Thermochemical Acidities in Three Superbase Systems

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Heats of deprotonation (ΔH_D) are compared for a number of weak carbon and nitrogen acids in dimethyl sulfoxide (Me_2SO) with potassium salts of tert-butyl alcohol (KOBu-t) or the solvent (KMe_2SYL) as bases and also for the potassium salt of 1,3-diaminopropane in the diamine (KAPA) as the solvent. For compounds which were deprotonated in all three media, ΔH_D values in KAPA are about 9 kcal/mol more exothermic than those in KMe_2SYL/Me_2SO which in turn are about 4 kcal/mol more exothermic than those in KOBu-t/Me_2SO. The heat of isomerization of 1,4-pentadiene to its 1,3-isomer in KAPA is calculated from heats of deprotonation values of the two compounds and found to be 7.96 kcal/mol. This compares well with literature estimates. Resonance energies are estimated for cyclopentadienyl and indenyl anions to be 31.7 and 19.2 kcal/mol, respectively. Heats of deprotonation for a large number of acids in the three bases are compared with free energies of ionization in dimethyl sulfoxide and cyclohexylamine and with heats of ionization in the gas phase.

Because of the great practical importance of base-promoted reactions, comparisons of the strengths of acids are fundamentally interesting to organic chemists. Likewise, an understanding of the similarities and differences of basic media is essential, since virtually all organic compounds can serve as proton donors if presented to a strong enough acceptor base.

A variety of means have been used to measure or estimate the driving force for deprotonation in terms of free energy by indicator methods,[1,2] by electrochemical means,[3,4] and through rate–equilibrium correlations, "kinetic acidities".[5,6] In several previous papers we have described the use of reaction calorimetry as a thermochemical approach for the comparison of bases in strong acids[7] or of acids in strong bases.[8] Particular effort was devoted to deprotonation of organic proton donors in dimethyl sulfoxide (Me_2SO) by using the potassium salt (KMe_2SYL) of this solvent as the base. The same system has been developed extensively by Bordwell and his colleagues to yield pK_as of the organic acids[1] and, more recently, the ion pair association constants of their potassium salts.[9] Rather good correlations were found between Bordwell's pK_as for many acids in KMe_2SYL/Me_2SO and our heats of deprotonation (ΔH_D) for the same acids in this medium. However, some fairly large discrepancies have also been noted.

The advantage of the thermochemical approach is that it allows comparison of an enormous range of compounds through one single type of measurement in the same medium. No special spectroscopic properties are required, nor is it necessary to develop an extensive series of overlapping indicators, or other means, for relating the strongest and weakest acids on the same scale. The greatest weakness of the thermochemical method is that enthalpy changes are not directly useful measures of chemical driving force. Free energies, equilibrium constants, and rate constants are without doubt the chemically important properties. However, thermochemical measurements can provide a reasonable guide to free energies

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of proton transfer, in the absence of the less accessible free energy scales needed for accurate pK_a measurements.

This paper reports our results from measurements of the heats of deprotonation for a variety of carbon and nitrogen acids in three strongly basic (superbase) systems.

Solutions of potassium *tert*-butoxide (KOBu-*t*) in Me$_2$SO are convenient to prepare since free-flowing anhydrous KOBu-*t* became available commercially. Although KOBu-*t*/Me$_2$SO is often used for base-promoted reactions, we know of no previous attempts to relate acidities in it to those in other media. Brauman and co-workers[10,11] demonstrated that solutions of KOBu-*t*/Me$_2$SO are essentially self-buffering since they quickly produce a complex equilibrium mixture also containing *t*-BuOH, KMe$_2$SYL, and other species. It is not, therefore, a system whose base strength can be varied over a wide range.

The KMe$_2$SYL/Me$_2$SO system has been used more than any other superbase to compare weak organic acids. Since some of our values for ΔH_D and some of Bordwell's pK_as in the same media have been modified during the past decade, we have summarized the most recent results from both groups.

Finally, we will present all of our results obtained to date in the KAPA superbase system produced from the potassium salt of 1,3-diaminopropane (DAP) in that diamine as the solvent. These include the use of this very powerful base to deprotonate several isomeric alkenes which produce the same carbanion. For these compounds, the differences in ΔH_D correspond to differences in the heats of formation of the initial alkenes in DAP. We have used an equivalent approach to determine heats of formation of isomeric alkyl halides which go to the same carbocation in superacid.[12]

Experimental Section

Purification and Handling of Solvents. Dimethyl sulfoxide (Me$_2$SO, Aldrich, 99%) was placed over 4A molecular sieves for several days. It was then transferred to a large round-bottomed flask and titrated to a pink end point with *n*-BuLi in hexane with triphenylmethane as an indicator. It was then vacuum distilled (~1 mm), maintaining the pot temperature below 60 °C. The middle fraction (~60%) was collected and stored in a dark bottle fitted with an automatic zeroing buret and was kept under a positive pressure of argon. Karl–Fischer titration of Me$_2$SO showed that the water content was usually less than 300 ppm. All transfers were done under argon by using syringes and cannulation needles.

1,3-Diaminopropane (DAP, Aldrich, 98%) was first dried by using 4A molecular sieves. It was dried further by distillation over sodium metal under reduced pressure, or the above method with *n*-BuLi and triphenylmethane was employed. The latter approach gave drier solvents and was used exclusively once this fact was discovered. Once purified, the solvent was stored in a round-bottomed flask fitted with a three-way stopcock and stored under a positive pressure of argon. Transferring the solvent was done by cannula.

Preparation, Estimation, and Storage of Potassium Dimsylate Solutions. Potassium dimsylate solutions (KMe$_2$SYL) were prepared as approximately 1 M solutions from purified Me$_2$SO and potassium hydride (Alfa). The procedure was that described by Bordwell.[1b] The base concentration was estimated by titrating it against a solution of diphenylacetic acid in Me$_2$SO.[13] The KMe$_2$SYL solution was used within 3 days and was stored protected from light at room temperature under argon.

KAPA was prepared in the same way as KMe$_2$SYL and its strength estimated similarly. The solutions were used within a few days.

Potassium *tert*-butoxide (KOBu-*t*, Aldrich) was sublimed under high vacuum before use. Stock solutions of KOBu-*t* in Me$_2$SO were made by dissolving a known amount of KOBu-*t* in Me$_2$SO, all solution transfers being made in a glovebox. They were diluted in 0.1 M and used within 1 day.

Purification of Compounds. Materials were purified as described below. In all cases, except those specified, the authenticity and purity were checked by NMR and by comparison of the melting point (Thomas-Hoover capillary apparatus) or boiling point against literature values.

Acetylacetone (Aldrich) was fractionally distilled through a Vigreaux column. The purity was verified by NMR.

Diisopropylamine (Aldrich) was dried over 4A molecular sieves and distilled from NaOH pellets through a Vigreaux column.

Toluene and *p*-xylene (Fisher 99%) were used as received.

Cycloheptatriene (Aldrich) was distilled under reduced pressure by using a short Vigreaux column and a short-path distillation head with ice-cold water circulation. The receiver flask was also cooled in ice. It was then washed three times with 10% Na$_2$CO$_3$, once with 10% KOH, and three time with water and then redistilled under reduced pressure. It was stored in the freezer and used within 1 week.

Phenylacetylene (Aldrich) was distilled through a Vigreaux column under reduced pressure and the 95–95.5 °C (200 mm) fraction taken. It was protected from light and air and used within 1 week.

Xanthene (Eastman Organic) was crystallized twice from absolute ethanol and dried in a vacuum oven.

tert-Butylamine (Aldrich) was dried over 4A molecular sieves and then distilled from sodium metal.

1,4-Pentadiene (Aldrich 99%) was used as such. The purity was checked by GC.

1,3-Pentadiene (Aldrich 99% trans) was used as received. The purity was checked by GC.

Cyclopentadiene was prepared by cracking the dimer (Aldrich, 90%) very close to its boiling point and distilling it through a Vigreaux column with a short distillation head with circulating ice-cold water. The distillation temperature was kept at 40 °C. The receiver was cooled in dry ice. The compound was stored at -20 °C or below until needed and used within 1 or 2 days. The purity was checked by NMR.

Fluorene (Eastman Organic) was recrystallized from absolute ethanol and dried in a vacuum oven at 50 °C for 1 day.

Indene (Eastman Organic, technical grade) was distilled just prior to use from molecular sieves through a glass column packed with helices. It was stored in the freezer.

Diphenylmethane (Eastman Organic) was stored over 4A molecular sieves, fractionated under reduced pressure, and recrystallized from methanol.

Triphenylmethane (Eastman Organic) was recrystallized from absolute ethanol and dried in air.

p-Phenyltoluene (Aldrich 95%) was recrystallized first from 95% ethanol and then from methanol.

1,8-Diaminonaphthalene (Aldrich 98%) was purified successfully by high-vacuum distillation to give a pale yellow solid. Recrystallization from deoxygenated benzene–ligroin gave almost colorless crystals. The material thus obtained was kept protected from light in a desiccator under argon.

1,5-Diaminonaphthalene (Aldrich, technical grade) was recrystallized repeatedly from deoxygenated aqueous ethanol until a satisfactory melting point was obtained.

Aniline (Fisher, ACS certified) and *m*-chloroaniline were distilled from KOH pellets under reduced pressure, stored in the freezer, and used within a few days.

Cyclohexylamine (Aldrich) was dried over 4A molecular sieves for several days. Then it was dried over LiAlH$_4$ (Alfa) for 1 day and distilled from sodium metal.

trans-β-Methylstyrene (Aldrich 95%) was distilled, and the 45–48 °C (0.05 mm) fraction was collected.

tert-Butyl alcohol was stored over 4A molecular sieves and distilled at atmospheric pressure under N$_2$. It was kept tightly stoppered until use and handled under N$_2$.

Dibenzo-18-crown-6 (Parish chemical) was recrystallized from benzene until a melting point of 162–163 °C was reached.

Dimedone (Aldrich) was purified by multiple recrystallization from acetone.

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UV spectra were recorded on a Cary 15 recording spectrophotometer. ^{1}H NMR spectra were taken on Varian A-60, EM-360, or FT-60 instruments. For higher sensitivity an IBM NR-80 instrument (80 MHz) was used. Sometimes spectra were recorded on a MH-100 (JEOL) instrument. Appropriate deuterated solvents such as Me$_2$SO-d_6, CDCl$_3$, or DAP-d_4 were used when needed.

Gas chromatograms were recorded on a Varian 920 or a Hewlett-Packard Model 5700A instrument.

Calorimetry. The solution calorimeter used for this study has been described.[8e,f] Since these solvent systems are air and moisture sensitive, the calorimeter was cleaned, dried with hot air from a heat gun, purged continuously for 0.5 h, and kept under argon purge during filling and measurements.

For the preparation of 0.1 M KOBu-t/Me$_2$SO solutions, the calculated quantity of KOBu-t was weighed out under argon, dissolved in the calculated amount of Me$_2$SO under argon, and transferred to the Dewar flask by means of a syringe. The KMe$_2$SYL solutions, roughly 0.5–1 M, were diluted to 0.1 M and transferred to the calorimeter by using cannulation under argon. KAPA solutions were handled similarly.

Liquid samples were introduced using the following three methods. (a) A 500-, 250-, or 100-μL gas-tight syringe with a Luer tip and Chaney adapter which had been calibrated to deliver known amounts of sample was used with calibrated metal stops.[8e,f] (b) Alternatively, a Glenco micrometer syringe with a Teflon needle immersed in the solvent was used. The syringe was calibrated before use and the sample injected simply by turning the micrometer to deliver desired volumes. (c) Volatile liquids, such as 1,4-pentadiene, were sealed in preweighed glass ampules which were broken by pressing them against a stainless steel loop suspended in the calorimeter.

Solid samples were introduced with disposable plastic syringes, the ends of which had been removed.[8e,f] Solids were also introduced into ampules by dissolving them in an inert, volatile solvent, injecting into preweighed glass ampules, evaporating the solvent, and then sealing the ampules which were broken as before.

Results

Calorimetry. The thermochemical method consists of measuring the partial molar heat of solution (ΔH_s) of a weak acid at high dilution (10^{-4}–10^{-2} M) first in the pure solvent and then in the 0.1 M base solution. The heat of solution in the pure solvent was measured to correct for enthalpy changes not due to deprotonation. At the concentrations involved, the molar heats of solution were independent of the amount of solute added.

ΔH_s^{DAP} and $\Delta H_s^{Me_2SO}$ stand for the heats of solution of the solute in pure DAP and Me$_2$SO, respectively. $\Delta H_s^{KMe_2SYL}$ and ΔH_s^{KAPA} stand for the heats of solution of the solute in 0.1 M KMe$_2$SYL/Me$_2$SO and 0.1 M KAPA/-DAP, respectively. ΔH_s^{KOBu-t} represents the heat of reaction of the solute with 0.1 M KOBu-t/Me$_2$SO. All reactions were carried out at 25 °C unless specified otherwise.

The enthalpy of deprotonation of a weak acid in a base system (ΔH_D) is defined as the heat of transfer of the solute from the pure solvent to the basic solution, e.g., eq 1. Each

$$\Delta H_D^{KMe_2SYL} = \Delta H_s^{KMe_2SYL} - \Delta H_s^{Me_2SO} \qquad (1)$$

heat of solution is the average of six or more numbers (i.e., at least one complete run with six injections of solute).

Completeness of proton transfer was inferred in most cases from the following facts, none of which should be considered as more than moderately strong evidence. (1) The pK_as of most of the compounds involved are much lower (by about 3 or more pK_a units) than that of the solvent. (2) NMR spectra of the reaction products were found to be identical with those of anions already reported in the literature or were consistent with the presumed structures of the anions. In view of the relative insensitivity of NMR to traces of thermochemically significant

impurities, this is a necessary but not decisive criterion in the absence of their neutral precursors. (3) In some cases, the reaction mixture was quenched and the starting material recovered (see below). (4) Thermograms showed that the heats of reaction were released immediately, indicating the absence of slow secondary reaction.

The results obtained in the three different base systems are presented in Table I where they are compared with published values for pK_as in Me$_2$SO[1] and cyclohexylamine[6] and for proton affinities of the anions in the gas phase.[14,15]

Table II lists complete, updated values for heats of ionization, $\Delta H_i°$, in Me$_2$SO from this laboratory, free energies of ionization, $\Delta G_i°$, from Bordwell's laboratory, and entropies of ionization derived from the two data sets. Since a significant number of these values from our laboratory and Bordwell's have undergone slight revision and since we do not forsee another extensive comparison of our work, we present the collected results here.

Proton Magnetic Resonance (^{1}H NMR) Studies of Anions in DAP-d_4 and KMe$_2$SYL/Me$_2$SO. Analysis of Quenched Anions. To verify the deprotonation process and to establish the identity of the anion formed, we obtained ^{1}H NMR spectra of solutions from reaction of the weak acids used in this study with excess KAPA in DAP. Whenever possible, these spectra were compared with literature spectra. In one or two cases ^{1}H NMR spectra of the anions in KMe$_2$SYL/Me$_2$SO were obtained.

In some cases we also obtained additional evidence for clean deprotonation of the weak acids used in our study by quenching the superbase solution of the deprotonated acid with ice-cold water and extracting with ether. In each case the reprotonated product exhibited a ^{1}H NMR spectrum identical with that of the starting material.

^{1}H NMR Spectra of Anions. ^{1}H NMR spectra were recorded with samples in sealed tubes under dry argon with reference to Me$_4$Si in that solvent or to one of the solvent peaks (once the frequency of that signal with reference to Me$_4$Si had been established). In general, the concentration of the weak acid was between 10 and 50 mM. Although DAP-d_{10} would have been the solvent of choice for examining KAPA solutions, its high cost led us to use DAP-d_4. This was obtained by exchanging protio DAP with pure D$_2$O, removing all the water by azeotroping with benzene. This process was repeated until a solvent with >90% deuterium content was obtained.

Unfortunately, the residual methylene protons made it difficult to detect signals due to the sample between 1 and 3.5 ppm. These intense peaks also caused distortion of other peaks in the ^{1}H NMR spectrum to some extent. The high viscosity of KAPA and KMe$_2$SYL solutions broadened signals, and this also made interpretation difficult. All the ^{1}H NMR spectra were recorded at the temperature of the ^{1}H NMR probe (usually 25–40 °C).

Whenever possible a Fourier transform instrument (e.g., IBM NR-80) was used. In cases where peak folding was a major problem, continuous-wave instruments such as the Varian T-60, A-60, or EM-360 were used. ^{1}H NMR spectra of the various anions are discussed below relative to Me$_4$Si.

(1) KOBu-t in Me$_2$SO-d_6 (Me$_4$Si Standard). This showed only two peaks, one attributed to the methyl group (0.56 ppm) and the other to the OH group of t-BuOH (2.03 ppm) produced in small concentrations by the reaction of KOBu-t with Me$_2$SO.

(2) KAPA in DAP. DAP (neat) showed two sets of peaks, one between 1.3 and 1.7 ppm and the other between

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Table I.   Comparison of the Three Base Systems KMe₂SYL/Me₂SO, KOBu-t/Me₂SO, and KAPA/1,3-DAP with Each Other and with Other Measures of Acidity

no.	compd	pK in Me_2SO (CHA)[a]	$\Delta H_D^{KMe_2SYL,f}$, kcal/mol	$\Delta H_D^{KOBu\text{-}t,j}$, kcal/mol	$\Delta H_D^{KAPA,j}$, kcal/mol	ΔH°_{acid} (gas phase)[k], kcal/mol	$\Delta H_S^{Me_2SO,f}$, kcal/mol	ΔH_S^{DAP}, kcal/mol
1	acetylacetone	13.3[b]	-31.73 ± 0.34	-26.9 ± 0.6		343.7	0.91 ± 0.01	
2	dimedone	11.2[b]	-33.93 ± 0.40	-31.6 ± 0.9		338.9	3.70 ± 0.09	
3	t-butyl alcohol	32.2[c]	-9.2 ± 0.2[g]	-3.99 ± 0.17		373.3	1.24 ± 0.02[g]	
4	1,5-diaminonaphthalene	29.2[d]	-8.5 ± 0.4[d]		-28.7 ± 0.4[d]	358.5[l]	-0.67 ± 0.19[i]	-0.33 ± 0.20
5	1,8-diaminonaphthalene	24.8[d]	-12.4 ± 0.8[d]		-28.7 ± 0.5[d]	353.2[l]	-0.6 ± 0.2[i]	-0.57 ± 0.20
6	aniline	30.7[e]	-7.1 ± 0.2[d]		-14.5 ± 0.8[d]	367.1	-2.38 ± 0.14[i]	-1.33 ± 0.06
7	m-chloroaniline	28.5	-11.0 ± 0.5[d]			351.1	-4.10 ± 0.27[f]	
8	cycloheptatriene		side reaction		side reaction		1.16 ± 0.02	1.31 ± 0.06
9	xanthene	30.0[e]	-8.34 ± 0.2	-4.3 ± 0.2	side reaction	373.9	5.60 ± 0.12	5.74 ± 0.26
10	1,3-pentadiene				-8.8 ± 0.2			1.36 ± 0.11
11	1,4-pentadiene		-8.08 ± 0.09		-16.7 ± 0.7	359.7[l]		1.01 ± 0.25
12	cyclopentadiene	18.0[e] (16.3)	-24.4 ± 0.4	-16.64 ± 0.88	-34.6 ± 0.9	356.1	1.05 ± 0.04	1.07 ± 0.06
13	indene	20.1 (20.0)	-22.8 ± 0.4[h]	-14.5 ± 0.5	-27.8 ± 1.1		0.63 ± 0.01	1.18 ± 0.06
14	fluorene	22.6 (23.1)	-18.2 ± 0.4[g]	-15.4 ± 0.3	-26.1 ± 0.9	353.3	0.77 ± 0.03[h]	4.74 ± 0.29
15	diphenylmethane	32.2[c] (33.4)	-6.56 ± 0.18	-3.00 ± 0.24	-12.5 ± 0.2	364.5	4.73 ± 0.07[g]	1.90 ± 0.07
16	triphenylmethane	30.7[c] (31.45)	-9.38 ± 0.32[h]	-2.43 ± 0.22	-19.1 ± 1.4		4.03 ± 0.04	6.79 ± 0.38
17	phenylacetylene	28.8[e]	-11.5 ± 0.2[g]	-3.1 to -5.3		370.3	5.80 ± 0.10[h]	
18	β-methylstyrene				-9.8 ± 0.2		-0.74 ± 0.02[g]	1.76 ± 0.14
19	p-phenyltoluene	(39.1)			incomplete deprotonation	379.0		4.32 ± 0.60
20	toluene				no reaction	380.5		1.35 ± 0.12
21	p-xylene				no reaction			1.63 ± 0.28
22	Me₂SO	35.1[e]			-8.5 to -9.8	372.7		0
23	cyclohexylamine	(40)			no reaction			0.76 ± 0.11
24	diisopropylamine				no reaction			1.22 ± 0.06

[a] These values are from ref 36 unless noted otherwise. The values in parentheses are those for CHA. [b] These values are from ref 1f. [c] These values are from ref 1b. [d] These values are from ref 27. [e] These values are from ref 1a unless mentioned otherwise. [f] These values are from ref 29 unless mentioned otherwise. [g] From ref 8. [h] From ref 34. [i] This work. [j] These are revised values from our earlier values published in ref 24. [k] From ref 15 unless noted otherwise. [l] ΔH°_{acid} values for compounds no. 4 and 5 were estimated from the equation $\Delta G^\circ_{acid} = \Delta H^\circ_{acid} - T\Delta S^\circ_{acid}$ by using $T = 298$ K and $\Delta S^\circ_{acid} = 22$ eu. The ΔH°_{acid} value for compound no. 11 was obtained as a private communication from Dr. R. T. McIver.

2.5 and 2.9 ppm. The signals are reported with reference to external Me$_4$Si (in parts per million) as follows. First set: 1.35, 1.50, 1.60, 1.70. Second set: 2.55, 2.70, 2.80. The peak at 1.35 ppm was a singlet and integrated to four protons. This was assigned to the N–H protons.

A ^{1}H NMR spectrum of KAPA in DAP was also obtained. This was identical with the spectrum of DAP except for the peak at 1.35 ppm which was exchange broadened.

The spectrum did not change its features even after 2–3 days, suggesting that the base solutions are reasonably stable.

The ^{1}H NMR spectrum of the KAPA–DAP solutions with Me$_4$Si (internal reference) was identical with the previous spectrum except that all the peaks were shifted toward Me$_4$Si by about 0.2 ppm. The ^{1}H NMR spectral listings (in parts per million) are as follows. First set: 1–1.25 (br), 1.30, 1.42, 1.53, 1.63. Second set: 2.39, 2.49, 2.59, 2.70, 2.81. All the following anion spectra are reported by using internal Me$_4$Si as the standard or by assigning one of the methylene signals of KAPA to be at 2.59 ppm (which had been measured with reference to Me$_4$Si).

(3) Indene in KAPA. An approximately 40 mM solution of indene in KAPA was prepared and transferred to an NMR tube and sealed tightly. The ^{1}H NMR spectrum was closely similar to that reported for sodium indenide.[16] The spectrum was recorded again after a few days and did not show any new features.

(4) Pentadienyl Anions. Spectra of mixtures of 1,4- and (*E*)-1,3-pentadiene with excess KAPA were recorded at 60 MHz. The spectra were identical in all respects, proving that both the 1,4- and the 1,3-dienes give the same product with KAPA. The spectral assignments (in parts per million from (Me$_4$Si) are as follows: 3.49, 3.70, 3.81, 6.06, 6.21. This agrees well with those of Nakamura and co-workers for pentadienylpotassium in THF as well as with the ^{1}H NMR spectrum of 1,1,5,5-tetradeuterated pentadienylpotassium in THF at –60 °C.[17]

The ^{1}H NMR spectra did not change during a period of 1 h, but after 10 h the solutions appeared to be more viscous and the ^{1}H NMR spectra indicated considerable decomposition.

(5) *p*-Phenyltoluene. Heats of reaction for *p*-phenyltoluene with KAPA were dependent on the total concentration of *p*-phenyltoluene in solution, suggesting that deprotonation was not complete. Comparison of ^{1}H NMR spectra in CDCl$_3$, DAP-d_4, and KAPA/DAP-d_4 confirmed that some deprotonation had occurred, but the resolution was too poor to allow quantitative analysis.

(6) 1-Phenylpropene. Spectral comparisons of 1-phenylpropene in CDCl$_3$,[18] DAP-d_4, KAPA/DAP-d_4, and potassium amide/liquid ammonia[19] confirmed that clean formation of the anion occurs in KAPA.

Discussion

Comparison of Acidities in KOBu-*t*/Me$_2$SO, KMe$_2$SYL/Me$_2$SO, KAPA/DAP, and the Gas Phase. The thermochemical data in Table I show a roughly constant difference of 5 ± 1 kcal/mol between heats of deprotonation by KOBu-*t*/Me$_2$SO and those in
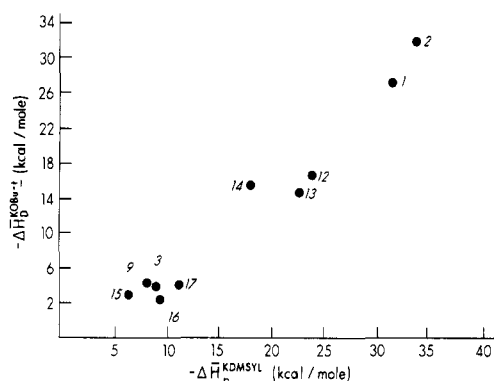
Figure 1. Plot of $\Delta H_D{}^{KMe_2SYL}$ (heat of deprotonation in KMe$_2$SYL) vs. $\Delta H_D{}^{KOBu\text{-}t}$ (heat of deprotonation in KOBu-*t*-Me$_2$SO) for compounds used in this study. The numbers correspond to those in Table I.

KMe$_2$SYL/Me$_2$SO, the latter system yielding more exothermic values. There is abundant evidence[1,8] that most, if not all, of the carbanions and nitranions formed by deprotonation of the acids listed in Table I are not associated with potassium ion at the low concentrations (10^{-2}–10^{-4} M) of our calorimetric runs. However, the association of the potassium bases, KOBu-*t* or KDMSYL, is more complicated in Me$_2$SO and is undoubtedly responsible for some of the observed difference in thermochemical acidity.

The Raman study by Brauman and co-workers[11] demonstrated the remarkable insensitivity of the $^-$OBu-*t*/*t*-BuOH ratio to concentration due to aggregation of one kind or another. The heat of solution of *t*-BuOH into 0.1 M KOBu-*t* in Me$_2$SO is –4 kcal/mol (Table I). It is reasonable, therefore, to expect the formation of hydrogen-bonded alkoxide (eq 2) to be an important factor in

$$AH + 2^-OBu\text{-}t \rightleftharpoons A^- + t\text{-BuOH}\cdots^-OBu\text{-}t \qquad (2)$$
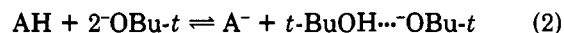
modifying the effective basicity of *tert*-butoxide ion as soon as protons are removed from any acid that is deprotonated in this medium.

Various attempts have been made to analyze the complex series of equilibria which coexist in KOBu-*t*/Me$_2$SO mixtures.[20] What seems clear is that the mixture of *tert*-butoxide and Me$_2$SYL anions which are produced are bound strongly to *tert*-butyl alcohol by hydrogen bonding and to potassium ions by coulombic attraction. We can go no further in trying to give a detailed accounting of how the sum of bonds made and broken contributes to the difference in thermochemical acidity. The fact that nearly the same equilibrium constant for deprotonation of triphenylmethane is found in both media[20b] implies that their effective basicity, in free energy terms, toward carbon acids is scarecely affected by the complexities which contribute to the thermochemistry. Figure 1 presents the relationship between ΔH_Ds in the two Me$_2$SO superbase systems. It is tempting to interpret the positions of various points to some average line which might be drawn. However, we see little value in such an exercise except to note that the weakest acids with points closest to the origin may not have been deprotonated completely.

Summary Correlations between Indicator ($\Delta G_i{}^\circ$) and Thermochemical ($\Delta H_i{}^\circ$) Acidities in KMe$_2$SYL/Me$_2$SO. Table II presents an updated complete listing of heats of ionization ($\Delta H_i{}^\circ$) in Me$_2$SO for all compounds where comparable free energy data are

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Table II. Thermodynamic Properties for Ionization of Protonic Acids in Dimethyl Sulfoxide at 25 °C[f]

no.	compd	ΔH_i°,[a] kcal/mol	ΔG_i°,[b] kcal/mol	ΔS_i°,[e] cal mol^{-1} deg^{-1}
	Hydrocarbons			
1	1,4-pentadiene	40.0 ± 0.8		
2	cyclopentadiene	23.6 ± 0.9	26.2	−8.7
3	indene	25.2 ± 0.9	29.0	−12.8
4	fluorene	29.8 ± 0.9	32.4	−8.7
5	2,3-benzofluorene[c]	33.4 ± 1.2	33.1	+1.0
6	*t*-butylacetylene	42.0 ± 0.8	44.8	−9.4
7	phenylacetylene	36.5 ± 0.8	40.9	−14.8
8	xanthene	39.7 ± 0.8	42.5	−9.4
9	diphenylmethane	41.4 ± 0.8	45.5	−13.8
10	triphenylmethane	38.6 ± 0.9	43.5	−16.4
11	biphenylyldiphenylmethane	37.7 ± 0.8	41.7	−13.4
12	9-phenylfluorene[c]	23.9 ± 1.1	26.0	−7.0
13	4,5-methylenephenanthrene[c]	29.7 ± 0.9	31.8	−7.0
14	1,1,3-triphenylpropene	30.6 ± 0.8	36.1	−18.5
	Nitriles			
15	acetonitrile	40.6 ± 0.8	44.3	−12.4
16	malonitrile	15.5 ± 0.9	16.9	−4.7
17	phenylacetonitrile	28.9 ± 0.8	31.5	−8.7
18	diphenylacetonitrile	22.8 ± 0.9	25.5	−9.1
19	(*m*-chlorophenyl)phenylacetonitrile	26.5 ± 0.9	28.2	−5.7
20	9-cyanofluorene	10.5 ± 0.9	12.9	−8.1
21	dimethyl sulfone	42.6 ± 0.8	44.0	−4.7
	Anilines			
22	aniline	40.9 ± 0.8	43.5	−8.7
24	*m*-chloroaniline[c]	37.0 ± 0.9	40.5	−11.7
25	4-chloro-2-nitroaniline[c]	25.8 ± 0.9	27.4	−5.4
26	imidazole	24.9 ± 0.9	27.0	−7.0
	Diphenylamines[c]			
27	diphenylamine	32.1 ± 1.0	35.6	−11.7
28	(4-nitrophenyl)phenylamine	21.4 ± 1.1	24.6	−10.7
29	(2-nitrophenyl)phenylamine	23.5 ± 0.9	25.7	−7.4
	Carboxylic Acids[c]			
30	benzoic acid	13.9 ± 0.8	16.6	−9.1
31	*p*-chlorobenzoic acid	13.4 ± 0.9	15.5	−7.0
32	*p*-methoxybenzoic acid	14.4 ± 1.0	17.1	−9.1
	Phenols			
33	phenol	23.7 ± 0.9	26.2	−8.4
34	*o*-cresol	23.1 ± 0.9	26.4	−11.1
35	*m*-cresol	23.8 ± 0.8	26.5	−9.1
36	*p*-cresol	25.4 ± 0.9	27.3	−6.4
37	*o*-chlorophenol	19.2 ± 0.9	22.1	−9.7
38	*m*-chlorophenol	20.9 ± 0.9	23.2	−7.7
39	*p*-chlorophenol	22.2 ± 1.0	24.4	−7.4
40	*p*-cyanophenol	18.1 ± 0.9	19.6	−5.0
41	*p*-nitrophenol	15.1 ± 1.0	16.3	−4.0
42	*p*-*tert*-butylphenol	24.8 ± 0.9	27.6	−9.4
43	2,6-di-*tert*-butylphenol	21.8 ± 1.1	25.1	−11.1
44	*p*-fluorophenol	21.0 ± 0.9	26.2	−17.4
45	*m*-fluorophenol	21.3 ± 0.8	23.2	−6.4
	Thiols[d]			
46	thiophenol	11.9 ± 1.0	15.6	−12.4
47	butanethiol	19.6 ± 0.8	24.8	−17.5
48	2-methyl-2-propanethiol	19.6 ± 0.8	26.0	−21.5
	Alcohols[d]			
49	methyl alcohol	32.0 ± 0.9	41.0	−30.2
50	ethyl alcohol	36.9 ± 0.9	42.2	−17.8
51	isopropyl alcohol	38.5 ± 0.8	42.9	−14.8
52	*tert*-butyl alcohol	38.8 ± 0.9	45.5	−22.5
53	2,2,2-trifluoroethanol	30.3 ± 1.0	33.8	−11.7
54	hexafluoroisopropyl alcohol	21.2 ± 1.0	26.1	−16.4
55	perfluoro-*tert*-butyl alcohol	14.2 ± 0.9	16.2	−6.7
56	water[d]	35.8 ± 0.9	44.4	−28.9
	Ketones			
57	acetone[d]	32.9 ± 0.8	37.6	−15.8
58	phenylacetone	24.6 ± 0.8	28.6	−13.4
59	acetophenone	30.7 ± 0.8	35.3	−15.4

Table II (*Continued*)

no.	compd	$\Delta H_i°$,[a] kcal/mol	$\Delta G_i°$,[b] kcal/mol	$\Delta S_i°$,[e] cal mol^{-1} deg^{-1}
60	benzoylacetone	15.1 ± 0.9	18.9	−12.8
61	dimedone	14.1 ± 0.8	16.8	−9.1
62	acetylacetone	16.3 ± 0.9	19.7	−11.4
63	dibenzoylmethane	14.8 ± 0.9	19.9	−17.1
64	deoxybenzoin	21.4 ± 0.9	25.6	−14.1
65	cyclopentanone	32.4 ± 0.8	36.8	−14.8
67	cyclohexanone[d]	32.5 ± 0.8	37.6	−17.1
68	cycloheptanone	34.2 ± 0.8	39.5	−17.8
69	cyclooctanone	33.3 ± 0.8	39.0	−19.1
70	cyclododecanone	34.3 ± 0.8	38.3	−13.4
71	camphor	38.1 ± 0.9	43.2	−17.1
	Nitro Compounds[b]			
72	nitromethane	20.1 ± 0.9	25.1	−16.8
73	nitroethane	18.3 ± 0.9	24.4	−20.5
74	nitropropane	19.1 ± 0.9	24.8	−19.1
75	2-nitropropane	19.3 ± 0.9	24.7	−18.1
76	nitrobutane	18.8 ± 0.8	24.5	−19.1
77	nitrocyclobutane	19.6 ± 0.9	26.0	−21.5

[a] These values are obtained from ref 29 unless mentioned otherwise and have been calculated by using the formula $\Delta H_i° = \Delta H_D{}^{KMe_2SYL} + 48.0$ (±0.8) where the value of 48.0 ± 0.8 kcal/mol is the heat of autoprotolysis of Me_2SO obtained from ref 8f. [b] These values are from ref 1, 30, 1b, and 1d. Some of these values have been updated (private communication from Dr. Bordwell), and the updated values have been used whenever possible. The $\Delta G_i°$ values are calculated from the formula $\Delta G_i° = 2.303 RT(pK_a + \log 14)$ and have a standard deviation of 0.1 kcal/mol. [c] The $\Delta H_i°$ values for these compounds are from ref 34. [d] The $\Delta H_i°$ values for these compounds are from ref 35. [e] The estimated errors for entropies of ionization may be considered as derived entirely from the enthalpies in column three in view of the much higher precision of pK_a measurements used to derive $\Delta G_i°$. Errors in $\Delta S_i°$ (in cal mol^{-1} deg^{-1}) can be estimated by tripling the error in $\Delta H_i°$ (i.e., dividing by 298 × 10^{-3}). [f] These data have been calculated (see text) for the process $AH + Me_2SO \rightleftharpoons A^- + Me_2SOH^+$ from the best available pK_a values from Bordwell's laboratory and ΔH_D values from this laboratory.

available. ΔH_i is the enthalpy change for process 3 under standard calorimetric conditions. Since ΔH_i cannot be measured directly, it is calculated from ΔH_D, the heat of deprotonation (eq 1), which in this system is simply the

$$HA + Me_2SO \rightarrow A^- + Me_2SOH^+ \qquad (3)$$
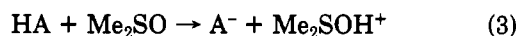
difference between the heat of solution of the acid HA in KMe_2SYL/Me_2SO solution and that in pure Me_2SO.

The difference between ΔH_D and ΔH_i is the heat of autoprotolysis, ΔH_{aut}, for the process in eq 4, which was

$$2Me_2SO \rightarrow Me_2SOH^+ + Me_2SYL^- \qquad (4)$$
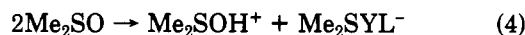
determined to be 48.0 ± 0.8 kcal/mol.[8f] $\Delta H_i°$, then, is appropriate for direct comparison with standard free energies of ionization $\Delta G_i°$ derived from the pK_as obtained by Bordwell and his colleagues, the only difference in the system being that our KMe_2SYL solutions are generally more concentrated (0.1 M compared to 10^{-3}–10^{-4} M for the indicator methods).

There is a formal standard state correction which is required for comparison of the two data sets. Bordwell's pK_a values neglect the constant term for the 14.0 molarity of solvent Me_2SO in the equation $pK_a = [A^-][Me_2SOH^+]/[AH][Me_2SO]$. Therefore, $\Delta G_i° = 2.303RT(pK_a + \log 14)$.

Table II also provides standard entropies of ionization data ($\Delta S°$) at 25 °C for those cases where free energy values are also available.

On several previous occasions we have presented correlation plots of Bordwell's free energies of ionization against our heats of ionization. If such a treatment is applied *to all compounds in Table II* for which both $\Delta H_i°$ and $\Delta G_i°$ are available, a fair ($R = 0.972$) correlation of nearly unit slope is obtained. However, the points which fall close to a common line and those which deviate from it tend to fall into families and can be examined more instructively through several correlation plots.

Figure 2 includes as carbon acids the hydrocarbons, nitriles, and dimethyl sulfone. We group them together
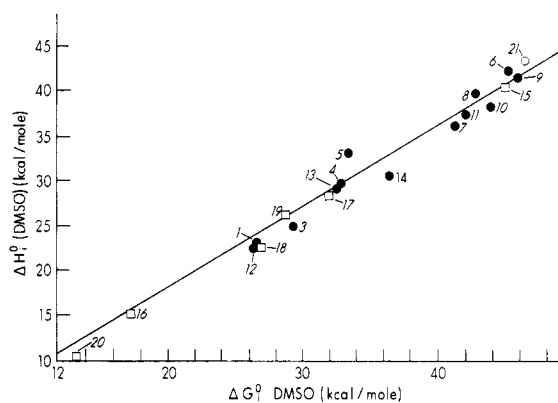

Figure 2. Plot of standard free energies vs. enthalpies of ionization for hydrocarbons, (●), nitriles (□), and dimethyl sulfone (○) in Me_2SO at 25 °C. The best correlation line is shown. The numbers correspond to those in Table II.

since their neutral initial states and ionic secondary states are clearly defined. The equation for this line is given in eq 5, and $R = 0.993$. Figure 3 is derived from data for

$$\Delta H_i° = 1.044\Delta G_i° - 0.735 \qquad (5)$$

phenols, benzoic acids, aromatic acids, thiophenols, aliphatic alcohols, and mercaptans. The line which runs across the plot is taken from Figure 2 and shows clearly that the oxygen and nitrogen acids which can form delocalized anions fall on the same correlation line as that for the hydrocarbons and nitriles. Most, but not all, of the alcohols fall below the line as do the sulfur acids. We are unable to arrive at a consistent and reasonable generalization for the behavior of all the alcohols and the thio acids (however, see below). If they are excluded from a least-squares treatment, the 22 nitrogen and oxygen acids which produce delocalized ions generate eq 6 with $R = 0.993$. In

$$\Delta H_i° = 1.029\Delta G_i° - 1.90 \qquad (6)$$

Figure 4 the data for ketones and nitro compounds are
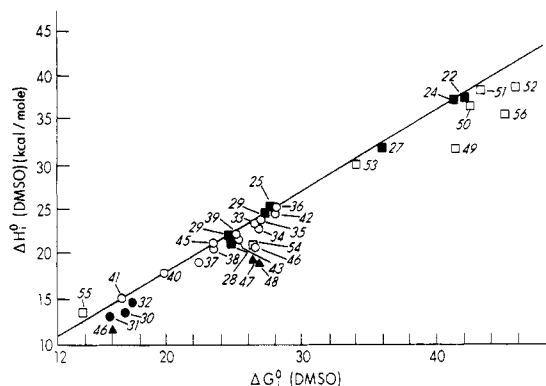
Figure 3. Plot of standard free energies vs. enthalpies of ionization for phenols (O), alcohols (□), benzoic acids (●), amines (■), thiophenol (△), and mercaptans (▲) in Me₂SO at 25 °C. The correlation line shown is that derived from the hydrocarbons and nitriles in Figure 2. The numbers correspond to those in Table II.
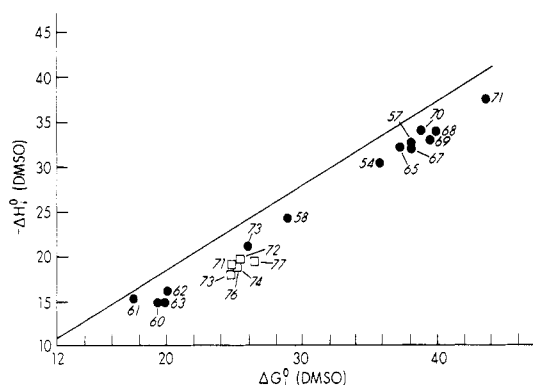
Figure 4. Plot of standard free energies vs. enthalpies of ionization for ketones (●) and nitroalkanes (□) in Me₂SO at 25 °C. The correlation line shown is that derived from the hydrocarbons and nitriles in Figure 2.

plotted. Again, the line shown on the plot is that from Figure 2, and all of the points, except that for dimedone (no. 61) fall clearly below it. The ketones and nitro compounds generate a good (R = 0.993) linear correlation of their own whose slope is very close to those for Figure 2 and 3 (eq 7). The behavior of the ketones is similar to

$$\Delta H_i^\circ = 1.015\Delta G_i^\circ - 4.43 \qquad (7)$$

that of the aliphatic alcohols which lie to the upper right of Figure 3 and suggests that the enolate anions behave much more like alkoxide ions than like phenoxy or carboxylate ions. The reason the nitro compounds fall here rather than being like the nitriles or anilines is not clear. The difference between the intercepts of various lines can also be expressed in terms of entropy units since the slopes are so similar and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. In these terms Table II indicates that the entropies of ionization of the ketones, nitro compounds, alcohols, and mercaptans are 2–4 times more negative than those for the other compounds. This may reasonably be ascribed in general to a greater degree of solvent electrostriction around charge-localized ions relative to delocalized ones but still leaves a number of individual cases unexplained.

In our opinion the most striking fact to emerge from Figures 2–4 is the similarity of their slopes and the remarkably consistent proportionality between the heats and free energies of ionization for a variety of types of compounds which produce delocalized anions. The limitations of calorimetric heats of ionization as a criterion of acidity are clear. It is surprising that this approach works as well

as it does. Similarly, good relationships between heats and free energies of protonation for neutral bases have been observed frequently in our laboratory. In general, the correlation between enthalpies and free energies of proton transfer is remarkably good over an enormous range of systems and processes.

Thermochemical Comparison of KMe₂SYL/Me₂SO with KAPA. Amide bases have been noted for their strength since the use of alkali amides in liquid ammonia which was introduced over a century ago.[21,22] Alkali salts of sterically hindered amines (e.g., lithium diisopropylamide) have become an increasingly valuable tool for the synthetic chemist. In the gas phase, NH₂⁻ is almost as strong a base as methide ion.[15] However, few quantitative comparisons of acidity are available in amide/amine systems.[5,6] Streitwieser's investigation of cesium cyclohexylamide/cyclohexylamine (CHA) is by far the most extensive and intensive acid–base study of such systems. His work suggests that CsCHA is five or six powers of ten more basic than is KMe₂SYL/Me₂SO but that ion pairing complicates comparisons of the two systems.[6]

Since the amide bases extend the range of organic acids which can be studied, we were intrigued by the reports of Brown that the potassium salt of 1,3-diaminopropane in the diamine as the solvent (KAPA) was a conveniently prepared superbase of great strength. Brown estimated from kinetic evidence that KAPA was about 10⁶ times stronger than KMe₂SYL/Me₂SO.[23]

We have already reported the heats of deprotonation of 19 weak acids including aliphatic amines, aromatic amines, and olefins in KAPA.[24] In general the ΔH_Ds in KAPA are about 6–10 kcal/mol more exothermic than those in KMe₂SYL. Me₂SO itself is deprotonated by KAPA, evolving 8–10 kcal/mol. This corresponds to a pK_a difference of about 6. Diisopropylamine and cyclohexylamine showed negligible deprotonation from which we conclude that their acidities are not appreciably greater than that of DAP. KAPA apparently is more active kinetically, especially where double bond isomerizations are concerned. This has been attributed to its ability to form a chelated ion pair.[23] Such chelation is possible in other diamines also, and the enhanced kinetic activity of such diamine base systems has been demonstrated.[25] It is known that diamines chelate alkali metal ions strongly in both the gas phase[26a] and in solution.[26b] One would expect the anion of a diamine to be an even better chelating agent than the neutral molecule and perhaps also be involved in nitranion hydrogen bonding.[27]

The weakest acid which was reacted with KAPA, p-phenyltoluene, has an ion-pair pK_a of 39.0 in cyclohexylamine.[6] This is only partially deprotonated in KAPA as evidenced by a small and decreasing heat of reaction as a function of concentration. Cesium cyclohexylamide (CsCHA) is also only able to partially deprotonate this hydrocarbon. Thus, one can conclude that the thermodynamic basicity of KAPA is close to that of CsCHA.

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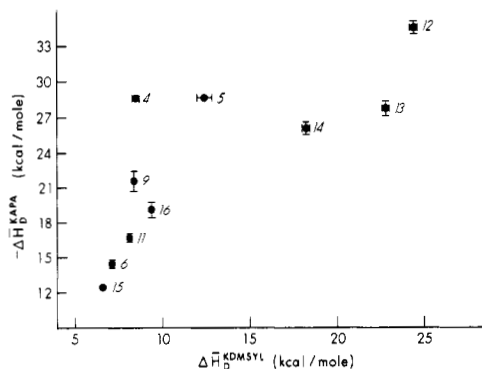
Figure 5. Plot of $\Delta H_D{}^{KMe_2SYL}$ vs. $\Delta H_D{}^{KAPA}$ for compounds used in this study. The numbers correspond to those in Table I.

Figure 6. Plot of $\Delta G_i{}^\circ$(CHA) (1.37pK_a) vs. $\Delta H_D{}^{KAPA}$ (heat of deprotonation in KAPA/DAP). The numbers refer to those in Table I.

Since our first ΔH_Ds in KAPA were published[24] we have improved our methods for purification and handling of DAP and its conversion to KAPA solutions. Therefore, we have remeasured our values and report them in Table I. The most important change is that for fluorene which is increased by 7 kcal/mol, thus eliminating the "anomaly" which had been reported. The rest of the values were also revised upward by a few kilocalories, but our basic conclusion that KAPA is a stronger base than KMe$_2$SYL by about 8 kcal/mol remains. The cases where the difference of ΔH_D values between KAPA and KMe$_2$SYL were much higher than 10 included xanthene, cycloheptatriene, and the naphthalenediamines. Cycloheptatriene mainly undergoes polymerization reactions with KAPA. The naphthalenediamines are a special case and have been discussed elsewhere.[27] Since KAPA is reported to attack ether,[28] it is likely that the "high" ΔH_D value for xanthene results from ring opening.

Excluding these exceptions, it is clear that the usual difference in ΔH_D is between 6 and 10 kcal/mol between the two systems. The values fluctuate somewhat. A plot of $\Delta H_D{}^{KAPA}$ values vs. $\Delta H_D{}^{KMe_2SYL}$ is presented in Figure 5. Deviations from linearity can be attributed to several factors. (a) DAP has a lower dielectric constant (9.55) than Me$_2$SO (46) so that ion pairing should be considerably more important in KAPA. (b) Some of the more bulky hydrocarbons as well as their anions do not dissolve quickly in DAP. This results in larger standard deviations for ΔH_D. The shape of the anion may also contribute to the extent of solvation of the anion by the solvent. DAP might be a somewhat better hydrogen bond donor to anions than Me$_2$SO and may show some selectivity.

Since ion pairing is probably important in KAPA but not in the gas phase, one would not expect the gas-phase and solution-phase acidities (in DAP) to be related in any straightforward manner (Table I).

Deprotonation in CHA should follow a pattern similar to that in KAPA. Figure 6 relates $\Delta H_D{}^{KAPA}$ to $\Delta G_i{}^\circ$ values derived from Streitwieser's pK_a values in CHA for the same compounds. The correlation is analogous to the $\Delta H_i{}^\circ$ vs. $\Delta G_i{}^\circ$ plot for KMe$_2$SYL/Me$_2$SO in Figures 2–4 and is obviously much better than Figure 5 which compares heats of deprotonation in KAPA and KMe$_2$SYL/Me$_2$SO for a wider range of structural types. The slope of the correlation line on Figure 6 is of opposite sign because of the different ways that ΔH_D and ΔH_i are defined (eq 1 and 3).

On consideration of the problems which could arise from comparing free energies in one solvent-base system of low dielectric constant with enthalpies measured in another,
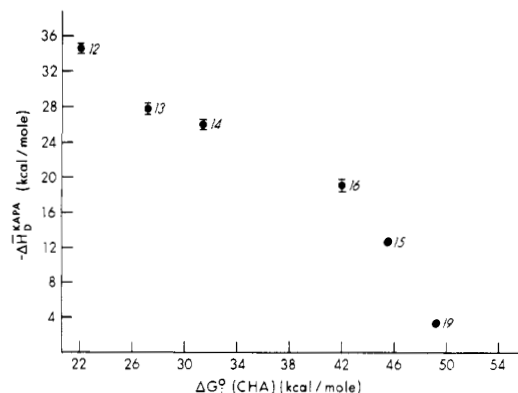
there is some satisfaction in seeing the correlation portrayed in Figure 6 although it may be limited to hydrocarbons which produce cyclic delocalized carbanions.

Estimation of Energy Differences between Isomeric Pentadienes and Calculation of Resonance Energies for Cyclopentadienyl and Indenyl Anions. Bordwell has discussed methods for estimating aromatic stabilization energies (ASE) for aromatic systems such as the indenyl (IN⁻) and cyclopentadienyl (CP⁻) anions using pK_a values and other thermochemical data by comparing the acidities of their conjugate acids with those of appropriate open-chain model compounds.[30]
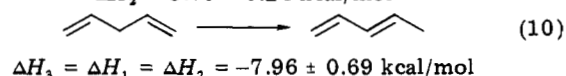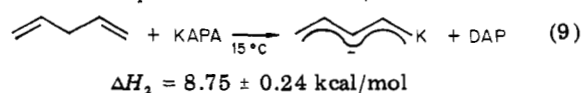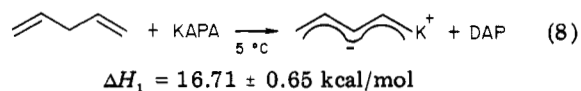
(E)-1,3-Pentadiene, (E)-1-phenylpropene (β-methylstyrene), and diphenylmethane were models for cyclopentadiene, indene, and fluorene. However, the pK_a values for (E)-1,3-pentadiene and (E)-1-phenylpropene could only be obtained by extrapolation from kinetic acidities, since neither compound is acidic enough to be deprotonated completely in Me$_2$SO.

We had observed earlier that 1,4-pentadiene gives a $\Delta H_D{}^{KMe_2SYL}$ value of -8.08 ± 0.09 kcal/mol.[29] Bordwell suggested that this heat was mainly due to isomerization of the 1,4-diene to the (E)-1,3-pentadiene on the basis of published heats of formation.[30]

In KAPA, however, both the 1,3- and the 1,4-diene are deprotonated completely. This is supported by the fact that the reaction is rapid and that the heat of reaction is not concentration dependent. Proton magnetic resonance spectra of the pentadienes in KAPA are identical with each other and with literature spectra of the pentadienyl anion.[17]

We have made $\Delta H_D{}^{KAPA}$ measurements for these two compounds. From these values and plots of $\Delta H_D{}^{KAPA}$ values vs. $\Delta G_i{}^\circ$s in Me$_2$SO or cyclohexylamine we are able to estimate the pK_a values of the dienes.

Since both the dienes go to the same final state, a difference in ΔH_D values gives the heat of isomerization (eqs 8–10).

$$\text{(diene)} + \text{KAPA} \xrightarrow{5\ ^\circ C} \text{(pentadienyl)}K^+ + \text{DAP} \quad (8)$$

$$\Delta H_1 = 16.71 \pm 0.65 \text{ kcal/mol}$$

$$\text{(diene)} + \text{KAPA} \xrightarrow{15\ ^\circ C} \text{(pentadienyl)}K + \text{DAP} \quad (9)$$

$$\Delta H_2 = 8.75 \pm 0.24 \text{ kcal/mol}$$

$$\text{(diene)} \longrightarrow \text{(diene)} \quad (10)$$

$$\Delta H_3 = \Delta H_1 = \Delta H_2 = -7.96 \pm 0.69 \text{ kcal/mol}$$

(28) Brown, C. A. *Synthesis* **1978**, 754; *J. Org. Chem.* **1978**, *43*, 3083.
(29) Johnston, D. E., M.S. Thesis, University of Pittsburgh, 1975.

(30) Bordwell, F. G.; Drucker, G. E.; Fried, H. E. *J. Org. Chem.* **1981**, *46*, 632.

The heat of isomerization from eq 8–10 compares well with the literature value of 6.6 kcal/mol[31] and the estimated value of 7.2 kcal/mol calculated by Bordwell[30] using Benson's additivity rules.[32]

Since both the dienes are low-boiling compounds and since it was difficult to make reproducible measurements at room temperature, we made the ΔH_D^{KAPA} measurements for the 1,4-diene and the 1,3-diene at 5 and 15 °C, respectively. We assume that the ion-pairing equilibria for this system do not vary enough with temperature to affect the observed heat changes appreciably.

From a plot of ΔG_i° in CHA vs. ΔH_D^{KAPA} values for the same compounds we can estimate a ΔG_i° value of 48.0 kcal/mol for (E)-1-Phenylpropene in CHA. Since the ΔG_i°s in CHA are about 1.36 kcal/mol/ΔG_i° higher than in Me$_2$SO, this gives a value of 46.6 kcal/mol in Me$_2$SO. On comparison of this with indene, which has a ΔG_i° of 27.4 kcal/mol, the difference in ΔG_i° values constitutes an ASE of 19.2 kcal/mol for IN$^-$. This is close to the ASE of 20 kcal/mol estimated by Bordwell by pK_a comparisons between indene and indole.

Another way to estimate the pK_a of (E)-1-phenylpropene would be to extrapolate it from a plot of ΔH_D^{KAPA} values vs. ΔG_i° values in Me$_2$SO, giving a ΔG_i° of 48.8 kcal/mol from which an ASE of 21.4 kcal/mol is calculated for the indenyl anion.

Similarly, one could estimate the ΔG_i° of (E)-1,3-pentadiene in Me$_2$SO from a plot of ΔH_D^{KAPA} values vs. ΔG_2° in Me$_2$SO. This gives a ΔG_i° = 49.8 kcal/mol for 1,3-pentadiene. Comparing this with the ΔG_i° of 24.6 kcal/mol for CPH, one gets an ASE of 25.2 kcal/mol for CP$^-$. This compares to a value of 26 kcal/mol obtained by Bordwell.

Cycloheptatriene. A ΔH_D^{KAPA} value of −18.2 kcal/mol was obtained by injecting cycloheptatriene into this superbase which seemed to indicate a pK_a of 30 in KAPA/DAP. The thermogram indicated that the reaction between KAPA and cycloheptatriene was over in less than 1 min. The apparent difference in ΔH_D^{KAPA} values between cycloheptatriene and cyclopentadiene, 16.4 kcal/mol, was close to the difference of 17.8 kcal/mol in the gas phase acidities[15] of these two compounds. Therefore, we were intrigued by the possibility that cycloheptatrienyl anion had been formed quantitatively and set about to test this proposition in view of previously reported difficulties

in making the ion.[33] However, we were unable to detect formation of cycloheptatriene-7-carboxylic acid following addition of CO$_2$ to KAPA solutions of the triene and conclude that the fortuitous heat of reaction arises from polymerization and side reactions.

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(33) Dauben, H. J., Jr.; Refi, M. R. J. Am. Chem. Soc. 1963, 85, 3041.
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