub>2</sub>(CN)<sub>2</sub> (6.6), CH<sub>2</sub>(CN)CO<sub>2</sub>Et (1.9), CH<sub>2</sub>(COCH<sub>3</sub>)<sub>2</sub> (-1.2), CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> (-6.8), whereas the normal  $\pi$ -charge-accepting ability is CN < CO<sub>2</sub>Et < COCH<sub>3</sub>.<sup>10</sup> Steric inhibition of resonance is avoided in the anions bearing the sterically small CN substituent, causing a reversal in the normal resonance effect order. The solution acidities parallel the gas-phase values<sup>14</sup> with effects that are about half as large ( $-\Delta G^\circ_{(s)}$  values are 9.1, 6.9, 6.1, and 2.0, respectively), so that  $\delta_s\Delta G^\circ$  values run in the reverse sequence. That is, as steric inhibition of resonance increases, the anion solvation increases with the increasing charge localization.

The steric effect caused by substitution of a *t*-Bu group for hydrogen in CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> provides a 3.2 kcal decrease in gas-phase acidity and a 10.9 kcal decrease in Me<sub>2</sub>SO acidity. The difference ( $\Delta\delta_s\Delta G^\circ$ ) corresponds to 7.9 kcal loss of solvation due to steric inhibition of solvation factors. This interpretation accords with very significant deviation for the *t*-BuCH(CO<sub>2</sub>Et)<sub>2</sub> diester point from the linear correlation of Arnett<sup>14</sup> between  $-\Delta G^\circ_{(g)}$  and the corresponding  $-\Delta G^\circ_{(s)}$  for a series of monoketones,  $\beta$ -diketones, and  $\beta$ -diesters.

**Summary and Conclusions.** For organic acids such as 9-phenylfluorene and triphenylmethane, which form large charge-dispersed anions on deprotonation, solvation of the anions is essentially constant in Me<sub>2</sub>SO solution, resulting in nearly the same gas-phase and solution relative acidities. The solvation energies of increasingly charge-localized anions derived from other types of acid increase progressively with diminished size and increasing lone pair-lone pair intraionic repulsion to values over 30 kcal greater for HO<sup>-</sup> and F<sup>-</sup> ions than for the 9-phenylfluorenyl anion. Accordingly, the intrinsic gas-phase order of acidities, CH < NH < OH < FH, is exaggerated in Me<sub>2</sub>SO, whereas the huge intrinsic acidifying effect of a positive charge (as in PhNH<sub>3</sub><sup>+</sup> vs PhNH<sub>2</sub>) and the differences in acidities in the series HF < HCl < HBr or the series H<sub>2</sub>O < H<sub>2</sub>S are attenuated. Lone pair-lone pair repulsion between adjacent atoms (as in pyrazide ion) frequently reverses the gas-phase and solution acidity order compared to the isomeric acid (pyrimidine). Field/inductive effects of heteroatom

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substituents in the gas phase are reduced by factors of 2-4 in Me<sub>2</sub>SO by larger effective dielectric constants. The 11 kcal decrease in solution acidity caused by introducing a *t*-Bu group into CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> is revealed by the δ<sub>s</sub>ΔG° value to be caused by steric inhibition of solvation of the carbanions. π delocalization of the anionic charge by the presence of a Ph substituent at the acidic site causes large increases in acidity, but the effects of successive Ph substitutions are decreased appreciably by leveling (saturation) effects and by steric inhibition of resonance in both media. The surprisingly small acidity increase in solution acidity for Ph<sub>3</sub>CH vs Ph<sub>2</sub>CH<sub>2</sub> (2.5 vs 5.4 kcal in the gas phase) is the result of a 3 kcal greater solvation energy for the Ph<sub>2</sub>CH<sup>-</sup> than the Ph<sub>3</sub>C<sup>-</sup> carbanion.

The solution order of acidities, cyclopentadiene > indene > fluorene, first reported over 50 years ago<sup>15</sup> is

shown to be caused by striking differences in the anion solvation energies (11.7, 5.8, and 1.8 kcal, relative to 9-phenylfluorenyl anion) that cause a reversal from the intrinsic acidity order. Solvation of substituent sites to which a significant fraction of anionic charge has been relayed by resonance (SSAR effects) is shown to be responsible for the dramatic near equalization of the solution acidities of *p*-nitrotoluene and *p*-nitroaniline. The SSAR effects are general and play important roles, not only in determining solution equilibrium positions but also in controlling reaction rates and physical properties.

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## Hydroxide Ion: An Effective One-Electron Reducing Agent?

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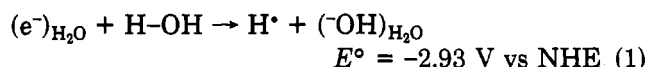
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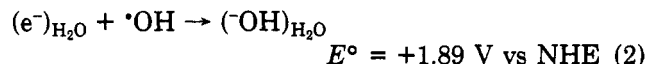
The reaction chemistry for hydroxide ion (<sup>-</sup>OH) includes Brønsted proton transfer, nucleophilic displacement (or addition), and electron transfer whereby <sup>-</sup>OH acts as a one-electron reducing agent.<sup>1</sup> In this Account, via examples from our own work and that of others, the reactivity of hydroxide ion (and by implication that of other anions) is interpreted in terms of two unifying principles: (a) the redox potential of the <sup>-</sup>OH/<sup>•</sup>OH couple (in a specific reaction) is controlled by the solvation energy of the <sup>-</sup>OH anion and the bond energy of the R-OH product (RX + <sup>-</sup>OH → R-OH + X<sup>-</sup>), and (b) the nucleophilic displacement and addition reactions of <sup>-</sup>OH occur via an inner-sphere *single-electron* shift.<sup>2</sup>

The electron is the ultimate base and one-electron reductant, which, upon introduction into a solvent, is transiently solvated before it is "leveled" (reacts) to give the conjugate base (anion reductant) of the solvent. Thus, in water the hydrated electron (e<sup>-</sup>)<sub>H<sub>2</sub>O</sub> yields <sup>-</sup>OH via addition to the H-OH bond of water.<sup>3</sup>



The product combination (H<sup>•</sup> + <sup>-</sup>OH) represents the ultimate thermodynamic reductant for aqueous sys-

tems. In the absence of an H<sup>•</sup> atom (and the stabilization afforded to <sup>•</sup>OH by formation of the 119-kcal H-OH bond),<sup>4</sup> the hydroxide ion becomes a much less effective reductant.<sup>3</sup>



### Solvent Effects on the Redox Chemistry of <sup>-</sup>OH

Table I summarizes the redox potentials in water and acetonitrile for the single-electron oxidation of <sup>-</sup>OH and other bases.<sup>3,5</sup> In MeCN the HO<sup>•</sup>/HO<sup>-</sup> redox potential is more negative by about 1.0 V and the O<sub>2</sub>/O<sub>2</sub><sup>-•</sup> redox potential by about 0.5 V relative to their values in H<sub>2</sub>O. Most of this is due to the decrease in the energy of solvation for HO<sup>-</sup> and O<sub>2</sub><sup>-•</sup> in MeCN (compared to water, where each has an estimated free energy of hydration of about -100 kcal/mol).<sup>6</sup> The increase in the ionization energy for <sup>-</sup>OH from 1.8 eV in the gas phase to 6.2 eV in water<sup>6</sup> attests to its large solvation energy and to its dramatic deactivation as a base and nucleophile in water.<sup>7,8</sup>

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