

Equilibrium Acidities in Dimethyl Sulfoxide Solution

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Equilibrium acidities provide a fundamental data base for assessment of the electronic and steric effects brought about by structural variations in organic molecules. The Hammett equation,¹ based on the aqueous acidities of meta- and para-substituted benzoic acids, and the Taft equation, based partially on the aqueous acidities of substituted acetic acids, $\text{GCH}_2\text{CO}_2\text{H}$,² have served chemists in this regard for over 40 years. The Hammett H_0 acidity function and the like have allowed the aqueous acidity scale, which has a practical $\text{p}K_a$ range of 0-12, to be extended downward into the negative $\text{p}K_a$ region by about an equal amount.³ The aqueous scale has also been extended upward by about 12 $\text{p}K_a$ units by the use of H_- acidity functions that employ cosolvents and strong bases.⁴ These models and functions have severe limitations, however.

The first acidity scale to be established in a pure solvent other than water was the result of the pioneering work of Conant, Wheland, and McEwen in ether or benzene.⁵ During the past 20 years an ion-pair acidity scale covering an "effective $\text{p}K_a$ range" from about 15 to 40 has been developed in cyclohexylamine (CHA),⁶ and similar studies in other low-dielectric-constant solvents including 1,2-dimethoxyethane (DME)^{7a} and tetrahydrofuran (THF)^{7b,c} have been carried out. A more limited ion-pair acidity scale has been developed in liquid NH_3 .^{7d} Also, during this period, acidity scales have been established in the polar non-hydrogen-bond-donor (NHB) solvents dimethyl sulfoxide (Me_2SO)⁸ and *N*-methylpyrrolidin-2-one (NMP),⁹ which have relatively high dielectric constants. The $\text{p}K_a$'s measured in these solvents differ from ion-pair $\text{p}K_a$'s in that they are absolute, in the sense that they are based on Me_2SO and NMP as the standard states, which allows direct comparisons to be made with H_2O and gas-phase $\text{p}K_a$'s. A truly absolute acidity scale has been established in the gas phase, which, for the first time, provides intrinsic measures of structural effects free of solvent effects.¹⁰ Our purpose in this Account is (a) to discuss briefly acidities in various solvent media, (b) to present a table of representative equilibrium acidity constants in Me_2SO solution, and (c) to illustrate ways in which these $\text{p}K_a$ data can be used. In an accompanying Account we compare acidities in Me_2SO solution with intrinsic gas-phase acidities and discuss some of the insights into solvation effects provided thereby.

Acidities in H_2O and Me_2SO . It is important to recognize that $\text{p}K_a$ values are solvent dependent. The

dissociation constant of an acid, formally defined by eq 1, depends on the ability of the solvent to solvate the



proton, the anion, and the undissociated acid. Since solvation of the proton is constant in a given solvent and solvation of most neutral acids is small compared to that of their conjugate bases, differences in acidities brought about by structural variations or solvent changes are usually caused by changes in the energies of the anions. The large acidity increases observed in changing from Me_2SO to H_2O for oxygen acids forming oxyanions that are strongly H-bonded to water provide examples (Table I).

In Table I we see that the acidities of very strong acids such as $\text{F}_3\text{CSO}_3\text{H}$, HBr , HCl , and $\text{CH}_3\text{SO}_3\text{H}$ are

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(7) (a) During the past 12 years A. I. Shatenshtein and his co-workers have developed an acidity scale in Me_2SO and an ion-pair acidity scale in DME, using Li^+ , K^+ , and Cs^+ counterions. (The $\text{p}K_a$'s measured in Me_2SO , when placed on an absolute scale, usually agree with ours to within ± 0.3 $\text{p}K$ unit.) For recent work and leading references, see: Shatenshtein, A. I., et al. *J. Org. Chem. USSR (Engl. Transl.)* **1978**, *14*, 829-833; **1980**, *16*, 2089-2092; **1981**, *17*, 260-265; **1982**, *18*, 6-10; **1983**, *19*, 405-408. (b) Bors, D. A.; Kaufman, M. J.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 6975-6982. (c) Fraser, R. R.; Mansour, T. S.; Savard, S. *J. Org. Chem.* **1985**, *50*, 3232-3234. (d) Lagowski, J. J. *Pure Appl. Chem.* **1971**, *25*, 429-456.

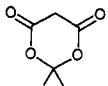
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Frederick G. Bordwell is Professor Emeritus at Northwestern University. (For a biography summarizing his earlier research activities, see *Acc. Chem. Res.* **1972**, *5*, 374). In the period 1970-1980 the Bordwell research group established acidity scales in Me_2SO 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 Me_2SO scale to problems in physical organic chemistry, the results of which are summarized in this Account.

Table I
Equilibrium Acidities in Dimethyl Sulfoxide and in Water

acid	pK _a (H ₂ O)	pK _a (Me ₂ SO) ^b	acid	pK _a (H ₂ O)	pK _a (Me ₂ SO) ^b
F ₃ CSO ₃ H	-14 ^a	0.3 ^c	F ₃ CSO ₂ NH ₂	6.3	9.7
HBr	-9 ^a	0.9 ^c	PhSH	6.5	10.31
HCl	-8 ^a	1.8 ^c	(CH ₃ CO) ₂ CH ₂	8.9	13.3
CH ₃ SO ₃ H	-0.6 ^a	1.6 ^c	HCN	9.1	12.9 ^e
2,4,6-(NO ₂) ₃ C ₆ H ₂ OH	0	~0 ^d	NH ₄ ⁺	9.2	10.5 ^d
4-Cl-2,6-(NO ₂) ₃ C ₆ H ₂ OH	3.0	3.6	CH ₃ NO ₂	10.0	17.2
HF	3.2	15 ± 2	PhOH	10.0	18.0
PhCO ₂ H	4.25	11.1	CH ₃ (CN) ₂	11.0	11.0 ^e
CH ₃ CO ₂ H	4.75	12.3	F ₃ CCH ₂ OH	12.4	23.6
PhNH ₃ ⁺	4.6	3.6 ^d	(CH ₃ SO) ₂ CH ₂	12.7	15.0
HN ₃	4.7	7.9 ^e	CH ₃ CONH ₂	15.1	25.5
	4.8	7.3 ^f	CH ₃ OH	15.5	29.0
PhSO ₂ H	3.5	7.1	H ₂ O	15.75	32
C ₆ H ₅ NH ⁺	5.2	3.4 ^d			

^a Estimated by the H₀ method; in pure H₂O their acidities are leveled to that of H₃O⁺ (pK_a = -1.75). ^b From measurements made in our laboratory, unless otherwise noted. ^c McCallum, C.; Pethybridge, A. D. *Electrochim. Acta* 1975, 20, 815-818. ^d Reference 8d. ^e Reference 8c. ^f Reference 34.

leveled in Me₂SO to that of Me₂SOH⁺, just as they are leveled to that of H₃O⁺ in H₂O. For strong oxygen acids such as picric acid and 4-chloro-2,6-dinitrophenol, which form highly delocalized anions on dissociation, acidities do not differ greatly in H₂O and Me₂SO. As the oxygen acids in Table I become weaker, charge delocalization in the anion decreases and the difference in acidity in H₂O vs Me₂SO (ΔpK_a) increases from near zero for picric acid to 15 pK_a units for the weakest acids, MeOH and H₂O. This change is due primarily to the strong H-bond donor properties of the water solvent, which achieve maximum effectiveness toward localized ions such as F⁻, F₃CCH₂O⁻, MeO⁻, or HO⁻. The strong H-bond acceptor properties of H₂O make PhNH₃⁺ and pyridinium ions (but not the NH₄⁺ ion) weaker acids in H₂O than in Me₂SO. (Me₂SO is also a good H-bond acceptor and solvates cations well.) Solvation of the CH(CN)₂⁻ by H₂O and Me₂SO appears to be nearly equal.

Acidities in Solvents of Low Dielectric Constant. Ion-Pair pK_a's. Ion-pair acidity scales in cyclohexylamine (CHA),⁶ DME, THF, or other solvents of low dielectric constant⁷ complement that in Me₂SO in some respects but are more limited in scope. These scales were originally anchored arbitrarily on the H. pK_a = 18.49 for 9-phenylfluorene (9-PhFlH) in H₂O/sulfolane, but more recently they have been anchored on the pK_a of fluorene in Me₂SO (22.3 on a per-hydrogen basis).¹¹

The size of ion-pairing effects will depend somewhat on the nature of the cation. For example, with Li⁺ counterion in CHA, PhC≡CH appears to be a stronger acid than in Me₂SO by 6.1 pK units, but with Cs⁺ counterion in DME ΔpK is only 2.4 units.¹² Ion-pairing effects of anions with K⁺ counterion are of little or no importance in dilute (millimolar) Me₂SO solution, except for strongly chelating anions such as that formed from CH₃COCH₂COCH₃. A method for detecting such ion-pairing effects and a spectroscopic method for

measuring ion-pair association constants (K_{as}) have been devised.^{13a} Ion pairing stabilizes the anion and leads to an apparent acidity increase. Small corrections of the pK_a values are therefore needed. For chelating anions the size of K_{as} increases along the series K⁺ < Na⁺ < Li⁺.

Acidities in Other NHBD Solvents. An acidity scale in *N*-methylpyrrolidin-2-one (NMP) has also been established by using the overlapping indicator method.⁹ Relative acidities in NMP and Me₂SO correlate beautifully (see Figure 5 in ref 9), and the absolute acidities do not differ greatly. Ion-pairing association constants with K⁺ counterion for chelating anions and homo-hydrogen bonding constants for phenols^{13b} are also similar in NMP and Me₂SO. Since differences in free energies of transfer from H₂O to solvents such as HMPA, Me₂SO, NMP, DMF, and MeCN do not differ greatly,¹⁴ we can expect relative acidities in Me₂SO to provide a good model for those in these NHBD solvents. Differences in free energies of transfer of the proton in these solvents may be appreciable, however, and can lead to sizable differences in absolute acidities. For example, the pK_a's for PhOH in Me₂SO, NMP,⁹ and MeCN^{8d} are 18.0, 20.1, and 27.2, respectively.

Acids in the pK_a range 32-35 are difficult to measure in Me₂SO (pK_a = 35) because of the leveling effect of the solvent.¹⁵ Very weak acids such as amines, alkyl sulfides or ethers, benzenes, alkylbenzenes, alkenes, and alkanes are not deprotonated by MeSOCH₂K in Me₂SO, showing that their pK_a's are above 35. Conceivably, the pK_a's for some of these compounds could be measured in a more weakly acidic solvent such as HMPA, but problems with ion pairing can be expected to increase. It is possible to obtain at least a rough estimate of the pK_a's of some of these compounds by extrapolation, however.¹⁶

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Table II
Equilibrium Acidities in Dimethyl Sulfoxide at 25 °C

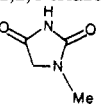
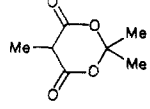
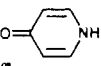
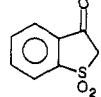
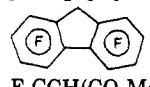
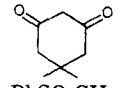
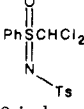
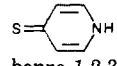
acid	pK _a ^a	acid	pK _a ^a
5-nitrobarbituric acid	0.8	PhCONHOH	13.65
(F ₃ CSO ₂) ₂ CH ₂	2.1	2,3-dihydroxynaphthalene	13.7
2,4-dinitronaphthol	2.1	<i>N</i> -acetyloxindol	13.8 ^g
PhN ⁺ HMe ₂	2.45	1,2,3-triazole	13.9
F ₃ CCO ₂ H	3.45	uracil	14.1
saccharin	4.0	adenine	14.2
PhCH(CN) ₂	4.2	CH ₃ COCH ₂ CO ₂ Et	14.2
2,6-dinitrophenol	4.9	(MeSO ₂) ₂ CHPh	14.3
2,4-dinitrophenol	5.1	2,5-diphenylcyclopentadiene	14.3
F ₃ CSO ₂ CH ₂ COPh	5.1	9-cyano-9,10-dihydroanthracene	14.3
PhCOSH	5.2 ^b		14.4
Cl ₂ CHCO ₂ H	6.4 ^c		
PhSCH(SO ₂ Ph) ₂	5.55	CH ₃ COCH ₂ CO ₂ Et	14.4
F ₃ CCH ₂ SO ₂ NHPh	5.7	fluorenone benzylimine	14.5
2,4,5-Cl ₃ C ₆ H ₂ SH	6.0	F ₃ CSO ₂ CH ₂ Ph	14.55
Ph ₃ P ⁺ CH ₂ COPh	6.1	succinimide	14.6
Ph ₃ P ⁺ CH ₂ CN	7.05	CH ₃ C(=S)NHPh	14.7
PhSO ₂ H	7.1	1,2,4-triazole	14.75
PhSO ₂ CH ₂ NO ₂	7.1		14.75
PhSeH	7.1 ^b		
	7.4 ^d		14.8
HONO	7.5	fluorenone phenylhydrazone	14.9
H ₃ N ⁺ CH ₂ CO ₂ H	7.5 ^e	MeCH(COCH ₃) ₂	15.05
CH ₂ =CHCH ₂ NO ₂	7.7	1,2,3-triphenylindene	15.2
(C ₆ F ₅) ₂ CHCN	7.95	PhCH ₂ SH	15.4
tetrazole	8.2	9-(phenylthio)fluorene	15.4
9-cyanofluorene	8.3	9-(benzylsulfinyl)fluorene	15.7
barbituric acid	8.4	PhSO ₂ NHNMe ₂	15.8
(CH ₃ CO) ₃ CH	8.6	nitrocycloheptane	15.8
H ₃ N ⁺ CH ₂ CO ₂ Et	8.7 ^e	C ₆ F ₅ CH ₂ CN	15.8
<i>p</i> -NO ₂ C ₆ H ₄ CO ₂ H	9.0	nitrocyclopentane	16.0
F ₃ CSO ₂ NH ₂	9.7	PhSO ₂ NH ₂	16.1
	10.1	(PhSe) ₂ CHPh	16.15
PhSH	10.3	fluorenone oxime	16.2
PhCOCH ₂ CN	10.2	CH ₂ (CO ₂ Et) ₂	16.4
1,3-cyclohexanedione	10.3 ^d	benzimidazole	16.4
9-(methoxycarbonyl)fluorene	10.35	CH ₃ CH(SO ₂ Et) ₂	16.7
fluoradene	10.5 ^f	NO ₂ NH(=NH)NH ₂	16.7
(F ₃ C) ₃ COH	10.7	3-((phenylsulfonyl)methyl)pyridine	16.7
<i>p</i> -NO ₂ C ₆ H ₄ OH	10.8	isonicotinic hydrazide	16.8
	10.8	2,6-di- <i>tert</i> -butylphenol	16.85
F ₃ CCH(CO ₂ Me) ₂	10.8	PhC(=S)NH ₂	16.9
PhCO ₂ H	11.0	H ₂ NCN	16.9
F ₃ CSO ₂ CH ₂ SPh	11.0	PhCH ₂ SO ₂ F	16.9
CH ₂ (CN) ₂	11.0	Me ₂ CHNO ₂	16.9
	11.2		16.95
PhSO ₂ CH ₂ COPh	11.4	2-indanone	16.95
	11.8	CH ₃ CH ₂ CH ₂ CH ₂ SH	17.0
benzo-1,2,3-triazole	11.9	2-pyridone	17.0
PhSO ₂ CH ₂ CN	12.0	PhSO ₂ NHNH ₂	17.1
(PhSO ₂) ₂ CH ₂	12.25	2-naphthol	17.1
PhCH ₂ NO ₂	12.3	PhCOCH ₂ SPh	17.1
CH ₃ CO ₂ H	12.3 ^c	F ₃ CCONH ₂	17.15
9-(ethylsulfonyl)fluorene	12.3	CH ₃ NO ₂	17.2
9-isocyanofluorene	12.3	nicotinic hydrazide	17.5
pentaphenylcyclopentadiene	12.5	CH ₃ SO ₂ NH ₂	17.5
5-fluorouracil	12.7	PhCOCH ₂ Ph	17.65
5,5-diethylbarbituric	13.0	nitrocyclobutane	17.8
(CH ₃ CO) ₂ CH ₂	13.3	nitrocyclohexane	17.9
2-thiopyridone	13.3	9-phenylfluorene	17.9
(PhCO) ₂ CH ₂	13.35	(CH ₃ CO) ₂ NH	17.9
(PhNH) ₂ C=S	13.4	cyclopentadiene	18.0
		PhOH	18.0
		(PhSO) ₂ CH ₂	18.1
		(CH ₃) ₃ S ⁺	18.2

Table II (Continued)

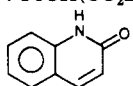
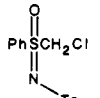
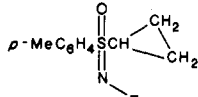
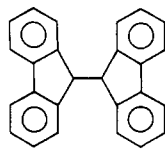
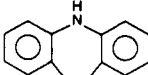
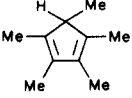
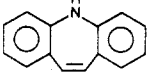
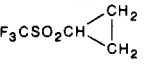
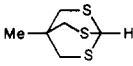
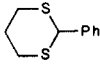
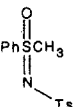
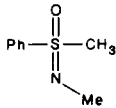
acid	pK_a^a	acid	pK_a^a
oxindole	18.2 ^g	F ₃ CSO ₂ CHMe ₂	21.8
(EtO) ₂ P(O)NHPH	18.3	2-methylindene	21.8
<i>p</i> -CH ₃ C ₆ H ₄ SO ₂ CH ₂ N=C	18.4	CH ₃ CONHNH ₂	21.8
CH ₃ C(=S)NH ₂	18.45	PhCH ₂ CN	21.9
PhCON(Me)OH	18.5	9-cyano-9,10-dihydrophenanthrene	21.9
<i>N</i> -methyloxindole	18.5 ^g	nicotinamide	22.0
imidazole	18.6	CH ₃ COCH ₂ SO ₂ Ph	22.1
PhCOCH ₂ SePh	18.6	PhC≡CCH ₂ SO ₂ Ph	22.1
1,3-dimethylbenzimidazolium ion	18.6	4,5-methylenepheneanthrene	22.2
PhCOCHPh ₂	18.7	2-thiophenecarboxamide	22.3
(PhCH ₂) ₂ C=O	18.7	PhSO ₂ CHPh ₂	22.3
F ₃ CSO ₂ CH ₃	18.75	2-((phenylsulfonyl)methyl)furan	22.3
PhCONHNH ₂	18.9	9-methylfluorene	22.3
4-chloro-2-nitroaniline	18.9	PhSO ₂ CH ₂ - 	22.35
PhCOCH ₂ SCH ₂ Ph	19.0	PhCH(CN)N- 	22.4
Me ₃ SiCH(CO ₂ Et) ₂	19.0	CH ₂ =CHCH ₂ SO ₂ Ph	22.5
PhCH ₂ SO ₂ SCH ₂ Ph	19.1	3-methylindene	22.5
Ph ₂ P(S)CH ₂ P(S)Ph ₂	19.3	Ph ₃ PCH ₃ ⁺	22.5
2-phenylindene	19.4	2-furancarboxamide	22.55
PhSO ₂ NHC(=NH)NH ₂	19.45	fluorene	22.6
PhCOCH ₂ S- 	19.45	PhCH ₂ CO ₂ Et	22.6
PhCH ₂ N=CHCO ₂ Et	19.5	phenothiazine	22.7
(PhNH) ₂ C=O	19.55	(PhS) ₃ CH	22.8
NH ₂ C(=NH)NHCN	19.6	pyrrole	23.0
pyrazole	19.8	PhCH(Me)CN	23.0
carbazole	19.9	PhOCH ₂ CONH ₂	23.0
PhCH ₂ SO ₃ Ph	19.9	1-indanone	23.0 ⁱ
PhCH ₂ COCH ₃	19.9		29.6 ⁱ (pK_a^{II})
10-cyano-9-methylanthracene	20.0	PhSCH ₂ CONH ₂	23.0
indene	20.1	PhSeCH ₂ CONH ₂	23.1
Ph ₂ C=NOH	20.1	2,3,4-trimethylimidazolium ion	23.2
PhCH=CHCH ₂ SO ₂ Ph	20.2	4-aminopyrimidine	23.3 ^j
PhCOCHF ₂	20.2	(H ₂ NNH) ₂ C=O	23.3
PhSO ₂ CH ₂ PPh ₂	20.2	PhCONH ₂	23.35
PhCOCH ₂ NPh ₂	20.3	(Ph ₂ C=CH) ₂ CHPh	23.4
<i>p</i> -NO ₂ C ₆ H ₄ CH ₃	20.4	PhSO ₂ CH ₂ Ph	23.4
F ₃ CSO ₂ CH ₂ Me	20.4	HCONH ₂	23.45
<i>i</i> -PrCH(CO ₂ Et) ₂	20.5	F ₃ CCH ₂ OH	23.45
	20.7	PhSO ₂ CH ₂ Cl	23.8
PhSCH ₂ Cl	20.7	(PhCH ₂) ₂ SO ₂	23.9
		MeOCH ₂ CONH ₂	23.9
2-benzylbenzothiazole	20.8	<i>t</i> -BuSCH ₂ CONH ₂	24.1
	20.8	<i>p</i> -F ₃ CSO ₂ C ₆ H ₄ CH ₃	24.1
	20.9 ^h	2-pyrrolidone	24.2
indole	20.95	3-((phenylsulfonyl)methyl)thiophene	24.2
PhCH=NNHPh	21.1	cyclohexanone oxime	24.3
PhCOCH ₂ OPh	21.1	Ph ₂ C=NCH ₂ Ph	24.3
(H ₂ N) ₂ C=S	21.1	benzoxazole	24.4
PhCONHC(=NH)NH ₂	21.25	CH ₃ COCH ₂ CH ₃	24.4
PhSO ₂ CH ₂ SiPh ₃	21.3	H ₂ NCO ₂ Et	24.6
PhCH ₂ C(=S)NMe ₂	21.3	<i>t</i> -BuCH(CO ₂ Et) ₂	24.7
PhSCH ₂ CO ₂ Me	21.4	H ₂ NCH ₂ CONH ₂	24.7
CH ₃ CONHPh	21.45	PhCH ₂ CONH ₂	24.7
isonicotinamide	21.5	PhCOCH ₃	24.7
PhC(Me)=NNHPh	21.5	Ph ₂ NH	24.95
phenoxazine	21.65	cyclobutanone	25.05
PhCOCH ₂ F	21.7	CH ₃ SO ₂ OPh	25.2
9-(trimethylsilyl)fluorene	21.7	PhCH ₂ SO ₂ NMe ₂	25.2
4-acetylpyridine	21.8		25.2 ^d
		4-benzylpyridine <i>N</i> -oxide	25.2
		2-aminopyrimidine	25.3 ^j
			25.5
			
		CH ₃ CONH ₂	25.5
		Ph ₂ C=CHCH ₂ Ph	25.6
		CH ₃ C(=S)NMe ₂	25.65
		Ph ₂ C=CHCHPh ₂	25.8
		<i>c</i> -C ₆ H ₅ COPh	25.8
		cyclopentanone	25.8

Table II (Continued)

acid	pK_a^a	acid	pK_a^a
	26.1	CH ₃ OH	29.0
	26.1	thiazole	29.4
c-C ₄ H ₇ COPh	26.15	p-PhSO ₂ C ₆ H ₄ CH ₃	29.85
PhNHNHPh	26.2	2-benzylthiophene	29.9
Me ₂ CHCOPh	26.25	xanthene	30.0
2-piperidone	26.4	3-benzylpyridine	30.15
cyclohexanone	26.4	(CH ₃) ₂ CHOH	30.25
CH ₃ COCH ₃	26.5	4-methylthiazole	30.3
4-aminopyridine	26.5	camphor	30.4
	26.6		30.6
c-C ₆ H ₁₁ COPh	26.7	PhNH ₂	30.6
4-benzylpyridine	26.7	Ph ₃ CH	30.6
cyclodecanone	26.8		30.65
PhSCHPh ₂	26.8	PhSO ₂ CH ₂ OMe	30.7
(H ₂ N) ₂ C=O	26.95	PhSCH ₂ Ph	30.8
benzothiazole	27.0	9-methylanthracene	31.1
PhS(O)CH ₂ Ph	27.2	CH ₃ SO ₂ CH ₃	31.1
PhCH ₂ N≡C	27.4	(n-PrS) ₃ CH	31.3
heptamethylindene	27.4	CH ₃ CN	31.3
(EtO) ₂ P(O)CH ₂ Ph	27.55	H ₂ O	31.2
2-methylbenzothiazole	27.6	Ph ₂ CH ₂	32.2
2-aminopyridine	27.7	(CH ₃) ₃ COH	32.2
	27.7		(33) ^k
cycloheptanone	27.8	CH ₃ S(O)CH ₃	35
9-phenylxanthene	27.9	4-methylpyridine	(35) ^k
PhSO ₂ CH ₂ OPh	27.9		(39) ^k
4-methyloxazole	28.0	NH ₃	(41) ^k
PhOCH ₂ CN	28.1	2-methylnaphthalene	(42) ^k
[(CH ₃) ₂ CH] ₂ C=O	28.2	PhSCH ₃	(42) ^k
2-benzylpyridine	28.2	2-methylthiophene	(42) ^k
c-C ₃ H ₅ COPh	28.25	2-methylfuran	(43) ^k
PhSO ₂ CH ₂ F	28.5	PhCH ₃	(43) ^k
3-aminopyridine	28.5	CH ₂ =CHCH ₃	(44) ^{k,l}
PhC≡CH	28.7	CH ₃ SCH ₃	(45) ^k
(EtO) ₂ P(O)CH ₂ SiMe ₃	28.7	PhOCH ₃	(49) ^k
		CH ₄	(56) ^k

^a The pK_a 's were selected from a list of about 1200 that have been measured in our laboratory. The pK_a 's of oxygen acids have been corrected for homohydrogen bonding, and pK_a 's of acids forming chelating anions have been corrected for ion pairing with K⁺. The ylides formed from cations are often reactive, and these values should be regarded as tentative. Most pK_a 's were measured by using two or more indicators or standard acids and are believed to be accurate to ± 0.1 unit. ^b Courtot-Coupez, J.; Le D  m  zet, M. *Bull. Soc. Chim. Fr.* 1969, 1033-1039. ^c Ritchie, C. D.; Lu, S., private communication. ^d Arnett, E. M.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* 1987, 109, 809-812. ^e Hughes, D. L.; Bergan, J. J.; Grabowski, E. J. *J. Org. Chem.* 1986, 51, 2579-2585. ^f Ritchie, C. D.; Uschold, R. E. *J. Am. Chem. Soc.* 1968, 90, 2821-2824. ^g Fried, H. E. Ph.D. Dissertation, Northwestern University, 1982. ^h Streitwieser, A., Jr. *Acc. Chem. Res.* 1984, 17, 353-357. ⁱ Cornforth, F. W. Ph.D. Dissertation, Northwestern University, 1974. ^j Shkurko, O. P.; Terekhova, M. J.; Petrov, E. S.; Mamaev, V. P.; Shatenshtein, A. J. *J. Org. Chem. USSR (Engl. Transl.)* 1981, 17, 260-264. ^k Values in parentheses were extrapolated by methods such as those described in ref 16. ^l From ref 52, assuming a BDE of 81 for the C-H bond in Ph₃CH.⁵¹

The Me₂SO Acidity Scale. Structural Effects on Acidities. In Table II we present data for equilibrium acidities in Me₂SO for over 300 compounds. The effects of structural variations on acidities for many of these have been discussed in papers from our laboratory, including the effects of cyclopropyl rings,²⁰ α -electron-

withdrawing groups,²¹ α -heteroatoms,²² phenyl groups,²³ phenylthio groups,²⁴ alkyl groups on C-H acids,²⁵ sp hybridization at carbon,²⁶ remote substituents (in

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(18) In CHA a Br  nsted-type extrapolation gives an ion-pair pK_a for toluene of 41,^{7b} and two extrapolations from azine acidities in DME have given a value of 42.

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fluorenes²⁷ and in acetophenones²⁸), ion pairing,¹³ steric inhibition of resonance,²⁹ alkyl groups in alcohols,¹⁵ aromaticity,³⁰ thiol groups,³¹ methyl effects on cyclopentadienes and indenenes,³² and homohydrogen bonding in phenols.^{13b} Papers from other laboratories have discussed the first and second ionization constants of 9,9'-bifluorenyl,³³ the effects of cyclization on acidities of ketones and carboxylic esters containing β -dicarbonyl groups,³⁴ and the effects of aza groups on acidities.³⁵ In the accompanying paper we compare some of these structural effects on solution acidities with those on intrinsic gas-phase acidities and discuss insights into solvation effects derived therefrom.³⁶

The Me₂SO acidity scale has proved useful in several ways. Jorgensen and his students have used the pK_a's as one of the parameters in an interactive computer program, CAMEO, that is being designed to predict products of organic reactions, given the starting materials and conditions.³⁷ By combining pK_a values in Me₂SO for 21 delocalized carbanions and 5 phenoxide ions with calculated π delocalization energies of 6 carbocations, Arnett has developed a "master equation" to correlate data for 30 reactions ($r = 0.9948$). Equations of this type are capable of providing a simple means of estimating heterolysis energies in solution for thousands of bonds that give resonance-stabilized anions and cations on cleavage.³⁸ In our laboratory we have found that rates ($\log k_{\text{obsd}}$) of reactions between the conjugate bases of various families of acids and electrophiles can be correlated generally with pK_{HA} values to give linear Brønsted plots,³⁹ as will be brought out in the next section.

Acid-Base Families and the Brønsted Relationship. For acids in Table II containing an aromatic nucleus, Hammett-type families can be prepared by placing substituents in remote positions. Taft-type families such as GCH₂CONH₂ and GCH₂COPh can also be prepared, and other types of families can be constructed from various groups of acids, e.g., an azole family (pyrrole, pyrazole, imidazole, etc.). The ρ values in Table III, when combined with literature σ and σ_p^-

Table III
Hammett ρ Values for Equilibrium Acidities in Me₂SO Solution at 25 °C

acid family	pK _a ^a	ρ^b	n^f	R ²	ref
ArCH(CN) ₂	4.2	4.2 ± 0.1	5	0.997	g
ArSO ₂ H	7.1	2.4 ± 0.2	4	0.986	h
ArSH	10.2	4.8 ± 0.3	5	0.988	31
ArCO ₂ H	11.0	2.6	9		i
ArCONHOH	13.65	2.6	4	0.989	j
ArOH	18.0	5.3 ± 0.1	8	0.991	13b
ArCH ₂ COCH ₃	19.9	4.7	4	0.999	k
ArNHCOCH ₃	21.45	4.1	6		k
ArCH ₂ CN	21.9	5.9	8	0.939	l
ArCH(NC ₄ H ₄ O)CN	22.4	7.0 ± 0.1	7	0.996	m
fluorenes	22.6	7.5 ± 0.53 ^c	14	0.939	27
fluorenes	22.6	5.7 ± 0.3 ^d	7	0.989	g
phenothiazines	22.7	5.21	5	0.982	n
ArCH ₂ SO ₂ Ph	23.4	4.8	10	0.999	g
ArCOCH ₃	24.7	3.55 ± 0.05	14	0.998	28
ArNHPh	24.95	5.4	3	0.997	n
GCH ₂ CONH ₂	25.5	3.1 ± 0.3	13	0.976	22b
ArNH ₂	30.6	5.7 ± 0.1	6	0.998	o
ArCHPh ₂	30.6	5.7 ± 0.3 ^d	7	0.989	p
9-methylanthracenes	36.1	>10 ^e	9		l

^apK_a of the parent acid. ^bThe Hammett plots are restricted for the most part to meta points; $\sigma_{m-\text{OMe}}$ is 0.02 in Me₂SO, however, rather than the value of 0.12 derived from benzoic acids in water.²⁸ The σ_p^- values for *p*-NO₂, *p*-RCO, and like substituents are made abnormally high, in part, by substituent solution-assisted resonance (SSAR) effects.³⁶ ^cFor 2- and 2,7-substituents; ρ is abnormally high because PhCO, CN, etc. groups are included and the 2- and 2,7-positions have some para character. ^dFor 3-substituents. ^e ρ is abnormally high; the correlation is poor since para substituents are used and steric effects in the 10-position are severe. ^fNumber of substituents. ^gBranca, J. C. Ph.D. Dissertation, Northwestern University, 1979. ^hHughes, D. L. Ph.D. Dissertation, Northwestern University, 1981. ⁱRitchie, C. D.; Uschold, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 2821-2824. ^jHughes, D. L.; Whang, Y., unpublished results. ^kChehel-Amiran, M., unpublished results. ^lBares, J. E. Ph.D. Dissertation, Northwestern University, 1976. ^mMueller, M. E., unpublished results. ⁿCheng, J.-P. Ph.D. Dissertation, Northwestern University, 1987. ^oAlgrim, D. J. Ph.D. Dissertation, Northwestern University, 1981. ^pTwyman, C. L. unpublished results.

values,⁴⁰ provide a means of estimating pK_a's for hundreds of additional acids.

Rates of reactions of electrophiles with the conjugate bases of acids within a family can be studied under conditions where steric, as well as solvent, effects are kept constant. Plots of $\log k_{\text{obsd}}$ vs pK_{HA} values give linear Brønsted plots, which are similar to Hammett plots but are much more precise since they do not depend on an arbitrary model (the pK_a's of benzoic acids in water). These Brønsted plots have been found to be linear for nearly all combinations of anions with electrophiles tried to date. The types of reactions include S_N2,⁴¹ S_N2',⁴² E2,⁴³ S_NAr,⁴⁴ H_T⁺,⁴⁵ and e_T⁻.⁴⁶ This means that for all of these reactions the nucleophilicities of the bases depend on only two factors, (a) their basicity, as measured by pK_{HA}, and (b) the sensitivity of the reac-

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(40) See Exner^{1b} for an extensive list of σ vs σ^- constants. The σ^- values for the NO₂, RCO, CN, and RSO₂ groups are exalted in Me₂SO in part by substituted solvation-assisted resonance (SSAR) effects.³⁶

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tion to changes in basicity, as measured by the slope of the Brønsted plot, β_{Nu} . β_{Nu} values usually fall in the range 0.2–0.5 for $\text{S}_{\text{N}}2$, $\text{S}_{\text{N}}2'$, and E2 reactions and in the range 0.5–1.0 for $\text{S}_{\text{N}}\text{Ar}$, H_{T}^{+} , and e_{T}^{-} reactions.

Reactions of PhCH_2Cl with families of delocalized anions bearing various types of donor atoms have been found to have similar β_{Nu} values. This has allowed the rate constant order for anions of the same basicity, but with different donor atoms, reacting with electrophiles such as PhCH_2Cl to be approximated: $\text{S}^{-} (10^3) > \text{C}^{-} (1.0) > \text{O}^{-} (0.3) > \text{N}^{-} (0.1)$.⁴⁷ For reactions having β_{Nu} values of 0.3 the total rate span is about 10^9 for delocalized anions derived from the acids in Table II, but the rate span increases exponentially as β_{Nu} increases. Thus, for some proton- or single-electron-transfer reactions, where β_{Nu} can approach unity, the rate span will be of the order of 10^{30} .

Acidities, Basicities, Reactivities, and Redox Potentials in Me_2SO . A plot of the oxidation potentials, $E_{\text{ox}}(\text{A}^{-})$, of 2- and 2,7-substituted fluorenone ions vs the $\text{p}K_{\text{HA}}$ values of their conjugate acids is linear with a slope near unity, indicating that substituents in the 2- and 2,7-positions do not stabilize (or destabilize) 9-fluorenyl radicals.⁴⁸ This explains the linearity of Brønsted plots, with slopes near unity, observed for 2-G- and 2,7-G₂FlH[−] ions reacting by single-electron transfer (SET) with acceptors such as 1,1-dinitrocyclohexane.⁴⁶ On the other hand, 9-G substituents have strong stabilizing (or destabilizing) effects on 9-G-Fl[•] radicals, the size of which can be measured, relative to 9-H-Fl[•], by eq 2.⁴⁸

$$\Delta E_{\text{s}} = 1.37\Delta\text{p}K_{\text{HA}} + 23.06\Delta E_{\text{ox}}(\text{A}^{-}) \quad (2)$$

In eq 2, ΔE_{s} provides an estimate of the effect of the 9-G substituent on the energy of the 9-G-Fl[•] radical, relative to that of the 9-H-Fl[•] radical. The ΔE_{s} values range from a stabilizing effect of as much as −10 kcal/mol for $\text{G} = \text{R}_2\text{N}$ to a destabilizing effect of +2 kcal/mol for $\text{G} = \text{RSO}_2$.⁴⁸ These ΔE_{s} values can be equated with the relative homolytic bond dissociation energies (ΔBDEs) of 9-C–H bonds in the corresponding fluorenes, 9-G-Fl–H.

Absolute BDEs for acidic C–H bonds in hydrocarbons or their derivatives can be estimated from eq 3, which

$$\text{BDE} = 1.37\text{p}K_{\text{HA}} + 23.06E_{\text{ox}}(\text{A}^{-}) + 55.9 \quad (3)$$

is based on a thermodynamic cycle derived by Nicholas and Arnold.⁴⁹ (Equation 3 was derived earlier in a different way by Friedrich and used to estimate BDEs in water for hydroquinone and phenol.⁵⁰) The BDEs in Me_2SO solution for the acidic C–H bonds in fluorene, indene, cyclopentadiene, 9-methylanthracene, diphenylmethane, triphenylmethane, xanthene, phenol, thiophenol, and aniline estimated in this way agree satisfactorily with gas-phase BDEs.⁵¹

The $\text{p}K_{\text{a}}$ values for a few hydrocarbons, including cyclopentadiene (CpH_2), toluene, propene, and iso-

butane, relative to triphenylmethane have been estimated from the algebraic sum of the differences in their BDEs and the differences in the oxidation potentials of their conjugate bases.⁵² For example, the $E_{\text{ox}}(\text{A}^{-})$ value for the CpH^{-} ion was found to be less negative than that of the Ph_3C^{-} ion by 18 kcal/mol. When the 6 kcal/mol difference in the BDEs of CpH_2 (81 kcal/mol) and Ph_3CH (75 kcal/mol) was taken into account, an estimated difference in acidities of 8.8 $\text{p}K_{\text{a}}$ units was arrived at. If we use the $\text{p}K_{\text{a}}$ of 30.6 for Ph_3CH in Me_2SO as a reference, the estimated relative $\text{p}K_{\text{a}}$ for CpH_2 is then 22. But, as Breslow points out, the $\text{p}K_{\text{a}}$ of 22 rests in part on the BDE of 75 for Ph_3CH , which has not been checked by modern methods.⁵² Indeed, if the BDE of 81 ± 3 estimated by eq 3 is used,⁵¹ the $\text{p}K_{\text{a}}$ calculated for CpH_2 becomes 17.6, which is in good agreement with the value of 18.0 determined in Me_2SO (Table II).

By combining $\text{p}K_{\text{HA}}$ values with $E_{\text{ox}}(\text{A}^{-})$ and $E_{\text{ox}}(\text{HA})$ values, according to eq 4, it is possible to estimate

$$\text{p}K_{\text{HA}}^{*+} = \text{p}K_{\text{HA}} + 23.06[E_{\text{ox}}(\text{A}^{-}) - E_{\text{ox}}(\text{HA})]/1.37 \quad (4)$$

acidities of radical cations of the type HA^{*+} , where A may be S, O, N, C, and the like.⁵³ Direct experimental determination of $\text{p}K_{\text{HA}}^{*+}$ values presents a formidable problem since establishment of the equilibrium $\text{HA}^{*+} \rightleftharpoons \text{H}^{+} + \text{A}^{•}$, which involves two radical species, is difficult, as is the measurement of the radical concentrations. The method is of particular value for estimating acidities of radical cation C–H acids, which generally have $\text{p}K_{\text{HA}}^{*+}$ values of 0 to −30.⁵⁴ A similar method, which is also based on a thermodynamic cycle, has been used to estimate the acidities of the conjugate acids of radical anions.⁵⁵

For single-electron-transfer (SET) reactions from fluorenone carbanions to an acceptor of the type 1,1-(NO_2)₂-c-C₆H₁₀ or 1- NO_2 -1-Ts-c-C₆H₁₀, Marcus-type plots of $\log k_{\text{obsd}}$ vs $E_{\text{ox}}(\text{A}^{-})$ have been found to be linear in several instances.^{46,56} Recently, a family of seven 9- R_2N -fluorenone ions having basicities that vary over a relatively small range ($\text{p}K_{\text{HA}}$'s = 20.4 ± 2.2) but have $E_{\text{ox}}(\text{A}^{-})$ values varying over a substantial range (0.427 V; 9.8 kcal/mol) has proved useful for testing for the presence of an SET component in $\text{S}_{\text{N}}2$ -type substitution reactions.⁵⁸ This family gave a linear Marcus-type plot for reactions with $\text{F}_3\text{CCH}_2\text{I}$, a known SET acceptor,⁵⁹ and the $\log k_{\text{SET}}$ values calculated with the Marcus equation, with λ and ΔG° values derived according to the method of Ebersson,⁶⁰ were found to correspond well

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with the experimental $\log k_{\text{obsd}}$ values. Application of the test to reactions with Ph_2CHCl , 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 Ph_2CHCl 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 Me_2SO acidity scale, for which about 300 representative values are given in Table II, furnishes (a) quantitative acidity data that can

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.

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Structural and Solvent Effects Evaluated from Acidities Measured in Dimethyl Sulfoxide and in the Gas Phase¹

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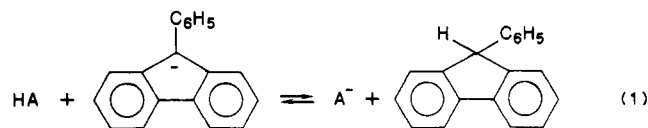
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The preceding paper gives extensive data for equilibrium acidities in dimethyl sulfoxide (Me_2SO) and makes comparisons with corresponding results in other condensed-phase media.² In the present paper the results of 76 selected gas-phase acidities³ are compared with corresponding results in Me_2SO 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 Me_2SO acidities, expressed by $1.364\Delta\text{p}K_{\text{a}} = -\Delta G^\circ$ values in

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



9-phenylfluorenyl ion (9- 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- PhFlH) and vice versa. The acidities from NH_4^+ to CH_4 cover a range of 211 kcal in the gas phase and 74 kcal in Me_2SO solution. The values in the table are arranged in order of increasing Me_2SO 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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(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 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.

Robert W. Taft is Professor of Chemistry at the University of California, Irvine. Born in Lawrence, KS, Taft received a B.S. in Chemistry from the University of Kansas and a Ph.D. from The Ohio State University where he worked with Melvin Newman. Following a postdoctoral year with Louis Hammett at Columbia University, Taft spent 15 years at The Pennsylvania State University. He has been at Irvine since it began in 1965. The present Account is taken from extensive studies of the effects of molecular structure on gas-phase proton-transfer equilibria, using ion cyclotron resonance spectroscopy. Current work also includes binding studies in the gas phase with a variety of univalent cations. Additional interests include studies of structural and solvent effects on hydrogen-bond acidities and basicities and their applications to treatments of solute partitioning between bilayers and biological activities.

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 Me_2SO 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 Me_2SO scale to problems in physical organic chemistry, the results of which are summarized in the preceding Account in this issue.