Weak Acids in Strong Bases. I. A Thermochemical Method for Comparing Acidities[1]

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Abstract: A technique is described for measuring directly the heat of deprotonation (ΔH_D) for Brønsted acids in dimethyl sulfoxide using the lyate anion of the solvent as a strong base. This permits direct comparison of a wide variety of acids, both strong and weak, under the same conditions. It is directly complementary to the use of heats of protonation in superacids (*e.g.*, HSO_3F) for comparing Brønsted bases. Excellent correlations are found between ΔH_D and pK_a's (from the work of Ritchie and Uschold) for a wide variety of acids in this system. The heat of autoprotolysis of DMSO is determined and used to calculate entropies of ionization in DMSO. The effect of changing cation is negligible within experimental error for most of the compounds studied showing that heats of ion pairing are not affecting the results. Heats of deprotonation (ΔH_D) are also presented for a series of nitroanilines and diphenylamines in strongly basic solutions of potassium and lithium dimsylate in DMSO. These values correlate well with the pK_a values for the same compounds in aqueous solutions of DMSO containing tetramethylammonium hydroxide (as reported by Stewart and coworkers). The slope of this correlation is nearly the same as that found for the correlation between the protonation properties, pK_{BH^+} and ΔH_{BH^+}, for a similar group of amines acting as weak bases in strong acids. This demonstrates a correlation of pK_a (standard state water) with heat of proton transfer over a range of at least 90 kcal/mol and 50 pK_a units from HSO_3F ($H_0 \approx -14$) to $K^+DMSYL^-/DMSO$ ($H_- \approx 34$).

Proton transfer is the most general reaction in organic chemistry since all organic compounds are potentially Bronsted acids or bases or both.[2] In addition to its practical value for activation of neutral molecules through conversion to carbonium ions[3,4] and carbanions,[5,6] the proton transfer reaction provides the broadest general structure–reactivity scale. However, the development of suitable acidity–basicity free energy functions for the quantitative comparison of weak bases or acids in a common standard state continues to give difficulty.[7-10]

Recently we have developed a thermochemical method for comparing a wide variety of bases in strong acids through their heats of protonation.[11] In this article we will describe a comparable approach to the deprotonation of acids (both strong and weak) in strong bases.

Ritchie and Uschold[12] and Steiner[13] have succeeded in measuring the pK_a's of a wide variety of Bronsted acids in dimethyl sulfoxide (DMSO) using the potassium or cesium salt of the lyate anion (DMSYL⁻) as a very strong base. Although other superbasic media could be used,[14-17] the wide current application of DMSO makes it a particularly important solvent for the initiation of our program.

Results

Our thermochemical approach involves simply the measurement[11,18] of partial molar heats of solution (ΔH_s) of the acid at high dilution (10^{-3}–10^{-2} *M*), first in DMSO (ΔH_s^{DMSO}) and then in 0.1 *M* alkali DMSYL⁻ solution in DMSO ($\Delta H_s^{DMSYL^-}$). The heat of deprotonation of the acid HA by the lyate anion

$$HA + DMSYL^- \longrightarrow DMSO + A^- \qquad (1)$$

is obtained from the difference

$$\Delta H_D = H_s^{DMSYL^-} - H_s^{DMSO} \qquad (2)$$

ΔH_D may be converted to the heat of ionization ΔH_i by

$$HA + DMSO \longrightarrow A^- + DMSOH^+ \qquad (3)$$

the process studied by Ritchie and Uschold,[12] through measurement of the heat of autoprotolysis (ΔH_{aut}) for the process

$$2DMSO \longrightarrow DMSOH^+ + DMSYL^- \qquad (4)$$

ΔH_{aut} was determined through the heat of transfer from high dilution in DMSO for acids strong enough to be completely dissociated in the solvent (eq 3) to high dilution in a solution of DMSYL⁻ (eq 1). Sub-

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Table I

	ΔH_s(DMSO), kcal/mol	ΔH_s(K^+DMSYL^-), kcal/mol	$\Delta H_i{}^a$, kcal/mol	$\Delta G^\circ{}_i{}^b$, kcal/mol	$\Delta S^\circ{}_i$, cal/(deg mol)
p-Chlorobenzoic acid	+2.74 ± 0.15	−32.0 ± 0.3	13.3 ± 1.2	13.8	−1.7 ± 5.4
p-Nitrophenol	−0.86 ± 0.10	−33.8 ± 0.5	15.1 ± 1.4	14.2	+3.0 ± 6.1
Benzoic acid	+1.26 ± 0.01	−33.7 ± 0.6	13.0 ± 1.4	15.0	−6.7 ± 6.1
p-Methoxybenzoic acid	+3.06 ± 0.15	−30.5 ± 0.4	14.5 ± 1.4	15.7	−4.0 ± 6.1
4-Nitrodiphenylamine	+2.55 ± 0.01	−24.4 ± 0.7	21.0 ± 1.5	19.5	+5.0 ± 6.4
4-Chloro-2-nitroaniline	+1.98 ± 0.13	−20.2 ± 0.2	25.8 ± 1.1	20.6	+17.5 ± 5.1
9-Phenylfluorene	+5.39 ± 0.40	−18.7 ± 0.3	23.9 ± 1.5	22.4	+5.0 ± 6.4
2,3,5,6-Tetrachloroaniline	+2.96 ± 0.02	−16.4 ± 0.2	28.7 ± 1.1	23.3	+18.1 ± 5.1
4,5-Methylenephenanthrene	+3.22 ± 0.15	−15.1 ± 0.2	29.7 ± 1.2	27.3	+8.1 ± 5.4
Fluorene	+4.73 ± 0.07	−13.5 ± 0.3	29.8 ± 1.2	28.0	+6.0 ± 5.4
Triphenylmethane	+5.8 ± 0.1	−3.58 ± 0.30	38.6 ± 1.2	39.3	−2.3 ± 5.4
t-Butyl alcohol	+1.21 ± 0.04	−8.00 ± 0.20	38.8 ± 1.0	39.8	−3.4 ± 4.7

[a] $\Delta H_i = \Delta H_D + 48.0$ kcal/mol. [b] Calculated from Ritchie's and Ushold's pK_a values. Errors in $\Delta G_i{}^\circ$ are ±0.41 kcal/mol (see ref 12).

traction of (1) from (3) gives (4). Such results for transfer of HSO_3F and F_3CSO_3H from DMSO to 0.1 *M* K^+DMSYL^- give 48.0 ± 0.8 and 44.7 ± 0.6 kcal/mol, respectively. We shall use the higher of these values for calculation of all ΔH_i terms reported in Table I. Control experiments with F_3CSO_3H into H_2O and 0.1 *M* Na^+ OH^- gave +13.7 ± 0.4 kcal/mol in agreement with the accepted value +13.34 kcal/mol for the heat of autoprotolysis of water.[19]

Evidence that deprotonation is the only reaction taking place for most compounds is provided not only by the instantaneous and reversible spectroscopic changes reported by previous workers, but also by the instantaneous and complete liberation of heat when each acid was added to the basic solution. Three other facts which support the validity of this simple reaction are: (1) development of a consistent acidity function scale for the aromatic amines studied here as observed by Dolman and Stewart; (2) the close, and nearly unit, correlation between the standard free energies of deprotonation (1.36 pK_a) obtained by Ritchie in DMSO *vs.* the heats of deprotonation obtained by us in DMSO solutions; (3) the interesting fact that the slope for the correlation between the pK_{BH^+} and ΔH_{BH^+} for the deprotonation of the conjugate acids of a series of aromatic amines in strong acids is almost identical with that which we find here for the correlation of pK_a and ΔH_D for the deprotonation of a similar group of amines in strong bases.

In order to verify the deprotonation reaction between these weak acids and the dimsylate anion, we have observed the nmr spectra for a few of the compounds listed in Table II in lithium dimsylate solution. The spectra for triphenylmethane and fluorene in $DMSYL^-$ solutions correspond exactly to the published spectra for the anions of these acids.[20] The spectrum for *p*-fluorophenol in DMSO was compared with that in DMSO in the presence of excess Li^+DMSYL^-. In the presence of base, the aromatic proton signal is broadened and shifted about 0.4 ppm upfield from its position in pure DMSO. No signal for the OH proton was observed in the lithium dimsylate solution. The signal for this proton in DMSO was a sharp singlet at δ 9.18 ppm.

All of the measurements discussed here were based on four to seven measurements of each heat of solution made by introducing successive weighed increments of the acid into the calorimeter solution. In the measurement of $\Delta H_s{}^{DMSYL^-}$, the $DMSYL^-$ ion was always maintained in threefold excess of the final amount of acid (0.03 *M*) even though the latter concentration in the calorimeter solution varied by as much as tenfold during a run. No concentration dependence of $\Delta H_s{}^{DMSYL^-}$ was found for any of the acids reported here. We take this as an indication of complete deprotonation of the acid HA over the entire concentration range and also as supporting evidence that heats of ion pairing are not significant in the processes reported here.

The reproducibility of the method was confirmed by frequent checks of ΔH_D of fluorene with different batches of DMSO and K^+DMSYL^-. Even though some trial runs employed samples of DMSO which contained more than 150 ppm of water by Karl Fischer titration, there was not statistically significant difference for the variation of ΔH_D between batches and within batches.

Discussion

Comparison with the Results of Ritchie and Uschold.[12] Results presented in Table I and in the following sections show the following important facts.

(1) Compounds of many kinds covering a wide range of acidity (pK_a from about 3 to 30) can be compared easily in a single medium under standardized conditions by our method.

(2) A plot of ΔH_D *vs.* Ritchie's[12] pK_a values gives a good linear correlation, $\Delta H_D = 1.35\text{p}K_a - 47.4$ ($r = 0.97$), over 30 kcal/mol for ΔH_D and 20 pK_a units. The pK_a intercept at $\Delta H_D = 0$ corresponds to an acid as strong as DMSO and is about 34 corresponding closely to Steiner's[13c] estimate of 33.

(3) The slope (1.35 ± 0.11) of this line corresponds to a unit slope correlation between ΔH_D or ΔH_i and $\Delta G^\circ{}_i$ (since $\Delta G^\circ{}_i = 1.36\text{p}K_a$ at 25°).

(4) Combination of $\Delta G^\circ{}_i{}^{12}$ and ΔH_i (eq 3) leads to standard entropies of deprotonation $\Delta S^\circ{}_i$ which are mostly in the neighborhood of zero within the sometimes considerable experimental error. Thus, although we are dealing with various types of acids over a wide range of strengths, their entropies of ionization are all close to that of DMSO and to each other.

Tests for Ion Pairing. Ritchie and Uschold conducted their experiments at high dilution and used

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Table II. Heats of Solution of Weak Acids in DMSO and $\Delta H_D{}^a$ for M^+DMSYL^- Solutions at 25° (All Values in kcal/mol)

Compd	H_s(DMSO)	$\Delta H_D(Li^+DMSYL^-)$	$\Delta H_D(Na^+DMSYL^-)$	$\Delta H_D(K^+DMSYL^-)$	$\Delta H_D(Cs^+DMSYL^-)$
FSO_3H	−26.6 ± 0.1			−48.0 ± 0.8	
CF_3SO_3H	−25.3 ± 0.1	−43.3 ± 0.5		−44.7 ± 0.6	
CH_3SO_3H	−14.1 ± 0.2	−38.1 ± 0.7		−40.0 ± 0.7	
p-Chlorobenzoic acid	+2.74 ± 0.15	−34.4 ± 0.6		−34.7 ± 0.7	
p-Fluorobenzoic acid	+1.70 ± 0.22			−34.6 ± 0.3	
Benzoic acid	+1.26 ± 0.01	−33.1 ± 0.5		−34.1 ± 0.4	−35.0 ± 0.7
p-Methoxybenzoic acid	+3.06 ± 0.15	−33.7 ± 0.5		−33.6 ± 0.6	
p-Nitrophenol	−0.86 ± 0.10	−33.3 ± 1.3	−33.3 ± 0.8	−32.9 ± 0.6	
p-Cyanophenol	0.00			−29.9 ± 0.5	
p-Chlorophenol	−0.97 ± 0.06	−27.5 ± 0.3	−26.9 ± 0.5		
m-Fluorophenol	−4.33 ± 0.05			−26.7 ± 0.3	
p-Fluorophenol	−0.66 ± 0.03			−27.0 ± 0.3	
Phenol	−0.72 ± 0.01	−27.0 ± 0.8	−25.2 ± 0.3	−24.3 ± 0.4	−24.8 ± 0.4
p-Methoxyphenol	+1.22 ± 0.13		−25.3 ± 0.8	−23.9 ± 0.5	
2,6-Di-*tert*-butylphenol	+2.34 ± 0.10			−26.2 ± 0.6	
9-Phenylfluorene	+5.39 ± 0.40	−22.7 ± 0.5		−24.1 ± 0.7	−23.9 ± 0.9
4,5-Methylenephenanthrene	+3.22 ± 0.15	−17.6 ± 0.6		−18.4 ± 0.4	
Fluorene	+4.73 ± 0.07	−16.4 ± 0.4	−18.1 ± 0.4	−18.2 ± 0.4	−17.9 ± 0.4
Phenylacetylene	−0.74 ± 0.02		−11.4 ± 0.1	−11.5 ± 0.2	
Triphenylmethane	+5.8 ± 0.1	−7.1 ± 0.2		−9.4 ± 0.4	

[a] ΔH_D is the heat of transfer of the acid from DMSO to 0.1 *M* M^+DMSYL^-.

Cs^+DMSYL^-, the alkali base which is most highly dissociated in DMSO. However, since there is good reason to suspect the intrusion of ion-pairing effects into at least some measurements[21–24] with 0.1 *M* alkali (M^+) $DMSYL^-$ we have investigated the variation of ΔH_D as a function of the alkali metal.

In Table II are presented values of ΔH_D for a variety of acids from very strong (*e.g.*, HSO_3F, $pK_a \sim -14$) to quite weak (*e.g.*, triphenylmethane, $pK_a = 28$[12]) as they are ionized by 0.1 *M* M^+DMSYL^- salts in DMSO. The results can be summarized easily.

For all compounds which produce charge-delocalized anions, except possibly phenol, there is very little if any difference (within the range of combined experimental error) between ΔH_D values measured with Li^+, Na^+, K^+, or Cs^+ as the counterion to $DMSYL^-$. The heats of solution of fluorene in 0.1 *M* K^+DMSYL^-, in 0.05 *M* K^+DMSYL^-, and in 0.05 *M* K^+DMSYL^- with 0.05 *M* dibenzo-18-crown-6-ether, a strong K^+ complexer, were all the same within experimental error. Therefore, although there are varying degrees of ion pairing for the different cations with the anions shown,[22] the differences are not thermochemically significant within experimental error.[25] Enthalpies of ion-pair dissociation for anions such as these amount to 4–5 kcal/mol in THF as solvent.[6,23] We believe that our failure to see a cation effect in ΔH_D here for highly delocalized anions indicates that the variation of M^+ in the process

$$HA + M^+DMSYL^- \longrightarrow DMSO + M^+A^-$$

has nearly equal effects on the energetics of ion pairing for M^+A^- and M^+DMSYL^-. If any trend in ΔH_D is observable for delocalized anions, it is towards a more exothermic value for the larger cations than for Li^+. If this trend is significant, it indicates a slightly "tighter" ion pair for Li^+DMSYL^- than for Li^+A^-.

Solvent and Charge Dispersal. The effect of solvent and charge delocalization can be estimated from a Hammett plot of pK_a's for phenols listed in Table II as determined from $\Delta H_D(K^+DMSYL^-$values) by the correlation equation $pK_a = 34.4 + 0.7407\ \Delta H_D$. The ρ value[26] for such a correlation is 5.3 which may be compared with 2.8 in water. The lower ρ value in water presumably reflects lessened demand for internal stabilization of phenolate anions in water because of external stabilization through hydrogen bonding. This interpretation is supported by Ritchie's determination of $\rho = 2.6$ for the benzoic acids in DMSO. The small ρ values for benzoate ions show that they enjoy less internal stabilization through resonance than do the phenolate anions.

Anilines and Diphenylamines. In this section we report the results of applying our method to a series of anilines and diphenylamines for which Stewart[27–30] has determined the pK_a values by the acidity function technique in DMSO–water mixtures using tetramethylammonium hydroxide as a base. The pK_a values determined by this method are referred, in principle, to a standard state in water; however, Stewart's pK_a values agree well with those determined by Ritchie (standard state pure DMSO) in most cases.

As a test for ion-pairing effects, we have measured ΔH_D for several of these anilines and diphenylamines in both lithium and potassium dimsylate solutions. The results are listed in Table III. From the data it is apparent that, except for 2-nitrodiphenylamine and 4-chloro-2-nitroaniline, the heats of deprotonation measured using either lithium or potassium dimsylate solutions are in fairly close agreement. A plot of ΔH_D *vs.* Stewart's pK_a values for the anilines and diphenylamines gives a good linear correlation for both lithium and potassium dimsylate values. From a least-squares

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Table III. Heats of Solution of Anilines and Diphenylamines in DMSO and in Li^+ and K^+ Dimsylate Solutions

Compd	$pK_a{}^a$	$pK_a{}^b$	ΔH(DMSO)	$\Delta H_D(K^+DMSYL^-)$	$\Delta H_D(Li^+DMSYL^-)$
			Anilines, AN = Aniline		
4-Cl-2-NO_2-AN	17.08	18.0	1.98 ± 0.13	−22.2 ± 0.3	−123.0 (*sic*)
4-NO_2-*N*-trityl-AN	17.98	17.0	0.55 ± 0.01	−23.5 ± 0.6	−20.1 ± 0.5
4-NO_2-2-CH_3-AN	18.83	20.3	1.04 ± 0.01	−19.1 ± 0.4	
4-NO_2-2,6-$(CH_3)_2$-AN	18.71	19.7	1.83 ± 0.05	−19.8 ± 0.4	−19.8 ± 0.5
2,3,5,6-$(Cl)_4$-AN	19.22	20.1	2.96 ± 0.02	−19.4 ± 0.2	−17.3 ± 0.4
4-NO_2-2,3,5,6-$(CH_3)_4$-AN	22.66	24.2	2.49 ± 0.09	−13.8 ± 0.2	−12.9 ± 0.4
4-CN-AN	22.68	25.6	−0.64 ± 0.04	−10.9 ± 0.2	
3,5-Dichloroaniline	23.59	26.3	0.80 ± 0.05	−10.9 ± 0.3	−11.6 ± 0.3
			Diphenylamines, DPA = Diphenylamine		
4-NO_2-DPA	15.67	14.7	2.25 ± 0.01	−26.7 ± 0.7	−23.9 ± 0.6
2-NO_2-DPA	17.91	16.3	6.04 ± 0.02	−24.5 ± 0.5	−160.0 ± 12.0 (*sic*)
4-$MeSO_2$-DPA	18.80	18.8	2.44 ± 0.03	−21.1 ± 0.3	−17.5 ± 0.6
3,4′-$(Cl)_2$-DPA	19.73	20.5	2.44 ± 0.05	−18.2 ± 0.5	
2,2′-Dipyridylamine	19.91	21.1	2.81 ± 0.04	−18.0 ± 0.3	−18.2 ± 0.2
4-Cl-DPA	21.33	21.4	2.52 ± 0.01	−17.4 ± 0.4	
Diphenylamine[c]	22.44	22.6	2.03 ± 0.08	−15.9 ± 0.6	−13.4 ± 0.5

[a] From ref 27 and 29. [b] Calculated from the equation $pK_a = 0.7407\Delta H + 34.4$. [c] ΔH_D for this compound in Cs^+DMSYL^+ is −14.1 kcal/mol.

fit of the data, for ΔH_D using Li^+ as counterion

$$\Delta H_D = 1.52 \pm 0.11 pK_a - 47.4 \pm 6.6 \qquad r = 0.98$$

for ΔH_D using K^+ as counterion

$$\Delta H_D = 1.85 \pm 0.17 pK_a - 55.5 \pm 8.2 \qquad r = 0.96$$

The standard deviations of the intercepts for these lines show that they are the same within the combined standard deviations. Applying Student's *t* test[31] to the slopes of these lines also indicates that they are statistically indistinguishable.

Protonation and Deprotonation of Nitroanilines. A remarkable result of the present work which is of significance to the whole question of the soundness of H_0 and H_- acidity scales as a measure of structural change on acidity arises by comparison of the slopes of the correlation lines for deprotonation of these nitro aromatic amines in strong base (see above) *vs.* pK_a with corresponding values for the protonation of similar compounds[11] in strong acid. In each case, the pK_a's are derived by an appropriate acidity function which refers them to a standard state in water for deprotonation either of the neutral amine (H_-) or deprotonation of its conjugate acid (H_0). In the former case we have seen an average slope of (1.69) relating ΔH_D to pK_a; in the latter case[11] the slope for $\Delta H_{a,b}$ *vs.* pK_a for amines is (1.78). Although the two processes for deprotonation are somewhat different and the superacid medium differs by about 50 pH units in proton donor ability from the superbasic one, we see an almost identical correlation between the enthalpy of deprotonation and the standard free energy change in water for this series of compounds and their ions.

These relationships between enthalpy and free energy imply that the effect of structural change on both of these thermodynamic properties is very close to the effect on the potential energies for the ionization reactions of the same compounds. They also strongly support the validity of the acidity function method when properly applied to a similar series of compounds.

Not all of the amines which we have studied fit these correlations. Several polynitroaromatic amines underwent an extremely exothermic (>100 kcal/mol) reaction with K^+DMSYL^-. This occurred when two or more nitro substituents were present in the same aromatic ring. For 2-nitrodiphenylamine and 4-chloro-2-nitroaniline, we find the very interesting result that with potassium dimsylate the only apparent reaction is proton transfer; but with lithium dimsylate these compounds undergo a very exothermic reaction which is obviously not simple proton transfer (2-nitroaniline does not give this extremely exothermic reaction with either Li^+ or K^+DMSYL^-). We are currently investigating the chemistry of these conversions.

Experimental Section

Most of the weak acids used were available commercially. 9-Phenylfluorene was prepared by the method of Ullman and von Wurstenberger.[32] Solids were recrystallized from appropriate solvents and dried or vacuum sublimed. Melting points agreed with literature values. Liquids were usually dried and distilled. Purity was checked by refractive index and/or glpc. When possible, the water content of hydroscopic materials was checked by Karl Fischer titration. Anilines and diphenylamines were supplied in pure form by Professor R. Stewart. Lithium dimsylate was prepared by the method of Corey and Chaykovsky[33] as a 1.0 *M* stock solution from 1.6 *M* butyllithium in hexane (Foote Mineral Co.) and DMSO.

Potassium dimsylate solutions were prepared as 1.0 *M* stock solutions by adding the calculated amount of DMSO to a weighed amount of potassium hydride in a vacuum line. Commercial potassium hydride (Alfa Inorganics) was freed from mineral oil by washing with light petroleum ether several times and drying on the vacuum line.

Cesium dimsylate was prepared in a manner similar to potassium dimsylate using $CsNH_2$ prepared on the vacuum line from cesium metal (>99.9% MSA Research Corp.) and liquid ammonia. The concentrated dimsyl solutions were stored under argon in the dark at −20°. About 20 ml of the 1.0 *M* solution was diluted with DMSO to 205 ml in the calorimeter for heat of solution measurements. The calorimeter solution was kept continually under a blanket of argon during the run. The red color of the trityl anion was stable for at least several hours in the calorimeter when protected from air in this way. The red color faded very rapidly when the solution was intentionally exposed to air. All calorimetric runs were made at 25 ± 1°.

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