4-methyl-1,8-decalindione were commercially available and were purified by distillation (>99% pure by GLC) or recrystallization (pure by TLC with good melting points). Commercial samples of KI, NaI, and LiI were dried at 350 °C to constant weight. A sample of 4-methyl-1,8-decalindione[34] was provided by H. E. Zaugg and was purified to 99+% purity by GLC through distillation [bp 72.5 °C (0.1 mmHg)].

Acknowledgment. We are grateful to Dr. H. E. Zaugg for a gift of 4-methyl-1,8-decalindione, to Dr. R. J. McCallum for much help in writing the computer program for the data treatment, to Donald Algrim for the data on ion pairing of carboxamide ions, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support. Suggestions of Timothy S. Ungermann were helpful in interpreting some of the acidity data.

Registry No. **1** (M = K), 19393-11-4; **1** (M = Na), 15435-71-9; **1** (M = Li), 18115-70-3; **2** (M = K), 72610-66-3; **2** (M = Na), 34916-51-3; **2** (M = Li), 70902-15-7; **3** (M = K), 22658-72-6; **3** (M = Na), 19269-14-8; **3** (M = Li), 22643-60-3; **4** (M = K), 37892-24-3; **4** (M = Na), 996-82-7; **4** (M = Li), 34727-00-9; **5** (M = K), 2421-91-2; **5** (M = Na), 2421-92-3; **5** (M = Li), 2421-93-4; **6** (M = K), 37892-21-0; **6** (M = Na), 17372-26-8; **6** (M = Li), 22643-61-4; **7** (M = K), 28273-52-1; **7** (M = Na), 25854-38-0; **7** (M = Li), 53328-79-3; **8** (M = K), 582-25-2; **8** (M = Na), 532-32-1; **8** (M = Li), 553-54-8.

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Equilibria Involving Organic Anions in Dimethyl Sulfoxide and *N*-Methylpyrrolidin-2-one: Acidities, Ion Pairing, and Hydrogen Bonding

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Four new indicators, 5-nitrobarbituric acid, 2,4-dinitro-1-naphthol, 4-chloro-2,6-dinitrophenol, and 2,4-dinitrophenol, have been used to complete the anchoring of the Me$_2$SO acidity scale. Two of these indicators plus 2-methyl-4,6-dinitrophenol were used to anchor a new acidity scale in the dipolar nonhydroxylic solvent *N*-methylpyrrolidin-2-one (NMP). Overlapping indicators and standard acids are now available to cover the pK_a range 0 to 32 in both solvents. Absolute acidities were found to be about 1 pK_a unit lower in NMP than in Me$_2$SO for most weak acids. This is attributed to a slightly lower basicity for NMP. For acids in which the negative charge in the anion is localized on oxygen the acidities were about 2 pK_a units lower in NMP. Homohydrogen bonding ("homoconjugation") constants for carboxylic acids and phenols were found to be about an order of magnitude larger in NMP than in Me$_2$SO. Ion association (ion pairing) constants were also found to be about an order of magnitude larger in NMP than in Me$_2$SO. The larger association constants for NMP are consistent with the more positive free energies of single-ion transfer from water to NMP than from water to Me$_2$SO that have been observed for small anions. Acidity constants for 48 weak acids for the pK_a range 2 to 31 in NMP are reported. Homohydrogen bonding constants for four phenols and two carboxylic acids and association constants for the anions of 10 weak acids with K$^+$ are given. It is suggested that solvents of the type NMP and Me$_2$SO be classified as "dipolar nonhydroxylic", rather than as "dipolar aprotic".

Organic chemists have been working to establish acidity scales for weak organic acids for almost 50 years to augment and complement the water acidity scale. An equilibrium acidity scale in benzene, which provided semiquantitative relative acidities for a few alcohols, ketones, hydrocarbons, and anilines, has been in use for most of this period.[1] More recently a quantitative scale of equilibrium acidities in cyclohexylamine (CHA) has provided relative acidities for many types of hydrocarbons and for some related compounds.[2] Although these scales provide important information concerning the relative acidities of groups of closely related compounds, the measured acidities are cation dependent,[3] and relative acidities may vary greatly with the medium if the structures of the acids being compared are not closely related.[4] Furthermore, since the "pK_a's" determined in such solvents are related to arbitrary reference standards in other solvents,[5] meaningful comparisons with pK_a's determined in any other medium cannot be made. For a time it appeared that a unique quantitative pK_a scale could be developed in mixed aqueous media using the H_- technique.[6] This hope was dashed, however, by the observation that compounds of different structural types showed divergent behavior in such mixtures.[7,8] Strongly dipolar nonhydroxylic ("aprotic") solvents, such as dimethyl sulfoxide (Me$_2$SO), dimethylformamide (DMF), acetonitrile, and hexamethylphosphoramide (HMPA), finally provided media in which equilibrium acidities directly comparable to those in water could be obtained.[9] Common oxygen acids such as carboxylic acids, phenols, and alcohols have been found to be less acidic in these media than in water by many

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(5) The acidity scale in benzene is based on the pK_a of MeOH in MeOH,[1] that in cyclohexylamine is based on the pK_a of 9-phenylfluorene in aqueous sulfolane determined by the H_- method.[2]

(6) Stewart, R.; O'Donnell, J. P. *J. Am. Chem. Soc.* **1962**, *84*, 493–494.

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Table I. Equilibrium Acidities in Dimethyl Sulfoxide Solution Determined by Direct Spectrophotometric Measurements

indicator acid	$\mathrm{p}K_a$	runs[a]	λ_{max}, nm[b]	ϵ (λ, nm)	selected $\mathrm{p}K_a$[c]
2,4-dinitrophenol (DNPH)	5.12 ± 0.04	2 (10)	438	1234 ± 0.9 (485 nm)	5.12
4-chloro-2,6-dinitrophenol (CDNPH)	3.56 ± 0.02	2 (11)	479	196.8 ± 0.5 (545 nm)	
	3.58 ± 0.02	2 (10)		370 ± 1.5 (540 nm)	3.56
2,4-dinitro-1-naphthol (DNNH)	2.11 ± 0.04	2 (9)	458	120 ± 0.4 (510 nm)	2.10
5-nitrobarbituric acid (NBAH)	0.77 ± 0.14	1 (4)	*d*	26.10 ± 0.1 (430 nm)	0.8 ± 0.2

[a] The number of runs with the number of points indicated in parentheses. [b] λ_{max} of the anion, in Me_2SO ±2 nm. [c] Standard deviation ± 0.05 or less unless otherwise indicated. [d] Obscured by glass absorption (λ_{max} <350 nm).

Table II. Equilibrium Acidities in Dimethyl Sulfoxide Determined in the 2 to 6 $\mathrm{p}K_a$ Region by the Overlapping Indicator Method

compd	indicator[a]	$\mathrm{p}K_{ind}$	runs[b]	$\mathrm{p}K_a$[c]	selected $\mathrm{p}K_a$[d]
CF_3SO_2NHPh	DNPH	5.12	2	5.66	
	CDNPH	3.56	2	5.71	5.69
$PhCOCH_2SO_2CF_3$	DNPH	5.12	2	5.05	
	CDNPH	3.56	2	5.20	5.13 ± 0.10
$PhCH(CN)_2$	DNPH	5.12	2	4.24 ± 0.07	
	CDNPH	3.56	2	4.25 ± 0.04	4.24
$(PhSO_2)_2CHSPh$	DNPH	5.12	1	5.52	5.52
$(CF_3SO_2)_2CH_2$	DNNH	2.12	1	2.10 ± 0.10	
	CDNPH	3.56	2	2.04 ± 0.10	2.07 ± 0.15

[a] DNPH is 2,4-dinitrophenol; CDNPH is 4-chloro-2,6-dinitrophenol; DNNH is 2,4-dinitronaphthol. [b] Three-point titrations. [c] ±0.02 unless otherwise indicated. [d] ±0.05 unless otherwise indicated.

powers of ten, primarily because stabilization of their anions by hydrogen bonding with the solvent is lacking. The absence of such hydrogen-bond donor properties is a distinguishing characteristic for these solvents, as compared to water, methanol, etc., and is the basis of our suggestion that these solvents be referred to henceforth as "dipolar nonhydroxylic", rather than "dipolar aprotic".[10]

Chemists were quick to take advantage of the favorable properties of dipolar nonhydroxylic solvents for measurements of acidities by conductometric, spectrophotometric, and potentiometric methods. Measurements in many laboratories using a variety of solvents including Me_2SO, DMF, acetonitrile, propylene carbonate, and HMPA have been made.[9] Dimethyl sulfoxide has many distinct advantages for acidity measurements. It is (a) readily available in a high state of purity, (b) nontoxic,[11] (c) stable to strong bases for considerable lengths of time (days), (d) an excellent solvent for most neutral organic compounds and reasonably good at solvating both cations and anions, and (e) a very weak acid ($\mathrm{p}K_a$ = 35.1 in Me_2SO[12]). Although Me_2SO is poor, as compared to water, at solvating small anions or large anions where the charge is localized on oxygen or nitrogen (because of its poor hydrogen-bond donor properties), it is better than water at solvating large delocalized anions[9] and is also better at solvating cations. The ability of Me_2SO to solvate neutral and charged organic species, together with its low acidity, makes it suitable as a solvent for measuring the acidity of a wide range of compounds (probably well over 50% of all organic compounds). (This is to be contrasted with water which, because of its relatively high acidity and poor solvating power for neutral organic compounds, is suitable for measuring acidities of only about 1% of organic compounds.) For these reasons Me_2SO is in many ways an ideal dipolar nonhydroxylic solvent in which to establish an acidity scale.[13] A considerable effort has been made, therefore, to extend the acidity scale from the low $\mathrm{p}K_a$ region into the 15 to 32 $\mathrm{p}K_a$ region by using potentiometric[14,15] and overlapping indicator methods.[13] Originally the Me_2SO scale was anchored by Steiner on the "aqueous reference state" by using the H_- $\mathrm{p}K_a$ for 4-nitroaniline.[7] Although the $\mathrm{p}K_a$ of fluorene obtained by using this standard in Me_2SO was identical with that obtained in H_2O–Me_2SO or CH_3OH–Me_2SO and with that obtained in Me_2SO by the potentiometric method,[14] this turned out to be fortuitous.[7,8] The $\mathrm{p}K_a$ values obtained by the potentiometric method in the low $\mathrm{p}K_a$ region (0 to 14) have been shown to agree with those obtained by the spectrophotometric method,[16] and provide a secure anchor for the Me_2SO scale.[13] (However, the values above $\mathrm{p}K_a$ 14 obtained by the potentiometric method have been shown to be unreliable, apparently because of slow electrode response.[13,17]) The present paper reports spectrophotometric measurements on five additional indicators and five additional standard acids, which completes the development of the overlapping indicator scale in the low $\mathrm{p}K_a$ region (0 to 8).

If the Me_2SO scale is to be generally useful it is important to be able to relate acidities in this scale to absolute acidities in other dipolar nonhydroxylic solvents and to see whether or not there will be appreciable differences

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[10] The term "aprotic" is incorrect for most of these solvents in any event.

[11] Although Me_2SO has low toxicity, its ability to penetrate the skin rapidly requires that its solutions be handled with care since they may contain toxic materials.

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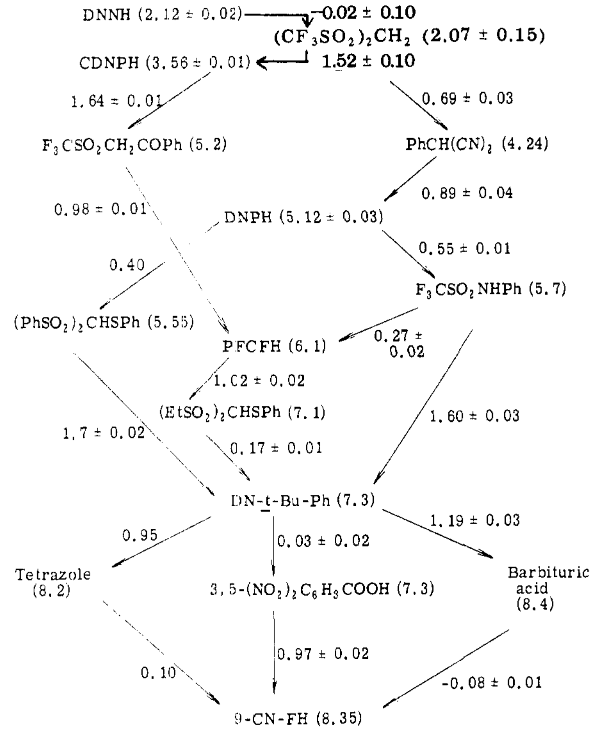

Figure 1. Ladder constructed for the pK_a region 2 to 8 in Me_2SO solution by using a combination of direct spectrophotometric measurements and an overlapping indicator method. Formulas are given for standard acids. Letter abbreviations are used for indicators (see Table III for a summary).

in relative acidities in different solvents of this type. As a start in that direction, we report in this paper the development of a parallel acidity scale in *N*-methylpyrrolidin-2-one (NMP).

Results and Discussion

Anchoring the Me_2SO and NMP Acidity Scales. Our Me_2SO acidity scale was originally anchored on the acidities of three carbon acids, 9-cyanofluorene ($pK_a = 8.3$), 9-(carbomethoxy)fluorene ($pK_a = 10.35$), and malononitrile ($pK_a = 11.1$), which had been determined by the potentiometric method. In order to extend the overlapping indicator method down to $pK_a = 0$, direct spectrophotometric measurements have now been made with four new indicators (Table I).

Table II illustrates the overlapping technique by showing measurements made against five compounds giving colorless anions, using three of these indicators. Note that agreement in pK_a determinations for a given compound using two different indicators is usually less than 0.1 pK_a unit. (Agreement better than ± 0.05 pK_a unit is usually obtained when the pK_a of the acid is intermediate to the pK_a's of the two indicators.)

Some of the additional measurements used to develop overlapping indicators and standard acids for use in the low pK_a region are shown in Figure 1. This ladder establishes the link between these indicators and 9-cyanofluorene.

Direct spectrophotometric measurements were made in NMP for the indicators 2,4-dinitro-1-naphthol, 4-chloro-2,6-dinitrophenol, and 2-methyl-4,6-dinitrophenol. These acidities were then used to anchor the NMP acidity scale by relating them to one another and/or to compounds giving colorless anions. A ladder in NMP, comparable to the partial ladder shown in Figure 1 for Me_2SO, was then constructed to cover the pK_a range 0 to 32 (Figures 2–4). Measurements in the region above about pK_a 20 presented difficulties when the NMP was not purified carefully (see the Experimental Section).

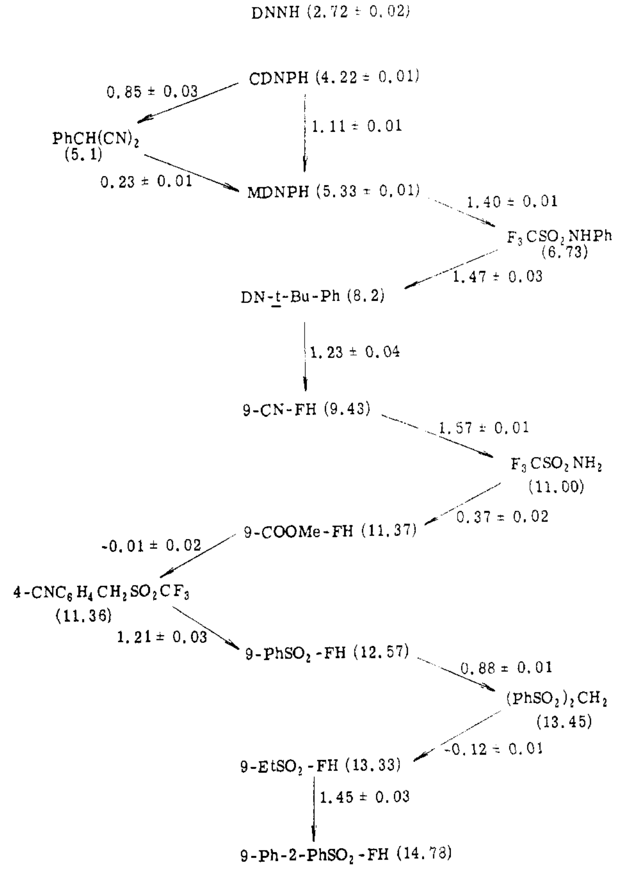

Figure 2. Ladder constructed for the pK_a region 2 to 15 in NMP solution by using a combination of direct spectrophotometric measurements and an overlapping indicator method. Formulas are given for standard acids. Letter abbreviations are used for indicators (see Table III for a summary).

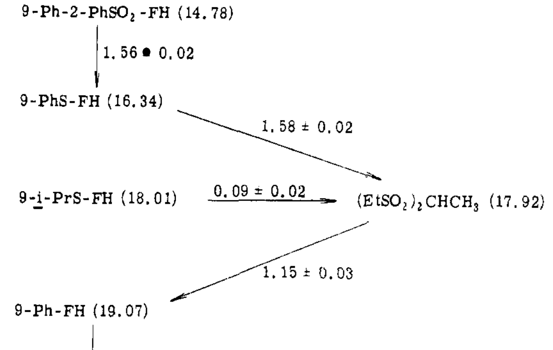

Figure 3. Ladder constructed for the pK_a region 15 to 25 in NMP solution by using an overlapping indicator method. Formulas are given for standard acids. Letter abbreviations are used for indicators (see Table III for a summary).

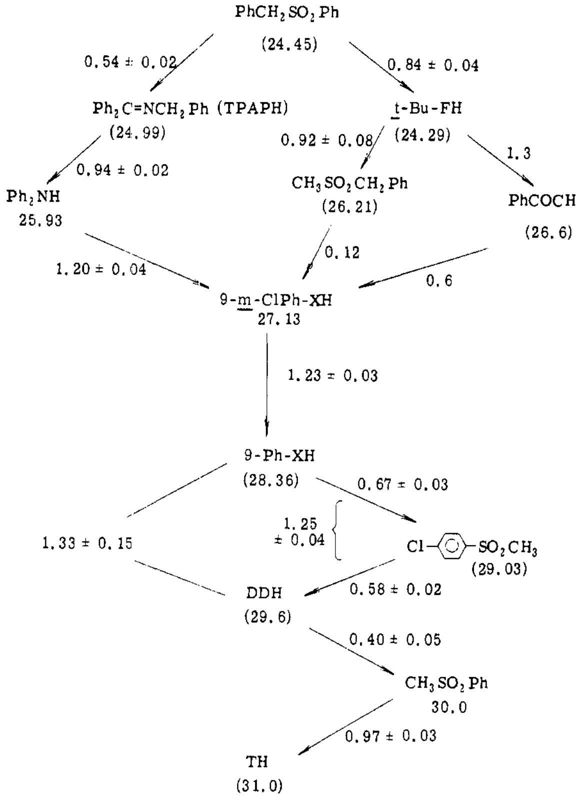

Figure 4. Ladder constructed for the pK_a region 25 to 32 in NMP solution by using an overlapping indicator method. Formulas are given for standard acids. Letter abbreviations are used for indicators (see Table III for a summary).

Comparisons of Acidities of Indicators and Standard Acids in Me$_2$SO and NMP. Absolute acidities may be defined by eq 1 and 2, where S is the solvent.

$$\mathrm{HA} + \mathrm{S} \rightleftarrows \mathrm{HS}^+ + \mathrm{A}^- \qquad (1)$$

$$K_{\mathrm{abs}} = \frac{[\mathrm{HS}^+][\mathrm{A}^-]}{[\mathrm{HA}][\mathrm{S}]} \qquad (2)$$

The absolute acidity constant, K_{abs}, is related to the conventional acidity constant, K_a, by dividing K_a by the solvent concentration, [S]. Direct comparisons of acidities can be made in solvents like Me$_2$SO, NMP, and H$_2$O, where ion-association effects can be avoided, but K_a's must be corrected to an absolute scale by dividing by the molar concentration of the solvent (14 for Me$_2$SO and 10 for NMP). Table III shows a comparison of acidities in Me$_2$SO and NMP for the indicators (mostly hydrocarbons) in the pK_a range 0 to 25. We report the experimentally determined pK_a values and make the correction to the absolute scale only for purposes of comparison (ΔpK_{abs}).

Examination of Table III shows that in NMP these hydrocarbon indicators are less acidic than in Me$_2$SO by 0.45 to 1.2 pK_a units. It seems likely that one factor causing the difference is a higher basicity for Me$_2$SO in Me$_2$SO than for NMP in NMP. This suggests that, when measured in a common solvent, Me$_2$SOH$^+$ will be less acidic than NMPH$^+$. Estimates of acidities in water of Me$_2$SOH$^+$ and NMPH$^+$ have been made by several techniques, but, unfortunately, the results are not consistent and no conclusions can be drawn.[18] The results for potentiometric titration with perchloric acid in acetic anhydride or nitromethane are more consistent. The pK_a for Me$_2$SOH$^+$ in H$_2$O, estimated from measurements in Ac$_2$O, is 1.0[19] and that for NMPH$^+$ is +0.2[25] or −0.3;[19] in CH$_3$NO$_2$ the values are 0.91[20] and −0.2.[26] From these results in

Table III. Acidities of Indicators Used to Anchor the pK_a Scales in Dimethyl Sulfoxide (Me$_2$SO) and *N*-Methylpyrrolidin-2-one (NMP)[a]

acids	pK_a- (Me$_2$SO)	pK_a- (NMP)	ΔpK_{abs}[b]
2,4-dinitro-1-naphthol (DNNH)	2.12	2.72	0.45
4-chloro-2,6-dinitrophenol (CDNPH)	3.56	4.22	0.51
2-methyl-4,6-dinitrophenol (MDNPH)	4.59	5.33	0.58
2,6-di-*tert*-butyl-4-nitrophenol (DN-*t*-BuPH)	7.3	8.2	0.8
9-cyanofluorene (9-CN-FH)	8.3	9.45	1.0
9-(carbomethoxy)-fluorene (9-CO$_2$Me-FH)	10.35	11.4	0.9
9-(phenylsulfonyl)-fluorene (9-PhSO$_2$-FH)	11.55	12.6	0.95
fluorenone 2,4-dichlorophenylhydrazone	11.95	12.7	0.60
9-(ethylsulfonyl)fluorene (9-EtSO$_2$-FH)	12.3	13.35	0.90
2-(phenylsulfonyl)-9-phenylfluorene (2-PhSO$_2$-9-Ph-FH)	13.8	14.8	0.90
9-(phenylthio)fluorene (9-PhS-FH)	15.4	16.35	0.80
9-(isopropylthio)-fluorene (9-*i*-PrS-FH)	16.9	18.0	1.0
9-phenylfluorene (9-Ph-FH)	17.9	19.05	1.0
4-chloro-2-nitroaniline (CNAH)	18.9	19.95	0.90
2-naphthylacetonitrile (2-Np-ANH)	20.65	21.7	0.90
9-methylfluorene (9-Me-FH)	22.35	23.4	0.90
1,1,3-triphenyl-2-aza-1-propene (TPAPH)	24.3	25.0	0.55
9-*tert*-butylfluorene (9-*t*-Bu-FH)	24.35	25.3	0.80
9-(*m*-chlorophenyl)-xanthene [9-(*m*-ClPh)-XH]	26.6	27.15	0.35
9-phenylxanthene (9-Ph-XH)	27.9	28.35	0.25
diphenylyldiphenyl-methane (DDH)	29.4	29.6	0.05
triphenylmethane (TH)	30.6	31.0	0.25

[a] The acidities of these indicators relative to the standard acids against which they were measured are shown in Figures 1–4 or in ref 13. [b] Corrected to an absolute scale by subtracting log (14/10) from the ΔpK_a.

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(18) For Me$_2$SOH$^+$ pK values in H$_2$O are 1.0,[19] 0.91,[20] 0,[21] −1.04,[22] −1.8,[23] and −2.7;[24] for NMPH$^+$ they are +0.20,[25] −0.3,[19] −0.2,[26] −0.17,[27] and −0.92.[28]

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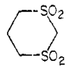
Table IV. **Acidities of Sulfone, Sulfonamide, and Nitrile Standard Carbon Acids in Me_2SO and NMP**[a]

acid	pK_a-(Me_2SO)	pK_a-(NMP)	ΔpK_{abs}[b]
$PhCH(CN)_2$	4.2	5.1	0.75
F_3CSO_2NHPh	5.7	6.7	0.85
$F_3CSO_2NH_2$	9.7	11.0	1.15
$CH_2(CN)_2$	11.1	12.6	1.35
$4\text{-}CNC_6H_4CH_2SO_2CF_3$	10.7	11.4	0.55
	15.5	16.9	1.25
$(PhSO_2)_2CH_2$	12.25	13.45	1.05
$(EtSO_2)_2CHCH_3$	16.73	17.9	1.0
$(m\text{-}CF_3C_6H_4CH_2)_2SO_2$	21.0	21.7	0.55
$PhSO_2CH_2Ph$	23.45	24.4	0.85
Ph_2NH	24.95	25.9	0.80
$CH_3SO_2CH_2Ph$	25.4	26.2	0.65
$p\text{-}ClC_6H_4SO_2CH_3$	28.0	29.0	0.85
$PhSO_2CH_3$	29.0	30.0	0.85

[a] The acidities of these standard acids relative to the indicators against which they were measured are shown in Figures 1-3 or in ref 13. [b] Corrected to an absolute scale by subtracting log (14/10) from ΔpK_a.

nonhydroxylic solvents we conclude that Me_2SO is about 1 p*K* unit more basic than NMP.

The nearly constant ΔpK of 0.9 ± 0.1 between acidities in Me_2SO vs. NMP for hydrocarbon indicators in the pK_a range 8–25 (Table III) is not surprising since ΔpK for these compounds is also nearly constant even for Me_2SO vs. CHA.[13] This result is consistent with a 1 p*K* unit lower basicity of NMP, and the constancy of the value gives us assurance that both scales have been developed properly.

Sulfones, sulfonamides, and nitriles have been compounds of choice for use as standard acids for our acidity scale because they are readily available and form stable, colorless, or nearly colorless anions. The pK_a's of a number of such standard acids that were used to develop the Me_2SO and NMP acidity scales are shown in Table IV.

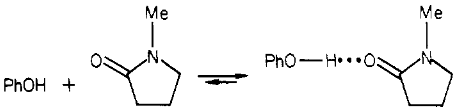
Examination of Table IV shows that ΔpK between the two scales is about 1.0 ± 0.4 p*K* unit. The ΔpK's are slightly larger than for the hydrocarbon indicators (Table III), but considerably smaller than for examples where the negative charge is localized on oxygen.

The hydrocarbon indicators with pK_a's above 25 used for the NMP scale were the following: 9-(*m*-chlorophenyl)xanthene (pK_a = 27.1), 9-phenylxanthene (pK_a = 28.3), diphenylyldiphenylmethane (pK_a = 29.6), and triphenylmethane (pK_a = 31.0). These compounds are 0.35, 0.25, 0.05, and 0.25 p*K* unit, respectively, less acidic in NMP than in Me_2SO.[13] Here the ΔpK's are smaller than the difference in basicity between Me_2SO and NMP, which suggests that NMP may be slightly better than Me_2SO in solvating strongly basic, highly delocalized anions. This is supported by the observation that the free energy of transfer of $(C_6H_5)_4B^-$ from Me_2SO to NMP is −0.7 kcal/mol.[37a]

Titration of a solution of triphenylmethane (TH) in NMP with a solution of the conjugate base of NMP gave a good Beer's law plot, signifying complete deprotonation. This contrasts with the behavior of TH in Me_2SO, where titration with dilute $CH_3SOCH_2^-K^+$ solutions gives curved plots.[12] Evidently the conjugate base of NMP, $C_5H_8NO^-K^+$, is more basic in NMP than is $CH_3SOCH_2^-K^+$ in Me_2SO. Titration of diphenylmethane (DH) in NMP with the conjugate base of NMP gave a curved Beer's law plot, signifying incomplete deprotonation. Since the p*K* of DH in Me_2SO is 1.8 units higher than that of TH, these results indicate that the pK_a of NMP in NMP is about 2 p*K* units higher than that of Me_2SO in Me_2SO, i.e., about 37. (The pK_a of Me_2SO is 35.1.[12]) Since, as we will see shortly, the pK_a's of carbon or nitrogen acids, such as NMP, in which the charge in the anion is delocalized to oxygen are about 2 units lower in Me_2SO than in NMP, we can expect the pK_a of NMP in Me_2SO to be about 35. This agrees with the estimates for the H–C acidities of carboxamides in Me_2SO that we have made by extrapolations. Initially we had hoped that NMP would be a weaker acid than Me_2SO, which would allow an upward extension of the dipolar nonhydroxylic solvent pK_a scale, but this is not the case. It may be possible, however, to develop other types of carboxamide solvents to serve this purpose. [Originally we considered using HMPA, but the reports that this compound is carcinogenic in parts per billion on long exposure (months)[29] caused us to abandon this idea.]

Acids in Which the Negative Charge in the Anion Resides Principally on Oxygen. There are three types of acids that fall into this category: (a) carbon acids, such as ketones, (b) oxygen acids, such as phenols or alcohols, and (c) acids whose anions can serve as bidentate ligands toward metal cations, e.g., carboxylic acids and β-diketones. Acidity measurements for the latter two types are often complicated by homohydrogen bonding or ion-association effects. Failure to recognize these complications is no doubt responsible, in part, for the frequent disagreement between p*K* values reported from different laboratories in Me_2SO, NMP, and other dipolar nonhydroxylic solvents. For example, pK_a's for 4-nitrophenol of 12.5,[30b] 11.4,[30c] and 10.6[30d] have been reported in NMP. Similarly, values for salicylic acid in NMP that have been reported include 9.8,[30a] 8.6,[30b] and 7.3;[30c] for benzoic acid the reported values are 9.9,[30a] 12.3,[30b] and 10.[30c] (See Table V for comparisons with our values.)

Kolthoff found that in dipolar nonhydroxylic solvents phenol and its monosubstituted derivatives hydrogen bond more strongly with their conjugate bases than they do with the solvent. As a consequence equilibria 3 and 4 are present for phenol in NMP.



(3)

$$PhO^- + PhOH \rightleftharpoons PhO^-\cdots H{-}OPh \qquad (4)$$

Kolthoff showed that the one-to-one homohydrogen bonded complex $PhO^-\cdots HOPh$ is the principal one present, which allowed him to measure the "homoconjugation" constant for PhOH in Me_2SO and to correct the pK_a (eq 1) for the presence of eq 4.[16,31] Even when this correction is made, however, the pK_a of PhOH obtained is 1.6 p*K* units lower than the corrected value obtained by the overlapping indicator method.[32] Presumably slow elec-

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(28) Virtanen, P. O.; Södervall, T. *Suom. Kemistil.* **1967**, *40*, 337–340.

(29) HMPA has gained widespread usage in both synthetic and physical organic studies but, in view of its toxicity, should be used with extreme caution. For reports on the carcinogenicity of HMPA see: *Nature* **1975**, *257*, 735; *Chem. Eng. News* 1976, Feb 2, p 3.

(30) (a) Dupin, M.; Terrat, J. P. *J. Electroanal. Chem.* **1972**, *35*, 261–273. (b) Kreshkov, A. P.; Gurvich, Y. A.; Galpern, G. M.; Kryuchkova, N. F. *Zh. Anal. Khim.* **1972**, *27*, 1166–1171. (c) Mouton, J. L.; Sinicki, C. *J. Electroanal. Chem.* **1973**, *48*, 285–295. (d) Breant, M.; Auroux, A.; Lavergne, M. *Anal. Chim. Acta* **1976**, *83*, 49–57.

(31) Kolthoff referred to the hydrogen bonding shown in eq 3 as homoconjugation. We prefer the term homohydrogen bonding because it is more descriptive and because the term "conjugation" usually refers to π–π bond or σ–π bond interactions, e.g., "homoconjugation" in bridged carbon cations or anions.

Table V. Acidity and Homohydrogen-Bonding Constants in Dimethyl Sulfoxide and *N*-Methylpyrrolidin-2-one

oxygen acid	$pK_a(NMP)^a$	$\Delta pK_{abs}{}^f$	$\log K_{hb}(NMP)^g$	$\Delta\log K_{hb}{}^h$
salicylic acid	8.4 (8.6,[b] 9.8,[c] 7.3[d])	1.45	1.8 ± 0.1	
benzoic acid	13.3 (12.3,[b] 9.9,[c] 10[d])	2.15	3.0 ± 0.1	1.1
4-nitrophenol	12.15 (12.5,[b] 11.4,[d] 10.6[e])	1.20	2.8 ± 0.15	1.1
4-acetylphenol	15.6	1.45	3.45 ± 0.05	1.2
3-chlorophenol	17.8 (14.3[e])	1.85	4.1 ± 0.2	0.8
phenol	20.1 (17.6,[b] 15.5[e])	1.95	4.1 ± 0.2	0.8

[a] Literature values are given in parentheses. [b] Reference 30b. [c] Reference 30a. [d] Reference 30c. [e] Reference 30d. [f] Corrected to an absolute scale by subtracting log (14/10) from $\Delta pK_a = pK_a(NMP) - pK_a(Me_2SO)$. [g] M^{-1}. [h] $\Delta\log K_{hb} = \log K_{hb}(NMP) - \log K_{hb}(Me_2SO)$.

trode response in the potentiometric method is responsible for the discrepancy.[13,17]

Homohydrogen-Bonding Constants in Me_2SO and NMP. Recently the overlapping indicator method has been modified to correct the acidities for homohydrogen bonding for phenols in Me_2SO and to determine homohydrogen-bonding constants (K_{hb}).[32] Table V presents pK_a and K_{hb} constants in NMP determined by this method. Comparisons with literature pK_a values and with K_{hb} in Me_2SO are also given.

Kolthoff found that the extent of homohydrogen bonding decreased as the acidity of the phenol increased. The K_{hb} constants for dinitrophenols in Me_2SO were too small to measure.[16] This is true also in NMP. Steric effects, caused by the presence of 2-substituents, are no doubt also important in inhibiting homohydrogen bonding. In the present work we obtained no evidence for homohydrogen bonding in NMP for 2,4-dinitro-1-naphthol, 4-chloro-2,6-dinitrophenol, 2-methyl-4,6-dinitrophenol, or 2,6-di-*tert*-butyl-4-nitrophenol (Table III). On the other hand, 4-nitrophenol exhibited appreciable homohydrogen bonding (Table V).

A plot of the pK_a's for phenol and six substituted phenols and 2,4-dinitro-1-naphthol in Me_2SO vs. NMP is linear over a range of 17.4 p*K* units (Figure 5) with a slope of 0.91. The remarkably good correlation observed (R^2 = 0.9998) gives added assurance that the Me_2SO and NMP acidity scales have been developed with precision.[33] It is also noteworthy that the correlation for a plot of pK_a's for seven of these phenols (omitting 4-nitro-2,6-di-*tert*-butylphenol) in Me_2SO vs. H_2O is much poorer (R^2 = 0.984).

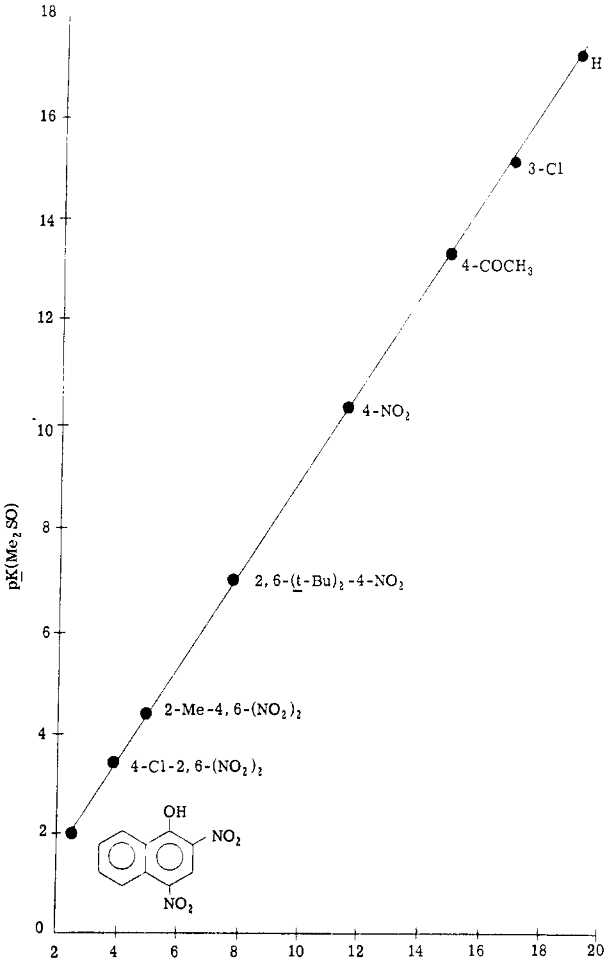

Figure 5. Correlation of acidities of phenols in Me_2SO vs. NMP; slope = 0.91, R^2 = 0.9998.[33]

Table VI. Single-Ion Free Energies of Transfer from Water (kcal/mol)[a]

ion	Me_2SO	NMP
Li^+	-4.5	
Na^+	-3.3	-3.9
K^+	-2.9	-3.3
Cl^-	9.2	13.2
Br^-	6.1	9.7
I^-	2.2	5.8
SCN^-	2.0	6.1
N_3^-	6.1	11.3
BPh_4^-	-8.8	-9.5

[a] Taken from ref 37a.

Examination of Table V shows that K_{hb}'s are about one order of magnitude larger in NMP than in Me_2SO. The difference is the same for carboxylic acids and phenols. Both the data of Arnett[34] and that of Kamlet and Taft[35] indicate that Me_2SO and NMP are about equally effective as hydrogen-bond acceptors for $4\text{-}FC_6H_4OH$ in CCl_4 solution. The larger K_{hb}'s in NMP than in Me_2SO are unexpected on these grounds. On the other hand, nucleophilicities of inorganic ions appear to be somewhat greater in NMP, although the data available for direct comparisons are limited.[36] Also, comparison of free energies of single-ion transfer from water to Me_2SO and from water to NMP indicate 3 to 5 kcal/mol weaker solvation of small inorganic ions in NMP.[37a] However, solvation of the Ph_4B^- ion is *stronger* by 0.7 kcal/mol in NMP than in Me_2SO (Table VI). (The enthalpies of single-ion transfer lead to similar conclusions.[37b]) The larger K_{hb} for phenols and carboxylic acids observed in NMP (Table V) is consistent

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[32] Olmstead, W. N., unpublished results.

[33] R^2, the square of the correlation coefficient *r*, is a measure of precision. It is that fraction of the variance in the plot that is explained by linear-regression analysis.

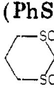
[34] Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875–3891.

[35] Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377–383.

[36] Alexander, R.; Ko, E. C. F.; Parker, A. J.; Broxton, T. J. *J. Am. Chem. Soc.* **1968**, *90*, 5049–5069.

[37] (a) Cox, B. G.; Hedwig, G. R.; Parker, A. J.; Watts, D. W. *Aust. J. Chem.* **1974**, *27*, 477–501. (b) Krishnan, C. V.; Friedman, H. L., ref 20, Chapter 9, pp 1–104.

Table VII. Comparison of Ion-Association Constants for Bidentate Ligands and Potassium Ion in NMP and Me_2SO

acid[a]	K_{as}(NMP), M^{-1}	K_{as}(Me_2SO), M^{-1}
$CH_2(CN)_2$	<10	<10
$CF_3SO_2NH_2$	20 ± 5	<10
$(PhSO_2)_2CH_2$	20 ± 5	<10
	110 ± 5	<10
$PhCONHNH_2$	130 ± 10	<10
$PhCH_2SCH_2COPh$	175 ± 10	26 ± 3
$CH_3COCH_2COCH_3$	250 ± 10	24 ± 5
$PhCOCH_2COPh$	9000 ± 1000	580 ± 90
PhCOOH	1050 ± 100	48 ± 3
CH_3NO_2	850 ± 30	55 ± 5

[a] The acidities for these compounds reported in this paper and in ref 41 have been corrected by calculation of pK_a at $[K^+] = 0$.[41] However, the pK_a's reported in earlier papers have not taken ion association into account. For $K_{as} < 100$ the correction is of the order of the experimental error in the pK_a measurements (±0.05 unit), but for $K_{as} \simeq 250$, 10^3, and 10^5 the corrections amount to roughly 0.1, 0.5, and 1 pK_a unit, respectively.

with weaker solvation of phenoxide and carboxylate ions in this solvent, which encourages greater hydrogen-bond acceptance by the anions.

The differences in acidities in NMP and Me_2SO for phenols increase progressively from a ΔpK of 0.45 to a ΔpK of 1.95 as the acidity of the phenol decreases (Tables III and V). Evidently, as the charge becomes more localized on oxygen in the more basic anion, NMP becomes increasingly less effective at stabilizing the charge, relative to Me_2SO. This is consistent with the observation that smaller ions, e.g., azide ion and chloride ion, have larger positive single-ion free energies of transfer from H_2O to NMP than from H_2O to Me_2SO (Table VI).

Ion Association in Me_2SO and in NMP. Ion association does not occur in dilute Me_2SO solutions between potassium ion and most organic anions.[13] Since NMP has a somewhat lower dielectric constant than Me_2SO (31.9[9] at 25 °C vs. 46.5 for Me_2SO[38]) one would expect from the Fuoss equation[39] that ion association would be greater in NMP than in Me_2SO.[40] A simple test for ion pairing in Me_2SO has been developed.[41] It consists of adding a solution of an alkali metal iodide in Me_2SO to perturb the equilibrium established in the overlapping indicator method (eq 5 and 6). Ion pairing is detected by a decrease

$$\text{H-A} + \text{In}^- \rightleftarrows \text{H-In} + \text{A}^- \qquad (5)$$

$$\text{M}^+ + \text{A}^- \rightleftarrows \text{M}^+\text{A}^- \qquad (6)$$

in absorbance of In^- greater than that caused by dilution. A general least squares procedure is used to calculate the true equilibrium constants for eq 5 and 6.[41]

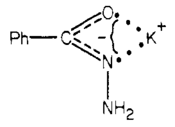
This test is applicable also to dilute NMP solutions, since alkali iodides have been shown to exist as free ions under these conditions.[42] Application of the test showed that anions derived from acids of the type shown in Tables I–IV are not subject to ion pairing in the dilute solutions (1–9 mM) used in our measurements. Phenoxide ions exhibit slight ion pairing. K_{as} in NMP for a number of bidentate anions with potassium ion are shown in Table VII.

As a check on the method, a measurement with the anion derived from dibenzoylmethane, which associates strongly with K^+, was made by using 1 equiv of [2.2.2]-cryptand, added to prevent ion pairing. The pK_a determined in ths manner was 15.45, which agrees well with the value of 15.41 determined by the least-squares method.

Examination of Table VII shows that K_{as} constants in NMP are greater than in Me_2SO by more than one order of magnitude. Anions from β-disulfones, sulfonamides, and benzhydrazides, which do not form chelates with K^+ in Me_2SO with measurable K_{as} constants, all exhibit appreciable ion pairing in NMP. The importance of geometry in stabilizing these chelates is brought out by the failure to observe chelation in the $CH(CN)_2^-$ ion, where the charge density on the two nitrogen atoms is probably comparable to that on the oxygen and nitrogen atoms in the $F_3CSO_2NH^-$ ion, but where the geometry is less favorable.

Chelation involving the oxygen atoms in β-diketone enolates is well-known, but examples of chelation involving the other ligands shown in Table VII are less common. It is noteworthy that in both NMP and Me_2SO the conjugate base of nitromethane, $CH_2{=}NO_2^-$, and the benzoate ion have larger K_{as} constants with K^+ than does the acetylacetonate ion. The four-membered-ring geometry required for chelation of K^+ with $CH_2{=}NO_2^-$ or $PhCO_2^-$ is probably less favorable than the six-membered-ring geometry required for chelation between K^+ and $(CH_3CO)_2CH^-$, but the latter geometry is achieved at the expense of converting the $(CH_3CO)_2CH^-$ ion to a cis conformation from its preferred trans conformation.[41] Conformational effects are no doubt also responsible for the larger K_{as} observed for $(PhCO)_2CH^-$, relative to $(CH_3CO)_2CH^-$, and for 1,3-dithiane tetroxide anion, relative to $(PhSO_2)_2CH^-$.

The K_{as} constants in NMP for the chelates formed from K^+ with the anions derived from benzhydrazide, ω-benzylthioacetophenone, and acetylacetone presumably all have planar structures (1, 2, and 3, respectively). Note that 4-, 5-, and 6-membered chelates are represented here and that all have K_{as} constants of the same order of magnitude. K_{as} for the chelate formed from K^+ and the anion derived from 1,3-dithiane tetroxide (4) is also of the same order of magnitude (Table VII), but here the chelate geometry is likely to be nonplanar, as shown. Ion formation in this case causes little or no rehybridization of the (sulfur) atom to which the oxygen atoms are attached, and there is relatively little delocalization of charge to oxygen compared to the open-chain carbon analogue (3). The restriction of rotation in anion 4 imposed by the ring structure greatly favors chelation, and K_{as} increases by



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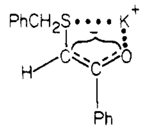

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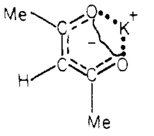

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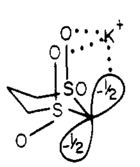

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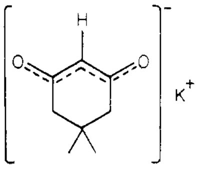

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(38) Casteel, J. F.; Sears, P. G. J. Chem. Eng. Data 1974, 19, 196.

(39) Fuoss, R. M. J. Am. Chem. Soc. 1958, 80, 5059–5061. Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions", 2nd ed; Butterworths: London, 1959; p 392–426.

(40) For a model electrolyte having an average radius of 5 Å, the Fuoss equation predicts a K_{as} of 3.3 in Me_2SO and 9.9 in NMP. For a radius of 2 Å, the calculated K_{as} values are 8.6 in Me_2SO and 130 in NMP.

(41) Olmstead, W. N.; Bordwell, F. G. J. Org. Chem., second in a series of six papers in this issue.

(42) Dyke, M. D.; Sears, P. G.; Popov, A. I. J. Phys. Chem. 1967, 71, 4140.

Table VIII. Carbon or Nitrogen Acids with Charges in the Anion Delocalized to Oxygen

acid	pK_a-(Me$_2$SO)[a]	pK_a-(NMP)[a]	ΔpK_{abs}[b]
$CH_3COCH_2COCH_3$	13.3	15.3	1.85
CH_3NO_2	17.2	19.8	2.45
$PhCH_2SCH_2COPh$	19.0	20.65	1.50
$PhCOCH_3$	24.7	26.5	1.65
$PhCOCH_2COPh$	13.35	15.4	1.90
$PhCONHNH_2$	18.9	20.6	1.55

[a] Ion association has been taken into account in calculating these pK_a's (see footnote *a* in Table VII). [b] Corrected to an absolute scale by subtracting log (14/10) from ΔpK_a.

almost an order of magnitude relative to the open-chain analogue (Table VII). On the other hand, in the dicarbonyl anion analogue (**5**) the ring imposes a planar structure in which the oxygen atoms are too far apart for chelation of the type shown in **3**. For **5** chelation is decreased sharply (K_{as}(Me$_2$SO) >10).[41]

When ion association occurs, the perturbation on eq 5 caused by eq 6 leads to errors in the observed pK_a's. Ion association was taken into account in calculating the pK_a's reported in Tables III–VIII for acids forming chelating ligands. The pK_a values calculated in the usual way[13] may be lower by as much as 1 pK unit if ion association is strong (footnote *a* in Table VII).[41]

Examination of Table VIII shows that ΔpK for acidities in NMP vs. Me$_2$SO has increased by about 1 pK unit when compared with the ΔpK's for hydrocarbon indicators (Table III) and sulfone, sulfonamide, and nitrile standard acids (Table IV). This can be rationalized by a lesser ability of NMP to solvate anions where the charge is localized on oxygen, which is consistent with predictions made on the basis of free energies of single-ion transfer from $H_2O \rightarrow$ NMP vs. $H_2O \rightarrow$ Me$_2$SO for inorganic anions (Table VI). The larger K_{as} constants observed in NMP may be rationalized similarly. It must be kept in mind, however, that inorganic anions may not be good models for organic anions and that the size of the dielectric constant may also play an important role.[39]

Comparisons with Other Strongly Dipolar Nonhydroxylic Solvents. We conclude that the principal cause of the difference in absolute acidities in NMP and Me$_2$SO resides in the relative basicities of the two solvents. It appears likely that absolute acidities in other carboxamide solvents in common use will not differ greatly from those observed in NMP. This view is supported by comparing our pK_a's with the literature values that have been reported in DMF and DMA, but, as has been pointed out above, the differences in values for the same compound from different laboratories are too large to place much confidence in the absolute values obtained in these solvents. In the much less basic solvents such as acetonitrile, absolute acidities are less by about 9 or 10 pK_a units than in Me$_2$SO. In such solvents Kolthoff has shown that homohydrogen bonding equilibria (eq 3 and 4) complete strongly with the acid-base equilibrium (eq 5).[16]

The nearly constant differences in relative acidities (ΔpK's) in NMP and Me$_2$SO with wide variations in structural types over wide ranges of acidities (Tables III–V) suggest that we can use the extensive compilation of acidities in Me$_2$SO (over 600 to date) to predict relative acidities in NMP and other carboxamide solvents. In the absence of strong ion-pairing effects it seems likely that relative acidities in other dipolar nonhydroxylic solvents may also be predicted from these data. The Me$_2$SO acidity scale can probably also be used, although with less assurance, to predict relative acidities in weakly dipolar nonhydroxylic solvents, such as DME, CHA, and benzene, *as long as comparisons are restricted to a given structural class, such as hydrocarbons forming anions that are strongly delocalized.* Comparisons between different structural classes are not possible, however.[13]

The order of magnitude larger ion-association constants observed in NMP than Me$_2$SO suggest that interactions between specific organic anions and specific cations are likely to be highly solvent dependent. Additional work is needed to establish the relationship, if any, between the size of these interactions and the bulk dielectric constant of the solvent. Correlations of ion-association constants with free energies of single-ion transfers for a given solvent look promising, but also require further investigation.

Experimental Section

Samples for Acidity Measurements. 2,4-Dinitro-1-naphthol, 4-chloro-2,6-dinitrophenol, 2,4-dinitrophenol, 2,4-dinitro-6-methylphenol, 4-nitrophenol, 3-chlorophenol, phenol, 5-nitrobarbituric acid, acetylacetone, dibenzoylmethane, 2-naphthylacetonitrile, diphenylamine, benzoylhydrazide, fluorene, triphenylmethane, benzoic acid, salicylic acid, 4-chloro-2-nitroaniline, nitromethane, malononitrile, acetophenone, 3,5-dinitrobenzoic acid, dibenzyl sulfone, benzyl methyl sulfone, and methyl phenyl sulfone were commercially available and purified to 99+% (GC, HPLC, or TLC) by recrystallization, distillation, or preparative GC. The syntheses and purifications of 9-cyanofluorene,[13] 9-(carbomethoxy)fluorene,[13] 9-methylfluorene,[13] 9-*tert*-butylfluorene,[13] 9-phenylfluorene,[13] diphenylyldiphenylmethane,[13] 9-(phenylsulfonyl)fluorene,[13] 9-(phenylthio)fluorene,[13] 9-phenylxanthene,[13] 2,6-di-*tert*-butyl-4-nitrophenol,[43] bis(phenylsulfonyl)methane,[43] benzyl phenyl sulfone,[43] bis(phenylsulfonyl)(phenylthio)methane,[43] bis(ethylsulfonyl)(phenylthio)methane,[43] 1,1-bis(ethylsulfonyl)ethane,[43] 9-(ethylsulfonyl)fluorene,[44] 9-(isopropylthio)fluorene,[44] and 9-phenyl-2-(phenylsulfonyl)fluorene[45] are described elsewhere.

Phenylmalononitrile was made by the method of Hindermayr.[46]

The 2,4-dichlorophenylhydrazone of fluorenone was prepared from the arylhydrazine and fluorenone; mp 194–196 °C.

We thank R. Filler, Illinois Institute of Technology, for a sample of 9-(carboethoxy)octafluorofluorene; R. J. Kosher, 3M Company, for bis((trifluoromethyl)sulfonyl)methane; R. W. Taft, University of California, Irvine, for 4-acetylphenol; and J. B. Hendrickson, Brandeis University, for samples of α-((trifluoromethyl)sulfonyl)acetophenone, *p*-cyanobenzyl trifluoromethyl sulfone, trifluoromethanesulfonamide, and trifluoromethanesulfonanilide.

Acidity Measurements. In the 0 to 6 pK_a region, acidities of compounds forming colored anions were determined in Me$_2$SO and NMP by measuring their self-dissociation in the solvent. The two step procedure is as follows: (1) The molar extinction coefficient (ϵ) of the indicator anion was determined at a fixed wavelength by titrating a solution of base (Et$_3$N) with a solution of the indicator acid and monitoring the absorbance of the indicator anion. (2) Several aliquots of the indicator acid were then added to the pure solvent, and the absorbance of the anion (due to auto-ionization) was recorded at the same wavelength used in determining ϵ. The concentration of the anion was calculated from ϵ and the pK_a was determined for each aliquot added.[47]

In the 6 to 30 pK_a region, acidities were determined by the overlapping indicator method described earlier.[13]

Ion-Pairing and Homohydrogen-Bonding Measurements. Both methods are an extension of the normal pK_a measurement[13]

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[43] Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; Drucker, G. E.; Gerhold, J.; McCollum, G. J.; van der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* **1977**, *42*, 326–332.

[44] Drucker, G. E. Ph.D. Dissertation, Northwestern University, 1978.

[45] McCollum, G. J. Ph.D. Dissertation, Northwestern University, 1976.

[46] Hindermayr, H. Ph.D. Dissertation, Ludwig-Maxmilians Universität, Munich, 1967.

[47] Similar measurements in water are described in King, E. J. "Acid–Base Equilibria"; Pergamon Press: New York, 1965; Chapter 5.

and are described elsewhere.[32,41] To prevent phenoxide and carboxylate anions from ion pairing with K^+ in NMP, an equivalent of [2.2.2]cryptand was added for the pK_a and homohydrogen-bonding measurements of the phenols and carboxylic acids.

Preparation of Bases. Below pK_a 6, Et_3N was used as a base in both solvents since stronger bases react with the low-region nitrophenolic indicators.

Above pK_a 6, $CH_3SOCH_2^-K^+$ was used as a base for measurements in Me_2SO, while both $CH_3SOCH_2^-K^+$ and the conjugate base of NMP, $C_5H_8NO^-K^+$, were used in NMP. (Identical results were obtained with both bases in NMP.) The preparation of $CH_3SOCH_2^-K^+$ has been described elsewhere;[12,13] $C_5H_8NO^-K^+$ was made in an analogous manner; the reaction of KH with NMP is much slower than with Me_2SO, taking several hours at room temperature under full vacuum.

In the pK_a region above 25 in NMP, low stock base strengths were obtained during the internal titration; e.g., the $C_5H_8NO^-K^+$ concentration was 30 mM when used with indicators below 9-methylfluorene ($pK_a = 23.4$), 26 mM with 9-*tert*-butylfluorene ($pK_a = 25.3$), 22 mM with 9-(*m*-chlorophenyl)xanthene ($pK_a = 27.1$), and 17.5 mM with diphenylyldiphenylmethane ($pK_a = 29.6$). With $CH_3SOCH_2^-K^+$ as a base, the base strength similarly decreased from 125 mM below p*K* 23 to 92 mM at p*K* 29. Since an internal titration of base strength was carried out for each pK_a measurement, a low base strength should not affect the results. Consistent results were obtained up to pK_a 31.

Purification of Solvents. Spectral-grade dimethyl sulfoxide was purified as described previously.[13]

The quality of *N*-methylpyrrolidin-2-one (NMP) varied with the source. We began our studies with an old Aldrich bottle of NMP. This sample was dried over molecular sieves and distilled from $NaNH_2$ at a pressure of about 5 mmHg (~70 °C). Treatment of this NMP with KH over a 3-h period produced a solution of the conjugate base, $C_5H_8NO^-K^+$, that completely deprotonated our indicator acids and gave good Beer's law titrations up to triphenylmethane ($pK_a = 30.6$ in Me_2SO). Consistent pK_a's were obtained up to pK_a 28 in this NMP.

The NMP subsequently purchased from Aldrich (98%) or Eastman (99%) was purified in a similar manner, but the $C_5H_8NO^-K^+$ made from this NMP, or $CH_3SOCH_2^-K^+$ in Me_2SO used in this NMP, would not completely deprotonate indicators above pK_a 20. Curved Beer's law plots were obtained in the 20–25 pK_a region, and little deprotonation occurred above pK_a 25. Good results were obtained, however, in the pK_a region below 20. A second distillation from $NaNH_2$ improved the quality of this NMP, but inconsistent results were still obtained in the 20 to 28 pK_a region.

A sample of 99.6% NMP made by GAF Corp., Texas City, TX, and obtained through the courtesy of Dr. T. D. Brown of the Phillips Petroleum Co. of Bartlesville, OK, gave better results.[48] After distillation from $NaNH_2$, the $C_5H_8NO^-K^+$ in NMP prepared with KH caused deprotonation of indicators up to pK_a 28 in this solvent. Repetition of acidity measurements in the 23 to 28 pK_a region gave results identical with those obtained earlier with the first batch of NMP. A second distillation from $NaNH_2$ gave a solvent which reacted with KH to give a base stock solution of $C_5H_8NO^-K^+$ in NMP that gave a good Beer's law plot with diphenylyldiphenylmethane ($pK_a = 29.6$ in NMP) and with triphenylmethane ($pK_a = 31.0$ in NMP).[49] This solvent and stock base gave pK_a's for $PhCH_2SO_2Ph$, *m*-ClPXH, PXH, and DDH within ±0.05 unit of those determined using the first sample of NMP.

The NMP that had been distilled from $NaNH_2$ contained about 0.1 mM basic impurity (probably either NH_3 or CH_3NH_2) that interfered with the direct measurements in the low region. Therefore, the NMP used for the low region was distilled again from a small amount of H_2SO_4.[50] This NMP gave reproducible results in the low region and also gave the same results in the middle region as the NMP that had been distilled only from $NaNH_2$.

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Registry No. Dimethyl sulfoxide, 67-68-5; 2,4-dinitrophenol, 51-28-5; 4-chloro-2,6-dinitrophenol, 88-87-9; 2,4-dinitro-1-naphthol, 605-69-6; 5-nitrobarbituric acid, 480-68-2; 1,1,1-trifluoro-*N*-phenylmethanesulfonamide, 456-64-4; α-[(trifluoromethyl)sulfonyl]acetophenone, 35896-48-1; phenylmalononitrile, 3041-40-5; bis(phenylsulfonyl)(phenylthio)methane, 73622-50-1; bis[(trifluoromethyl)sulfonyl]methane, 428-76-2; *N*-methylpyrrolidin-2-one, 872-50-4; 2-methyl-4,6-dinitrophenol, 534-52-1; 2,6-di-*tert*-butyl-4-nitrophenol, 728-40-5; 9-cyanofluorene, 1529-40-4; 9-(carbomethoxy)fluorene, 3002-30-0; 9-(phenylsulfonyl)fluorene, 22010-78-2; fluorenone 2,4-dichlorophenylhydrazone, 73622-51-2; 9-(ethylsulfonyl)fluorene, 60147-56-0; 2-(phenylsulfonyl)-9-phenylfluorene, 73636-50-7; 9-(phenylthio)fluorene, 28114-92-3; 9-(isopropylthio)fluorene, 60147-54-8; 9-phenylfluorene, 789-24-2; 4-chloro-2-nitroaniline, 89-63-4; 2-naphthylacetonitrile, 7498-57-9; 9-methylfluorene, 2523-37-7; 1,1,3-triphenyl-2-aza-1-propene, 7699-79-8; 9-*tert*-butylfluorene, 17114-78-2; 9-(*m*-chlorophenyl)xanthene, 58208-48-3; 9-phenylxanthene, 3246-80-8; diphenylyldiphenylmethane, 33661-35-7; triphenylmethane, 519-73-3; trifluoromethanesulfonamide, 421-85-2; malononitrile, 109-77-3; *p*-cyanobenzyl trifluoromethyl sulfone, 73622-52-3; *m*-dithiane 1,1,3,3-tetraoxide, 26413-18-3; bis(phenylsulfonyl)methane, 3406-02-8; 1,1-bis(ethylsulfonyl)ethane, 32341-85-8; bis[*m*-(trifluoromethyl)benzyl] sulfone, 34277-85-5; benzyl phenyl sulfone, 3112-88-7; diphenylamine, 122-39-4; benzyl methyl sulfone, 3112-90-1; *p*-chlorophenyl methyl sulfone, 98-57-7; methyl phenyl sulfone, 3112-85-4; salicyclic acid, 69-72-7; benzoic acid, 65-85-0; 4-nitrophenol, 100-02-7; 4-acetylphenol, 99-93-4; 3-chlorophenol, 108-43-0; phenol, 108-95-2; benzoylhydrazide, 613-94-5; 2-(benzylthio)acetophenone, 2408-88-0; acetylacetone, 123-54-6; dibenzoylmethane, 120-46-7; nitromethane, 75-52-5; acetophenone, 98-86-2; fluorenone, 486-25-9; 2,4-dichlorophenylhydrazine, 13123-92-7.

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(48) The NMP analysis made at Phillips was the following: NMP = 99.58%, lights = 0.10%, mol wt - 113 = 0.16%, 1,3-dimethylpyrrolidin-2-one = 0.13%, mol wt - 127 = 0.03%.

(49) The impurity present in 99.6% NMP that reacts with base is presumably butyrolactone, although chromatographic analysis indicates that its concentration in the sample prior to distillation was <0.001 area %.

(50) Kolthoff and Knecht found that methylamine could not be completely removed from *N*-methylacetamide (NMA) by fractional distillation at atmospheric pressure, although the boiling range of NMA was 204–206 °C. Methylamine was removed by distillation from H_2SO_4 at reduced pressure. Knecht, L. A.; Kolthoff, I. M. *Inorg. Chem.* **1962**, *1*, 195–203.