lower field, since it is known that the introduction of a heavier isotope into a compound usually induces shifts to higher field in neighboring nuclei.[16] All current theories based on vibrational effects predict an upfield shift due to heavy-isotope introduction, significantly decreasing with the number of bonds.[16] A possible explanation of the present results might be found in the occurrence of vibronic effects induced by the heavier isotope in tritiated benzenes, as indicated by the different ortho-ortho vs. meta-meta H-H distance measured in [^{3}H]benzene.[17] Perhaps the symmetry differences between [1,4-$^3H_2$]benzene and [^{3}H]-, [1,2-$^3H_2$]-, and [1,3-$^3H_2$]benzenes might play some role. The assessment of these effects deserves further investigation.

Finally, comparison of the product distribution in the [^3H_x]benzene sample ($C_6H_5{}^3H/C_6H_4{}^3H_2 \simeq 1$) with that measured in the blank ^2H_2O runs ($C_6H_5{}^2H/C_6H_4{}^2H_2 \simeq 0.1$) suggests that the observed discrepancy is mainly attributable to the isotopic purity of the starting water. In conclusion, we indicate in the proposed synthetic method a convenient route for obtaining [1,4-$^3H_2$]benzene with high chemical purity. For the specific purpose of the present study, the isotopic purity of the [1,4-$^3H_2$]benzene is also quite satisfactory, but, if necessary, it can be further improved by using a much larger excess of isotopically pure ^3H_2O.

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Registry No. II, 2425-81-2; III, 73728-29-7; [^{3}H]benzene, 3508-32-5; ^3H_2O, 14940-65-9; $BrC_6H_4{}^3H$, 61862-35-9; [1,2-$^3H_2$]benzene, 73713-15-2; [1,3-$^3H_2$]benzene, 73713-16-3; C_6H_6, 71-43-2; $C_6H_5{}^2H$, 1120-89-4; $C_6H_4{}^2H_2$, 25323-71-1; 1,4-dibromobenzene, 106-37-6.

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Acidities of Water and Simple Alcohols in Dimethyl Sulfoxide Solution

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A method is described for determining equilibrium constants between the indicators triphenylmethane and diphenylmethane (DH) and the solvent Me_2SO; pK_a values of 32.1 and 35.1 are assigned to DH and Me_2SO, respectively. This method is then extended to the determination of pK_a values for MeOH, EtOH, *i*-PrOH, and H_2O in Me_2SO, taking into account the leveling effect of the solvent, homohydrogen bonding ("homoconjugation"), and ion pairing. The pK_a values of the simple alcohols in Me_2SO were found to increase progressively with molecular size: MeOH (29.0) < EtOH (29.8) < *i*-PrOH (30.2). The pK_a of H_2O in Me_2SO is higher (31.4), but is lower than that of *t*-BuOH (32.2).

The observation that the intrinsic acidities of the simple alcohols in the gas phase follow the order *t*-BuOH > *i*-PrOH > EtOH > MeOH and that the gas-phase acidity of water is *much* less than that of methanol attracted attention, in part, because the solution acidity order was generally believed to be in the opposite direction.[1] Actually, the solution order is rather dependent on medium. In aqueous solution the statistically corrected order is MeOH > EtOH $\simeq$ H_2O, MeOH being only 0.4 pK unit more acidic than EtOH or H_2O. (The pK_a's in water are 15.50, ~15.9, and 15.75, respectively.[2]) The relative acidities in benzene are MeOH > EtOH, *i*-PrOH > *t*-BuOH, the "pK_a's" being 16, 18, 18, and 19, respectively.[3a] It is uncertain, however, that this is a true acidity order because the position of the equilibria used to determine the order in this medium (eq 1) could be as dependent (or

$$\mathrm{RO{-}H + R'O^-Na^+ \overset{C_6H_6}{\rightleftharpoons} RO^-Na^+ + R'O{-}H} \qquad (1)$$

more so) on the relative stabilities of the ion pairs (or aggregates), RO^-Na^+ and $R'O^-Na^+$, as on the relative acidities of ROH and R'OH. In isopropyl alcohol the relative order MeOH > H_2O > EtOH > *i*-PrOH has been observed, the ΔpK_a's relative to *i*-PrOH being 1.7, 1.2, and 1.1, respectively; *t*-BuOH was too weakly acidic to measure.[3b] Ion association no doubt occurs to some extent also in isopropyl alcohol, since the dielectric constant is rather low (ϵ = 18.3) and the counterion was Na^+, which is now known to ion pair strongly with alkoxide ions.[8]

In dimethyl sulfoxide solution a somewhat different relative acidity order, MeOH > EtOH > *t*-BuOH, H_2O,[4] has been reported. The acidities were determined by a potentiometric method[4a] and an overlapping indicator method.[4b,c] The pK_a's reported are actually about 2 pK_a units too low[5] because of (a) problems with the potentiometric method[5] and (b) the decision to anchor the overlapping indicator scale on the pK_a of *p*-nitroaniline determined by the H_- method in aqueous media.[4c] The acidities of alcohols in Me_2SO, as determined from enthalpies of deprotonation, are in the same order, but the

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0022-3263/80/1945-3295$01.00/0

position of water is reversed.[6] The pK_a values calculated from these data, using a correlation derived from the enthalpies and pK_a's of a large number of acids of all structural types, are as follows: H_2O (27.5), CH_3OH (27.9),[7] EtOH (28.2), *i*-PrOH (29.3), and *t*-BuOH (29.4).[6] It is possible that the enthalpies may be affected by ion pairing and/or homohydrogen bonding, i.e., eq 5 and/or eq 6.[8] Equilibrium acidity measurements with alcohols in Me_2SO need to be corrected for both of these effects.[8] They are also subject to the leveling effect of the solvent.[9] In view of all of these complications it seemed to be worthwhile to make measurements on this important group of compounds under conditions where competing equilibria involving the solvent, ion pairing, and homohydrogen bonding could be taken into account. In order to do so it was first necessary to determine the leveling effect of the solvent by measuring pK_a values of indicators near to that of the solvent. This allowed the pK_a of the solvent itself to be determined. The pK_a values for the alcohols and water were then measured under conditions where the effects of homohydrogen bonding and ion pairing were negligible. In this paper we report quantitative data which establish the acidity order in Me_2SO as the following: MeOH > EtOH > *i*-PrOH > H_2O > *t*-BuOH.

Results

Accurate determination of equilibrium solution acidities generally becomes difficult when one approaches to within about 4 to 5 pK_a units of the solvent acidity because of leveling effects.[9] For example, since the molar concentration of Me_2SO is 14.0, it follows from eq 2 that a 2 to

$$CH_3SOCH_2^- + HA \rightleftarrows CH_3SOCH_3 + A^- \qquad (2)$$

8 mM solution of $[CH_3SOCH_2]^-$, which is the concentration ordinarily used in our measurements,[5] will fail to completely deprotonate an acid, HA, of concentration 10^{-2} M, if the pK_a of HA is within about 4 pK_a units of that of Me_2SO.

Extrapolations from H_- measurements and studies of deprotonation rates have placed the pK_a of Me_2SO at between 32 and 33 in a H_2O–Me_2SO medium.[10] Acceptance of this value for pure Me_2SO would place the upper limit for our method[5] at about pK_a 28 to 29. Our present results show, however, that the upper limit is about 31 to 32, and that somewhat higher values can be reached by modification of the method.

Determination of the pK_a's of Triphenylmethane and Dimethyl Sulfoxide. Measurement of an extinction coefficient for diphenylyldiphenylmethane (DDH) from a Beer's law plot using potassium dimsyl solutions ranging in concentration from 2 to 8 mM gave values agreeing closely with those obtained using higher base concentrations (up to 150 mM). This was not true for triphenylmethane (TH), which gave an (apparent) extinction coefficient that increased with increasing base concentration. It is evident that TH is not being deprotonated completely at the base concentrations ordinarily used in our method. In order to use TH as an indicator in the usual manner[5] it is necessary, therefore, to use higher base concentrations (ca. 12 mM). By use of DDH as an indicator (pK_a = 29.4[5]) the pK_a of TH was determined to be 30.6.

Table I. Equilibrium Constant (K) at 25 °C between Triphenylmethane (TH), Dimethyl Sulfoxide (SH), and Their Conjugate Bases (T^- and S^-) (pK_a of Me_2SO in Me_2SO)

ϵ'[a]	S^-, mM	$10^{-4}K$	pK (Me_2SO)[d]
Experiment A[b]			
729	3.08	3.39	35.1
746	5.51	2.34	35.0
649	1.65	4.32	35.2
757	7.35	2.08	34.9
748	4.34	3.06	35.1
Experiment B[c]			
629	1.98	2.87	35.1
732	5.91	2.34	35.1
739	8.64	2.66	35.0
747	10.87	2.60	35.0
		3.0 ± 0.6	35.1 ± 0.1

[a] The apparent extinction coefficient. [b] The "true" extinction coefficient, ϵ, measured at 596 nm using 155 mM K^+S^- solution was 827. [c] The "true" extinction coefficient, ϵ, measured at 596 nm using 155 mM $CH_3SOCH_2^-K^+$ solution was 784. [d] Calculated assuming that the pK_a of TH is 30.6.

Table II. Determination of the Equilibrium Constant (K) at 25 °C between Diphenylmethane (DH) and Dimethyl Sulfoxide (SH) and Their Conjugate Bases (D^- and S^-), and Determination of the pK_a of DH

ϵ'[a]	S^-, mM	$10^{-3}K$	pK_a (DH)[b]
409	4.60	1.07	32.1
541	6.84	1.07	32.1
654	8.80	1.13	32.1
792	12.85	1.11	32.1
		1.09_5 ± 0.03	

[a] The apparent extinction coefficient; the "true" extinction coefficient, ϵ, obtained by using 540 mM K^+S^- was 1572 at 522 nm. [b] Calculated assuming that the pK_a of Me_2SO is 35.1.

For measurements of the equilibrium constant, K, between triphenylmethane (TH) and Me_2SO (SH) (eq 3 and 4), it was necessary to measure the concentration of S^-

$$TH + S^- \rightleftarrows T^- + SH \qquad (3)$$

$$K = \frac{[T^-][SH]}{[TH][S^-]} = \frac{\epsilon'}{\epsilon - \epsilon'}\left(\frac{[SH]}{[S^-]}\right) \qquad (4)$$

externally by titration of standard indicator solutions instead of internally as in the pK method.[5] Since the pK_a of TH has been established as 30.6 by relationship with the indicator DDH, determination of K provides a measure of the pK_a of Me_2SO. The results of two separate experiments in which 155 mM base solution was used to determine the "true" extinction coefficient, ϵ, at 596 nm ($\lambda_{max} \simeq$ 495 nm) are summarized in Table I.

The apparent extinction coefficients, ϵ', were obtained by adding successive aliquots of potassium dimsyl (K^+S^-) in Me_2SO solution to a solution of TH in Me_2SO and dividing the absorbance by the base strength. The concentrations of K^+S^- used ranged from 1.98 to 10.87 mM. The equilibrium constant obtained, $K = 3 \times 10^4$, is in close agreement with that of Steiner[11] and of the same order of

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(7) Calculated using ΔH_D = −11.7 kcal/mol in place of the value of −16.0 kcal/mol reported in ref 6. We are indebted to Professor Arnett for providing the corrected value.

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Table III. Determination of the Equilibrium Constant (K) at 25 °C between Diphenylmethane (DH) and Dimethyl Sulfoxide (SH) and Their Conjugate Bases (D^- and S^-) by the Wheland Method, and Determination of the pK_a of DH

ϵ'	S^-, mM[a]	$10^{-2}K$	pK_a
634	8.86	7.8	32.2
780	12.87	7.5	32.2
936	16.61	8.0	32.2
		7.8 ± 0.2	

[a] A plot of $1/\epsilon'$ vs. $1/[S^-]$ gave an intercept of 5.2×10^{-4}.

magnitude as that of Ritchie (1.6×10^4).[12] Using the pK_a of TH of 30.6 and the equilibrium constant 3×10^4 places the pK_a of Me_2SO in Me_2SO at 35.1.

Determination of the pK_a of Diphenylmethane (DH). Since DH is a weaker acid than TH, it was necessary to use a higher base concentration to effect complete deprotonation (540 mM). Using this higher base concentration to obtain an extinction coefficient, the equilibrium constant between DH and Me_2SO in Me_2SO was found to be $1.1 \pm 0.03 \times 10^3$ (Table II). This is the same as that determined previously by Steiner.[11] The pK_a of DH is then 32.1, relative to Me_2SO, $pK = 35.1$.

In instances where an extinction coefficient (ϵ) of an anion cannot be obtained because of incomplete deprotonation, it is possible to use a method developed by Stearns and Wheland to obtain ϵ from extrapolation of a plot of the reciprocal of the apparent extinction coefficient vs. the reciprocal of the base concentration.[13] As a check on the direct method just described, the Wheland method was used to obtain ϵ for D^- in Me_2SO from a series of potassium dimsyl concentrations ranging from 8.86 to 16.61 mM. The equilibrium constant determined in this way, $0.78 \pm 0.02 \times 10^3$ (Table III), agreed reasonably well with that obtained by the direct method (Table II), and the pK_a agrees within ±0.1 pK_a unit with that in Table II.

Temperature Effects. The equilibrium constant between TH and Me_2SO at 38 °C obtained as above was found to be $1.8 \pm 0.8 \times 10^4$, and that between DH and Me_2SO at 38 °C was found to be $6.7 \pm 0.2 \times 10^2$. The small differences between these values and those obtained at 25 °C are probably within the experimental error of the measurements. It is not surprising that temperature effects are small on an equilibrium of this type (eq 2) where the charge type is the same on each side. As a consequence, the pK_a's measured by the indicator method are usually insensitive to temperature, and therefore have sometimes been measured at ambient temperature.[5]

Determination of the pK_a's of Methanol, Ethanol, and 2-Propanol. Measurements of acid-base equilibria for water and alcohols in Me_2SO solutions are not only complicated by the leveling effects of solvent mentioned above but also by the presence of further equilibria involving hydrogen-bond formation (eq 5) and ion-pair formation (eq 6).[8] At high concentrations there are further

$$RO^- + ROH \rightleftarrows RO^-\cdots H\text{-}OR \qquad (5)$$

$$RO^- + M^+ \rightleftarrows RO^-Me^+ \qquad (6)$$

equilibria which result in association of three or more of the species in solution.[8] Methods are used in the present work to correct for these effects.

Table IV. Summary of Experimental Runs Determining the pK_a's of Methanol, Ethanol, Isopropyl Alcohol, and Water in Me_2SO at 25 °C

acid	indicator (pK_a)	pK_a (ROH)[a]	$\log K_{hb}$[b] (eq 2)
CH_3OH	DDH (29.4)	29.15	3.91
		29.05	3.75
	TH (30.6)	28.90	3.92
		28.83	3.94
		29.00	3.96
		28.99 ± 0.13	3.90 ± 0.08
CH_3CH_2OH	DDH (29.4)	29.90	3.54
		29.78	3.47
	TH (30.6)	29.72	3.64
		29.78	3.59
		29.80 ± 0.08	3.56 ± 0.07
$(CH_3)_2CHOH$	TH (30.6)	30.31	3.21
		30.26	3.15
		30.16	3.18
		30.26	3.15
		30.25 ± 0.06	3.17 ± 0.03
H_2O	DH (32.1)	31.45	3.29
		31.40	3.52
		31.35	2.93
		31.20	3.04
		31.40	3.11
		31.36 ± 0.10	3.18 ± 0.23

[a] Steiner's values for CH_3OH and CH_3CH_2OH are 27.0 and 27.4, respectively.[4] Adding the correction of 2.1 pK units to these values to put them on an absolute scale[5] brings them to within 0.1 and 0.3 pK unit, respectively, of our values. Steiner reported water to be too weakly acidic for an accurate measurement. [b] Steiner's values for CH_3OH and CH_3CH_2OH are 3.9 and 3.6, respectively.[4b]

Exner and Steiner found the association constant for t-BuO^- ion and K^+ ion in Me_2SO to be 270. The other simple alcohols ion pair more strongly.[8] In order to eliminate the complications that ion pairing can cause, we have used the cation (K^+) complexing agent [2.2.2]cryptand. In another more detailed study of the effects of ion pairing on acidity measurements in Me_2SO, we have shown that this reagent effectively eliminates ion-pair formation.[14] A 5–10 point titration of the indicator solution with a solution of the alcohol in Me_2SO was performed by the method described previously[5] and in the Experimental Section. Residual $CH_3SOCH_2^-$ concentrations were calculated from the known pK_a of the indicator and the pK_a of 35.1 for Me_2SO reported above. The data were then fitted to the remaining two equilibrium constants for the indicator–alcohol acid–base equilibrium (eq 7) and eq 5. The

$$In^- + ROH \rightleftarrows InH + RO^- \qquad (7)$$

equilibrium constant for (7) determined in this way agreed very well (within 5–10%) with the value measured experimentally at the point where $[ROH] = [RO^-]$. (At this point eq 5 does not affect the experimentally measured pK_a.[15]) The results for the three alcohols are summarized in Table IV.

As indicated in Table IV, our pK_a values for MeOH and EtOH agree to within a few tenths of a pK unit with those obtained by Steiner,[4] once his scale has been adjusted to ours. Our pK_a for EtOH is, however, 7.8 pK_a units higher than one reported recently.[16]

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(15) A more complete description of the effects of homo-H bonding (eq 5) on the indicator method will be published later.

Determination of the pK_a of Water. A similar method was used to determine the pK_a of water in Me_2SO. Cryptand served to eliminate the effects of ion pairing, as for the alcohols, and also solubilized the hydroxide salt, which has been reported to have very low solubility in Me_2SO in the absence of a large excess of water.[11] Poor results were obtained by using the same data treatment as for the alcohols. Vast improvement was obtained if the equilibrium constant between DH and Me_2SO (eq 8) was

$$K = \frac{[DH][CH_3SOCH_2^-]}{[D^-][CH_3SOCH_3]} = \frac{([D]_t - A/\epsilon)([A^-]_T - A/\epsilon)}{14.0(A/\epsilon)} \quad (8)$$

determined internally in each run, before the addition of water, by using the known concentration of all anions $[A^-]_T$ derived from the known base strength of the stock $CH_3SOCH_2^-K^+$ solution, the extinction coefficient for D^- determined in concentrated $CH_3SOCH_2^-K^+$ (ϵ), the total amount of indicator added $[D]_T$, and the absorbance of the solution (A). Determination of K in this manner gave results very similar to those shown in Table II ((1.10–1.20) × 10^3). Use of the value determined internally within each run gave much better results for the treatment of the data from the water titration than use of the externally determined average value.

Discussion

The methods presented here enable the measurement of the acidities of acids which have pK_a's close to the value of the solvent itself. The establishment of the pK_a of Me_2SO as 35.1 completes the pK_a scale, which is based on a number of acids with pK_a < 12, which can be accurately measured directly by potentiometric, spectrophotometric, or conductometric methods. Indicators are now available which allow the overlapping indicator method to be used readily between pK_a's 0 and 32.[5,18] The method can be applied over this range to other relatively nonacidic dipolar nonhydroxylic solvents, such as *N*-methylpyrrolidin-2-one.[18] The higher pK_a regions are inaccessible in hydroxylic solvents because the solvents themselves have pK_a's less than 20.

Acidities of Alcohols and Water. In the gas phase the acidity order of alcohols and water is *t*-BuOH > *i*-PrOH > EtOH > MeOH ≫ HOH. The low acidity of water can be rationalized in terms of its surprisingly large H–O bond dissociation energy (119 kcal/mol, as compared to 104 kcal/mol for the H–O bond in MeOH).[19] The increasing acidity of the alcohols with increasing size of alkyl groups has been explained as being due to the increasing stabilization of the alkoxide ions by polarizability effects.[1] The polarizability effects override small acid-weakening inductive effects, which would dictate an opposite order.[20] In Me_2SO and in *i*-PrOH solutions the order of the acidity of the alcohols is reversed as compared to the gas phase (Table V). The principal factor behind this reversal is the relative solvation of the alkoxide ions in the order MeO^- > EtO^- > *i*-PrO^- > *t*-BuO^-,[6] the differences being large enough to dominate the small polarizability effects that are present in solution.[20] The position of water relative to alcohols changes drastically in different media. In the two hydroxylic solvents, water and isopropyl alcohol, the acidity of water lies between methyl and ethyl alcohols (Table V). In Me_2SO it lies between isopropyl and *tert*-butyl alcohols, while in the gas phase water is much less acidic than any of the alcohols. The reason appears to be that hydroxide ion is particularly sensitive to changes in solvation because of its small size. The heats of deprotonation, ΔH_D, of MeOH, EtOH, and *i*-PrOH by $CH_3SOCH_2^-K^+$ in Me_2SO[6] correlate fairly well with the pK's measured herein, being −11.7,[7] −11.1, and −9.5, respectively. However, application of the equation successfully relating ΔH_D and pK_a for a variety of other types of acids[21] gives pK_a values for the methyl, ethyl, and isopropyl alcohols that are too low by about 1 unit. For *tert*-butyl alcohol and water the values calculated from ΔH_D are low by about 3 and 4 pK units, respectively. These differences could be due to a number of factors. One possibility is that an unfavorable entropy effect makes the alcohols less acidic than the heats would predict. (For most other types of acids $\Delta S°$ is near zero.[21]) A second possibility is that the experimentally measured heats are too large due to the effects of homohydrogen bonding and/or ion pairing (eq 2 and 3). These errors might be larger for the least acidic compounds, *t*-BuOH and H_2O, where the agreement is poorest.

Table V. Acidities of Alcohols and Water

acid	pK_a (Me_2SO)	pK_a (H_2O)[b]	relative pK_a (*i*-PrOH)[c]	ΔH_i(g)[e]
H_2O	31.4	15.75	−0.2	390.8
MeOH	29.0	15.50	(0.0)	379.1
EtOH	29.8	≈15.9	0.62	375.9
i-PrOH	30.25		2.72	374.3
t-BuOH	32.2,[a] 32.5[a]		*d*	372.9

[a] These values are obtained from the pK_a of Me_2SO reported here (35.1) and the acid-base equilibrium constants between *t*-BuOH and Me_2SO reported by Exner and Steiner[8] by conductivity (K = 800) and indicator (K = 400) methods. [b] Reference 2. [c] Reference 3; statistically corrected for the number of acidic protons. [d] Too high to measure. [e] Reference 19.

Experimental Section

Indicators were prepared and purified as described previously.[5] Alcohols were dried over Linde 4A molecular sieves for at least several days and distilled at atmospheric pressure under nitrogen. House distilled water was redistilled using a Corning MEGA-PURE distillation apparatus. [2.2.2]Cryptand (Parish) was used without further purification. Me_2SO was dried and freed of oxygen by distillation from sodium amide as described previously,[5] except that prepurified argon (Matheson), which was further purified by passing over 4A molecular sieves (Linde) and Ridox oxygen scavenger (Fisher), was used instead of nitrogen.

Potassium Dimsyl ($CH_3SOCH_2^-K^+$). Under a flow of argon, 2–3 mL of commercial potassium hydride dispersed in mineral oil (Alfa) was syringed into a dry degassed Airless-Ware (Kontes) fritted funnel. The mineral oil was washed off with pentane, which had been distilled from P_2O_5, stored over molecular sieves, and degassed, and the hydride, which remained on the glass frit, was vacuum dried. A flask of dry freshly distilled Me_2SO was fitted to the glass joint at the top of the funnel while argon was blowing

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[16] Delpuech, J. J.; Nicole, D. J. *J. Chem. Soc., Perkin Trans. 2* 1977, 570–576. As much as 3.2 pK_a units of this discrepancy has been traced to improper anchoring of the acidity scale.[17] Failure to correct for ion association and homohydrogen bonding probably accounts for much of the remaining difference.

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through both pieces. The apparatus was tipped so that the Me_2SO covered the hydride and the glass frit. Evolution of hydrogen began immediately. After the reaction was over, the solution was filtered through the frit directly into a storage flask fitted with a three way stopcock by evacuating the bottom of the fritted funnel. The storage flask was removed from the apparatus, again with a flow of argon going through both pieces. The flask was stoppered, degassed three times, and wrapped in aluminum foil. Solutions (~100 mM) prepared in this manner were colorless.

Indicator Method. The details of the method of measurement using indicator anions have been previously described.[5] Very briefly, it involves three parts: (1) determination of the extinction coefficient of the indicator anion via a Beer's law plot through the addition of a few aliquots of an Me_2SO solution of the indicator acid (pK_a known) to a solution of potassium dimsyl ($[K^+\text{-}CH_2SOCH_3^-]$ = 1–5 mM) in Me_2SO; (2) addition of an excess of indicator acid and measurement of the absorbance of the solution to determine the anion concentration; (3) addition of aliquots of an Me_2SO solution of the acid of unknown pK_a and measurement of the absorbance. Modifications to this method that have been developed in the past several years include a change in the method of preparation of potassium dimsyl (see above) and the use of extra precautions for compounds in the high pK_a region (see below). As mentioned above, argon is now used in place of nitrogen, a modification which seems to decrease the amount of oxygen coming into contact with the oxygen-sensitive carbanion solutions during runs. (The presence of oxygen during titrations makes itself evident by absorbance changes with time or after shaking the spectrophotometric cell.) The indicator anions in this study are particularly sensitive to oxygen, so only freshly distilled Me_2SO and freshly prepared $CH_3SOCH_2^-K^+$ were used. Normal acid–base equilibria in Me_2SO (eq 1) are insensitive to temperature but secondary equilibria (e.g., eq 2 and 3) can be, so the cell compartment in the Cary 14 spectrophotometer was thermostatted to 25 ± 1 °C with a Beckman recirculating water bath.

Enough of a solution of cryptand in Me_2SO was added to the spectrophotometric cell so that it was in excess of the amount of potassium for all of the alcohol and water runs.

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Registry No. Me_2SO, 67-68-5; H_2O, 7732-18-5; MeOH, 67-56-1; EtOH, 64-17-5; *i*-PrOH, 67-63-0; *t*-BuOH, 75-65-0.

Ion-Pair Association Constants in Dimethyl Sulfoxide

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A method of detecting ion-pair formation between the anions of organic acids and metal cations in conjunction with acidity measurements is presented. The equilibrium between an indicator anion which does not ion pair, an anion which does ion pair, and their conjugate acids is perturbed by the addition of a metal iodide salt. The association constant for ion-pair formation is derived from the spectrophotometric data. This allows pK_a values to be corrected for ion pairing. Most organic anions do not form ion pairs with potassium cations in dilute (1–5 mM) dimethyl sulfoxide solution. For β-diketones, conformational changes were found to produce large effects, not only on the association constants, K_{as}, for their anions but also on their acidities in Me_2SO relative to H_2O. With K^+ ion, β-keto enolate ions fixed in the *E,E* (*W*) conformation chelated least, acyclic β-keto enolate ions (*E,Z*) chelated more, and β-keto enolate ions fixed in the *Z,Z* (*U*) conformation chelated most. With these anions the size of K_{as} varied with the nature of the cation in the order $K^+ < Na^+ < Li^+$. For $PhCO_2^-$ and $H_2C{=}NO_2^-$ anions the differences in K_{as} were smaller, and the order was $K^+ < Li^+ < Na^+$. The chelating ability of $[\mathrm{O}\overset{\cdots}{-}\mathrm{C(R)}\overset{\cdots}{-}\mathrm{X}]^-$ anions toward K^+ ion was found to be $RCO_2^- > RCONR^- > RCOCR_2^-$. The anion derived from a cyclic carboxamide, 1-azacyclohexan-2-one, chelated with K^+ ion much more strongly than did an acyclic analogue anion, $EtCONEt^-$. MeO^- ion pairs strongly with K^+ whereas the equally basic carbanions, $PhC{\equiv}C^-$ and thiazolide ion, do not.

The formation of ion pairs in organic chemistry is widespread. Several recent reviews have been devoted to their detection and to studies of their spectroscopic properties, chemical reactivity, and association constants.[1-3] The existence of two types of ion pairs,[1] contact (or tight) and solvent separated (or loose), has been demonstrated by a variety of kinetic and spectroscopic techniques. Many of the factors which influence the formation of these two types of ion pairs have been delineated. These include solvent, temperature, anion and cation identity and structure, and the addition of ion-complexing agents. Most of the ions which have been studied are hydrocarbon anions and radical anions. There have been few studies of anions with functional groups such as carbonyl, nitrile, or nitro.

Parallel to the development of these physical chemical studies, many organic chemists have been varying the conditions of synthetic reactions to promote or suppress ion-pair formation in order to improve yields, speed up reactions, or favor product ratios or stereochemistry.[4] The primary result of changing from a weakly dipolar nonhydroxylic solvent such as tetrahydrofuran to a strongly dipolar nonhydroxylic solvent such as hexamethyl-

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