Dissociation Constants of Uncharged and Monovalent Cation Acids in Dimethyl Sulfoxide[1]

I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik

Contribution from the School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received August 3, 1967*

Abstract: Dissociation constants in dimethyl sulfoxide (DMSO) of various uncharged acids, monovalent cation acids, and some sulfonephthaleins have been determined. For uncharged acids, the anions of which have a localized charge, the difference between $\mathrm{p}K^{\mathrm{d}}_{\mathrm{HA}}$ in acetonitrile (AN) and DMSO is 9.7 to 10. For acids, the undissociated forms of which have intramolecular hydrogen bonding in AN, the difference is of the order of 11.5. This larger difference is attributed to breaking of these bonds by the strongly protophylic aprotic solvent DMSO. For ammonium and aliphatic amine cations, $\Delta\mathrm{p}K^{\mathrm{d}}_{\mathrm{BH^+}}$ in AN and DMSO varies between 6 and 10, whereas $\Delta\mathrm{p}K^{\mathrm{d}}_{\mathrm{BH^+}}$ in AN and water is 7.5 ± 0.3. Taking the logarithm of the medium activity coefficient $\log \gamma_{\mathrm{H^+}}$ in DMSO with reference to water equal to -1.5 ± 0.5 yields $\log \gamma_{\mathrm{H^+}}$ in AN with reference to water of $+7.9$ as derived from $\Delta\mathrm{p}K^{\mathrm{d}}_{\mathrm{HA}}$ of carboxylic acids. Based on these values a medium activity coefficient of the order of 1 of the picrate ion is found between AN and water. Using solubility products of potassium picrate in water and AN, a value of $\log \gamma_{\mathrm{K^+}}$ of 1.3 ± 0.5 in AN with reference to water was obtained. Because of hydrogen bonding of DMSO with acids, values of homoconjugation constants $K^{\mathrm{f}}_{\mathrm{HA_2^-}}$ in DMSO are some 100 times smaller than in AN. In isodielectric aprotic solvents the difference between $\mathrm{p}K^{\mathrm{d}}_{\mathrm{HA}}$ gives a better indication of the difference in basicity of the solvents than the difference between $\mathrm{p}K^{\mathrm{d}}_{\mathrm{BH^+}}$.

In exploratory work the dissociation constant of several uncharged acids and one cation acid in dimethyl sulfoxide has been determined.[2] In the present paper the dissociation constant of quite a number of acids of the above type and also a few sulfonephthalein indicators has been determined with an accuracy much greater than that in the preliminary study. The data obtained in the protophylic aprotic solvent DMSO have been compared with those obtained with uncharged acids[3] and with monovalent cation acids[4] in the protophobic aprotic solvent acetonitrile (AN) and also with those in water. The previously reported[2] preliminary value of $\mathrm{p}K^{\mathrm{d}}_{\mathrm{HA}}$ of benzoic acid in DMSO of 10.0 has been adopted by Parker[5] as a standard reference value. Actually in the present work this value is found to be 11.0 instead of 10.0.

In the present investigation the homoconjugation constant $K^{\mathrm{f}}_{\mathrm{HA_2^-}} = [\mathrm{HA_2^-}]/[\mathrm{A^-}][\mathrm{HA}]$ of several acids has also been determined. An estimate has been made of the medium activity coefficient of the proton in DMSO and in AN with reference to water and also of the picrate ion in AN (*vs.* water).

Experimental Section

Dimethyl sulfoxide (DMSO), Fisher certified reagent grade product, was purified as reported previously.[2] The water content of the purified solvent as found by Karl Fischer titration was less than 0.005%. The specific conductance of the solvent was about 1.0×10^{-7} ohm^{-1} cm^{-1}. The acid content determined by titration with thymol blue was found to be of the order of 4.0×10^{-6} *M* or less. The solvent was stored in dark bottles and protected from moisture. Acetonitrile, AN, was purified and preserved as described before.[6]

Solutions of perchloric acid in acetic acid and of perchloric acid monohydrate in nitromethane were prepared as described elsewhere.[7]

2,6-Dinitrophenol, 2,6-di-*t*-butyl-4-nitrophenol, *o*-nitrophenol, *p*-nitrophenol, phenol, and their respective tetraalkylammonium salts were prepared and purified as similarly as reported before.[3c] 4-Chloro-2,6-dinitrophenol obtained from Eastman Organic Chemicals was recrystallized as described previously.[2] Tetraethylammonium 4-chloro-2,6-dinitrophenolate was prepared by titrating potentiometrically with the glass electrode a solution of the nitrophenol in ethanol with aqueous tetraethylammonium hydroxide. The solution was evaporated to dryness and the residue, after washing with anhydrous ether to remove the excess of phenol, recrystallized from ethyl acetate and petroleum ether "B" (bp 60–80°) mixture and dried under vacuum at 70°. The salt was found to have an assay of 99% as found from titration in AN with standard perchloric acid solution in acetic acid using dibromothymolbenzein as indicator. Diethylbarbituric, benzoic, salicylic, and 3,5-dinitrobenzoic acids and their corresponding tetraalkylammonium salts were prepared and purified as before.[3a,8]

2,6-Dihydroxybenzoic acid obtained from K and K Laboratories, Inc., was recrystallized from water and dried under vacuum at 70°. Its tetraethylammonium salt was prepared by titrating potentiometrically a solution in ethanol with aqueous tetraethylammonium hydroxide. The solution was evaporated to dryness and the residue was recrystallized twice from ethanol–ethyl acetate mixture (1:10). The crystals were dried *in vacuo* at 50°. Titration in AN with perchloric acid with dibromothymolbenzein as indicator gave an assay of 99%. Acetic acid, Baker's analyzed reagent, was purified as described elsewhere.[9]

Tetraethylammonium acetate was prepared by adding to 12 g of tetraethylammonium bromide in 100 ml of ethanol to the equivalent amount of silver nitrate. To the filtrate an equivalent amount of potassium acetate (5.6 g) was added. The precipitate of potassium nitrate was filtered off and the filtrate evaporated to dryness. The residue was recrystallized three times from a mixture of 1:100 ethanol–ethyl acetate. The crystals were dried overnight *in vacuo* at 40°. Titration in AN with perchloric acid using dibromothymolbenzein as indicator yielded an assay of 99.2%.

Bromcresol green, bromthymol blue, dibromothymolbenzein, phenol red, thymol blue, phenolphthalein, dimethylaminoazobenzene, and methyl red were the same samples as reported previously.[10]

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[1] This research was supported by a grant from the National Science Foundation.

[2] I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.*, 1, 189 (1962).

[3] (a) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, 70, 856 (1966); (b) *J. Am. Chem. Soc.*, 87, 4428 (1965); (c) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *ibid.*, **88**, 5430 (1966).

[4] J. F. Coetzee and G. R. Padmanabhan, *ibid.*, **87**, 5005 (1965).

[5] B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *ibid.*, **88**, 1911 (1966).

[6] I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *ibid.*, **83**, 3927 (1961).

[7] I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *Anal. Chem.*, **39**, 1627 (1967).

[8] I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **85**, 426 (1963).

[9] S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 2974 (1956).

[10] I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *Anal. Chem.*, **39**, 315 (1967).

Stock solutions (1.0×10^{-3} M) of the indicators were prepared in DMSO.

Ammonia gas, generated by mixing AR grade ammonium chloride and sodium hydroxide, was passed through DMSO, and the solution after diluting ten times with water was titrated with standard hydrochloric acid, using the mixed indicator methyl red and bromcresol green.

Ethylamine obtained from the Matheson Co. was passed through DMSO and the solution titrated in the same way as that of ammonia. Tetramethylguanidine (American Cyanamid Co.) was purified by distillation under dry nitrogen at atmospheric pressure. The middle fraction, boiling at 160-161°, was collected.

Tetramethylguanidinium picrate was prepared by titrating potentiometrically a saturated solution of picric acid in ethanol with tetramethylguanidine until the end point. The solution was evaporated to a small volume. The crystals which separated on cooling were recrystallized from a 1:1 mixture of ethanol and petroleum ether "B." The crystals were dried *in vacuo* at 50°.

Triethylamine,[8] *n*-butylamine,[8] di-*n*-butylamine, pyridine,[11] aniline,[11] and lutidine[11] were purified as before, and perchlorates of triethylamine,[10] aniline,[10] pyridine,[7] and *n*-butylammonium picrate[8] were prepared and purified as described previously. Diethylamine (Baker's analyzed reagent) and tri-*n*-butylamine (Eastman Organic Chemicals) were used without further purification. Equimolar mixtures of amines and their perchlorates in DMSO were prepared by half-neutralizing the base with perchloric acid monohydrate (in nitromethane).

Conductometric Measurements. The conductance cell and conductivity bridge were the same as described before.[8] All measurements were made at 25°.

Spectrophotometric Measurements. A pair of 1-cm glass-stoppered quartz cells was used for all spectrophotometric measurements. Other experimental details are the same as reported before.[10] The molar absorptivities of the red forms of dimethylaminoazobenzene and methyl red were determined in 3.5 M sulfuric acid; the blue forms of bromcresol green, dibromothymolbenzein, bromthymol blue, thymol blue, and the red forms of phenol red and phenolphthalein were obtained in about 5.0×10^{-3} M tetrabutylammonium hydroxide. The molar absorptivities of the indicators at the designated wavelength at which the measurements were taken were found to be: 4-chloro-2,6-dinitrophenol, ϵ_{482} 9.7×10^3; 2,6-dinitrophenol, ϵ_{475} 1.20×10^4 and ϵ_{520} 1.22×10^3; dimethylaminoazobenzene, ϵ_{540} 1.62×10^4; methyl red, ϵ_{560} 1.24×10^4; bromcresol green, ϵ_{630} 6.51×10^4; dibromothymolbenzein, ϵ_{650} 6.25×10^4; bromthymol blue, ϵ_{638} 6.19×10^4; phenol red, ϵ_{583} 1.08×10^5; thymol blue, ϵ_{622} 5.33×10^4; phenolphthalein, ϵ_{578} 11.5×10^4; and picric acid, ϵ_{385} 1.92×10^4. Beer's law was found to hold at least up to 5.0×10^{-3} M solutions of all indicators. The absorbance due to other forms of the above indicators were found to be negligible at the wavelengths used.

Potentiometric Measurements. A Beckman, 40495, E-2 glass electrode was used for all emf measurements. The glass electrode gave a response of 59.1 mv/pH in aqueous solutions with reference to 0.05 M potassium acid tartrate and Beckman pH 7.0 buffer. When not in use, the electrode was stored in water. The reference electrode was a flowing junction silver-0.01 M silver nitrate (in DMSO) half-cell as designed by Kolthoff and Reddy.[2] Other experimental details are similar to those reported earlier.[3a] In general, stable potentials were obtained within 10 min, except for phenolate and acetate mixtures in which about 45 min are required.[12,13]

Results

Calculations of K^{d}_{HA}, $K^{d}_{BH^+}$, and $K^{f}_{HA_2^-}$ were made from conductometric, potentiometric, and spectrophotometric data as described in previous publications.[3a-c] The Debye-Hückel limiting law, $-\log f = 1.12\sqrt{\mu}$, was applied in solutions having an ionic strength <0.003, while the extended form, $-\log f = 1.12\sqrt{\mu}/(1 + 3.9 \times 10^7 a \sqrt{\mu})$, a taken as 6 A, for organic anions was used at higher ionic strengths.

Calibration of the Glass Electrode. In order to calibrate the glass electrode it was necessary to have available buffer solutions of known pa_H. For this purpose mixtures of 2,6-dinitro- and 2,6-dinitro-4-chlorophenol and their tetraethylammonium salts have been used. The pa_H of each mixture was calculated in the conventional way after the determination of the dissociation constants of the nitrophenols. These constants were determined conductometrically and also spectrophotometrically.

Dissociation constants calculated from conductivity data are presented in Table I. The constants calculated from spectrophotometric data are presented in Table II. Excellent agreement is obtained between the two methods. The average value of pK^{d}_{HA} equal to 3.54 for 2,6-dinitro-4-chlorophenol agrees satisfactorily with the value of 3.65 reported by Kolthoff and Reddy.[2]

Table I. Conductivity of Nitrophenols

Concn of nitrophenol, $M \times 10^3$	Λ	K^{d}_{HA}[a] $\times 10^4$
	2,6-Dinitrophenol	
1.0	3.89	1.6
1.87	2.94	1.6
3.17	2.31	1.6
7.52	1.48	1.5
13.3	1.09	1.5
20.6	0.89	1.5
27.3	0.79	1.5
	$\Lambda_0 = 32.0$	Av 1.5×10^{-4}
	2,6-Dinitro-4-chlorophenol	
0.75	14.9	3.4
1.5	11.7	3.4
3.0	9.0	3.2
6.0	6.5	3.2
8.9	5.6	3.1
19.2	4.1	3.2
38.0	3.0	3.2
88.5	2.0	3.2
	$\Lambda_0 = 30.0$	Av 3.2×10^{-4}

[a] Activity coefficient taken as unity and Onsager corrections neglected in all cases.

Table II. Spectrophotometry of Nitrophenols

Concn of nitrophenol, $M \times 10^5$	$[I^-]$, $M \times 10^5$	f^2	K^{d}_{HA} $\times 10^4$
	2,6-Dinitrophenol		
1.0	1.11[a]	0.94	0.13
4.08	2.35	0.92	0.13
5.35	2.77	0.90	0.14
7.70	3.3	0.89	0.13
11.3	4.23	0.88	0.15
13.9	4.92	0.86	0.15
			Av 14×10^{-5}
	2,6-Dinitro-4-chlorophenol		
1.9	1.79[b]	0.99	3.0
3.76	3.29	0.98	2.3
4.9	4.34	0.98	3.4
6.03	5.21	0.97	3.3
7.52	6.26	0.96	3.1
9.42	7.56	0.96	3.1
11.3	8.73	0.95	3.1
			Av 3.1×10^{-4}

[a] Wavelength taken, 520 mμ. [b] 482 mμ.

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(11) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **87**, 1004 (1965).

(12) A similar long period for attainment of constant potential in solutions of high pH was encountered by Ritchie.[13]

(13) C. Ritchie and R. Uschold, *ibid.*, **89**, 1721 (1967).

Table III. pK^{d}_{HA} and $K^{f}_{HA_2^-}$ of Uncharged Acids (D = DMSO)

Acid	DMSO (pK^{d}_{HA})$_D$	 $K^{f}_{HA_2^-}$ $\times 10^{-1}$	AN (pK^{d}_{HA})$_{AN}$	 $K^{f}_{HA_2^-}$ $\times 10^{-3}$	(pK^{d}_{HA})$_W$	pK^{d}_{AN-W}	pK^{d}_{D-W}	pK^{d}_{AN-D}
Picric	∼−1.0	0	11.0	0.002	0.3	10.7	−1.3	∼12.0
2,6-Dihydroxy-benzoic	3.1	0	12.6	0.4	1.2	11.4	1.9	9.5
4-Chloro-2,6-di-nitrophenol	3.5	0	15.3	0	3.0	12.3	0.5	11.8
2,6-Dinitrophenol	4.9	0	16.45	0	3.6	12.8	1.3	11.5
Salicylic	6.8	3	16.7	2	3.0	13.7	3.8	9.9
3,5-Dinitrobenzoic	7.4	2.3	16.9	10	2.8	14.1	4.6	9.5
2,6-Di-*t*-butyl-4-nitrophenol	7.6	0	19.0	0	7.2	11.8	0.4	11.4
3,5-Dinitrophenol	10.6	3	20.5	44	6.7	13.8	3.9	9.9
p-Nitrophenol	11.0	4	20.7	5	7.2	13.5	3.8	9.7
o-Nitrophenol	11.0	6	22.0	0.10	7.2	14.8	3.8	11.0
Benzoic	11.1	6	20.7	4	4.2	16.5	6.9	9.6
Acetic	12.6	3	22.3	4.7	4.8	17.5	7.8	9.7
5,5-Diethyl-barbituric	13.0	0	23.4	0.040	8.0	15.4	5.0	∼10.4
Phenol	16.4	40	27.2	11	10.0	17.2	6.4	∼10.8

For the sake of brevity the results of the calibration of the glass electrode are presented only in the form of a graph in Figure 1. The best line with a slope of 59.1 mv has been drawn through the experimental points. $E°$ of our electrode was found equal to +0.185 v.

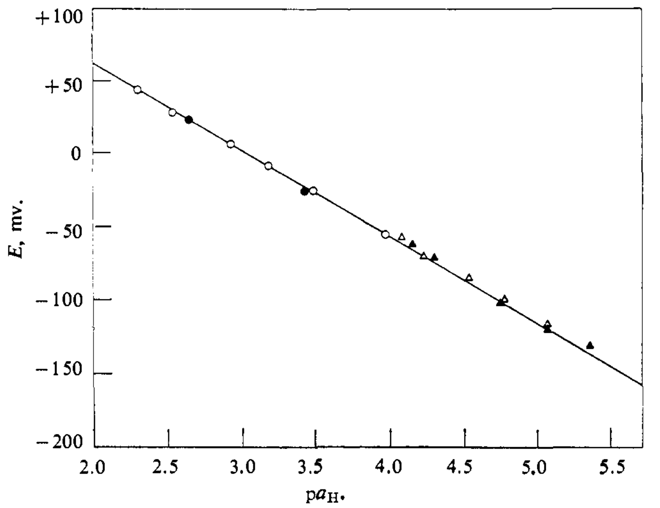

Figure 1. Calibration of the glass electrode in mixtures of nitrophenols and their tetraethylammonium salts in DMSO: △, 1.30 × 10^{-3}; and ▲, 1.41 × 10^{-2} *M* tetraethylammonium 2,6-dinitrophenolate; ○, 3.64 × 10^{-3}, and ●, 1.04 × 10^{-2} *M* tetraethylammonium 2,6-dinitro-4-chlorophenolate (concentration of nitrophenol 6 × 10^{-4} to 5 × 10^{-2} *M;* slope 59.1 ml).

Dissociation Constants of Uncharged Acids. With the exception of picric acid and the two dinitrophenols discussed above, the dissociation constants of the other uncharged acids, tabulated in Table III, were calculated from potentiometrically determined pa_H values of mixtures of the acids and their tetraalkylammonium salts at various salt concentrations (Figure 2). It is quite evident from the curvature of the plots in Figure 2 that homoconjugation between the anion of the acid and the undissociated acid occurs. The homoconjugation constants, calculated in the same way as described in a previous paper in acetonitrile,[3b] are also introduced into Table III. Kolthoff and Reddy[2] had already concluded that acetic acid can homoconjugate with its anion in DMSO, and they had estimated the value of the homoconjugation constant to be 1.0 × 10^2. Omitted in Figure 2 are the data of 2,6-dihydroxybenzoic acid and of 2,6-di-*t*-butyl-4-nitrophenol. These acids do not homoconjugate with their anions in DMSO.

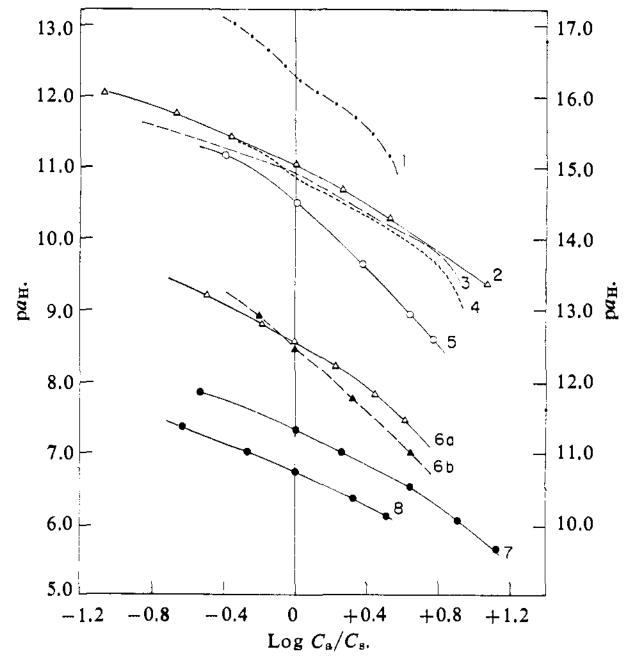

Figure 2. Plots of pa_H *vs.* log C_a/C_s in mixtures of acids and their tetraalkylammonium salts: (1) phenol, C_s = 5.0 × 10^{-3} *M;* (2) benzoic acid, C_s = 5.70 × 10^{-3} *M;* (3) *p*-nitrophenol, C_s = 7.91 × 10^{-3} *M;* (4) *o*-nitrophenol, C_s = 1.0 × 10^{-2} *M;* (5) 3,5-dinitrophenol, C_s = 1.28 × 10^{-2} *M;* (6a) acetic acid, △, C_s = 2.90 × 10^{-3} *M;* (6b) C_s = 9.0 × 10^{-3} *M;* (7) 3,5-dinitrobenzoic acid, C_s = 1.1 × 10^{-2} *M;* and (8) salicylic acid, C_s = 4.61 × 10^{-3} *M.* Right-hand scale for acetic acid and phenol; left-hand scale for others.

As a check on the reliability of the calibration curve of the glass electrode, we also have measured the dissociation constant of salicylic acid in mixtures of the acid and its tetraalkylammonium salt spectrophotometrically, using 2,6-dinitrophenol as indicator. Results are given in Table IV. Since the concentration of salt is very small,

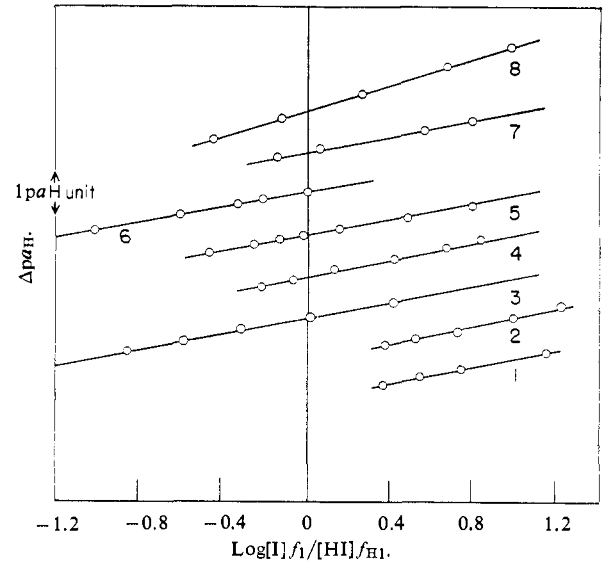

Figure 3. pK^d_{HI} of indicators in DMSO: (1) *p*-dimethylaminoazobenzene, (2) methyl red, (3) bromcresol green, (4) dibromothymolbenzein, (5) bromthymol blue, (6) phenol red, (7) thymol blue, and (8) phenolphthalein.

homoconjugation was neglected in the calculation of pK^d_{HSal}. A value of pK^d_{HSal} equal to 6.7 was obtained in satisfactory agreement with the potentiometric value, 6.8.

Picric acid has a very large dissociation constant. Kolthoff and Reddy[2] estimated its value from spectrophotometric measurements in 2–4 *M* sulfuric acid solutions in DMSO, assuming that sulfuric acid at these concentrations is completely dissociated as a monoprotic acid. We carried out spectrophotometric measurements using two sulfonic acids, assuming that these acids are completely dissociated at the concentrations used. The results are reported in Table V. The constant given here is a concentration constant. It would seem that the constant of 10 ($pK = -1.0$) is a maximum value, because it is doubtful whether the two sulfonic acids are completely dissociated into the ions at the concentrations used. Moreover, the values reported are concentration "constants." It seems fair to conclude that the p*K* of picric acid in DMSO is of the order of −0.5.

Table IV. Spectrophotometric Determination of pK^d_{HA} of Salicylic Acid[a]

C_{HSal}, $M \times 10^2$	A_{475}	pa_H	pK^d_{HSal}[b]
0.32	0.78	6.1	6.73
0.714	0.73	5.6	6.7
1.19	0.68	5.4	6.7
1.98	0.615	5.2	6.7
3.17	0.525	5.1	6.7

[a] 6.9×10^{-5} *M* 2,6-dinitrophenol as indicator; $C_s = 7.6 \times 10^{-4}$ *M* Et_4NSal, $f = 0.93$, cell path length 1.00 cm. [b] $pK^d_{HI} = 4.8$.

$pK^d_{BH^+}$ of Monoprotonated Bases. Values of $pK^d_{BH^+}$ entered in Table VI were obtained from potentiometric measurements of equimolar mixtures of the uncharged base and its perchlorate or picrate. The picrates were those of tetramethylguanidine and *n*-butylamine; the rest were perchlorates.

Table V. Concentration Dissociation Constant of Picric Acid from Spectrophotometric Data in Solutions of Methane or 2,5-Dichlorobenzenesulfonic Acid

Concn, $M \times 10$	A_{385}[a]	pK_{HI}
	MSA	
4.5	0.69	−0.90
8.9	0.662	−0.95
14.9	0.64	−1.02
22.4	0.612	−1.07
	DClBSA	
4.9	0.69	−0.93
9.0	0.664	−0.96

[a] Cell path length 1.00 cm.

Dissociation Constants of Some Sulfonephthaleins. These constants, referring to the color change from yellow to that of the strongly alkaline form, have been determined spectrophotometrically in the same way as had been done in acetonitrile.[10] Plots of Δpa_H ($= pa_H - pK^d_{HI}$) *vs.* log [I]f_I/[HI]f_{HI} are given in Figure 3, and the slopes of the lines with the values of pK^d_{HI} are entered into Table VII. Included is also the indicator dibromothymolbenzein. pK^d_{HI} values of dimethylaminoazobenzene and methyl red presented in Table VI have been determined spectrophotometrically in solutions of the strong acid 2,5-dichlorobenzenesulfonic acid. For both indicators the slopes of the lines (Figure 3) were equal to 1.0.

Discussion

It is of interest to compare dissociation constants of uncharged acids and of monovalent cation acids in the protophobic aprotic solvent acetonitrile (AN) with those in the protophylic aprotic solvent DMSO. Neither of the two solvents is a hydrogen-bond donor, but both are hydrogen-bond acceptors, DMSO being a very much stronger base than AN. The pK^d_{HA} of carboxylic acids and nitrophenols which do not exhibit intramolecular hydrogen bonding is 9.7 ± 0.3 units smaller in the stronger base DMSO than in AN (Table III), and with reference to these two solvents there is no "resolution" of acid strength. This is to be expected because anions in both solvents are not (DMSO, AN) or possibly only slightly solvated (AN). The ratio of the medium activity coefficient of the uncharged acids to that of the anions is assumed to be close to constant. Considering the great uncertainty of ±0.5 in the estimation of the basicity of DMSO as referred to water, the above assumption seems reasonable. The difference in dielectric constant between AN (36) and DMSO (44) is small; it tends to promote the dissociation of uncharged acids in DMSO. However, the effect is small. Using the Born equation, and taking $r_{H^+} = 3$ A and $r_{A^-} = 7$ A, would make the acid 0.3 unit stronger in DMSO than in AN. With $r_{H^+} = 5$ A and $r_{A^-} = 7$ A the difference would amount to 0.2 unit. On an isodielectric basis, the difference in pK^d_{HA} between the two solvents is 9.4 ± 0.3, this being attributed mainly to the difference in their basic strength.

Acids which are characterized by intramolecular hydrogen bonding (*o*-nitro- and 2,6-dinitrophenol) (Table III) have a pK^d_{HA} difference of about 11.5 units between DMSO and AN. The solvent DMSO is such a strong base that it breaks the intramolecular hydrogen

Table VI. $\mathrm{p}K^{d}_{\mathrm{BH^+}}$ of Monoprotonated Bases (D = DMSO)

Amine	$(\mathrm{p}K^{d}_{\mathrm{BH^+}})_{\mathrm{D}}$	$(\mathrm{p}K^{d}_{\mathrm{BH^+}})_{\mathrm{AN}}$	$(\mathrm{p}K^{d}_{\mathrm{BH^+}})_{\mathrm{W}}$	$\Delta\mathrm{p}K^{d}_{\mathrm{AN-W}}$	$\Delta\mathrm{p}K^{d}_{\mathrm{D-W}}$	$\Delta\mathrm{p}K^{d}_{\mathrm{AN-D}}$
Tetramethylguanidine	13.2	23.3	13.6	9.7	−0.4	10.1
n-Butylamine	11.1	18.3	10.6	7.7	0.5	7.2
Ethylamine	11.0	18.4	10.6	7.8	0.4	7.4
Ammonia	10.5	16.5	9.2	7.3	1.3	6.0
Diethylamine	10.5	18.8	11.0	7.8	−0.5	8.3
Di-*n*-butylamine	10.0	18.3	11.3	7.0	−1.3	8.3
Triethylamine	9.0	18.5	10.7	7.8	−1.7	9.5
Tri-*n*-butylamine	8.4	18.1	10.9	7.2	−1.5	9.7
Aniline	3.6	10.6	4.6	6.0	−1.0	7.0
Pyridine	3.4	12.3	5.2	7.1	−1.8	8.9
Methyl red	0.7	10.2	4.9	5.3	−4.2	9.5
Dimethylaminoazobenzene	0.7	10.1	3.3	6.8	−2.6	9.4

Table VII. $\mathrm{p}K^{d}_{\mathrm{HI}}$ of Sulfonephthaleins and Dibromothymolbenzein

Indicator	DMSO						
	slope	$(\mathrm{p}K^{d}_{\mathrm{HI}})_{\mathrm{D}}$	$(\mathrm{p}K^{d}_{\mathrm{HI}})_{\mathrm{AN}}$	$(\mathrm{p}K^{d}_{\mathrm{HI}})_{\mathrm{W}}$	$\Delta\mathrm{p}K^{d}_{\mathrm{AN-W}}$	$\Delta\mathrm{p}K^{d}_{\mathrm{D-W}}$	$\Delta\mathrm{p}K^{d}_{\mathrm{AN-D}}$
Bromcresol green	1.0	7.3	18.5	4.7	13.8	2.6	11.2
Dibromothymolbenzein	1.0	9.5	20.5	~6.7	13.8	2.8	11.0
Bromthymol blue	1.0	11.3	22.3	7.1	15.2	4.2	11.0
Phenol red	1.0	13.7	25.0	7.9	17.1	5.8	11.3
Thymol blue	0.95	~15.3	~27.2	8.9	18.3	6.4	~11.9
Phenolphthalein	1.5	~16.3	~29.2	~9.5	19.7	6.8	~12.9

bonds, thus making them more comparable in DMSO to acids without intramolecular hydrogen bonds. Relative to the latter acids, the acids with intramolecular hydrogen bonding are weaker acids in AN. For example, $\mathrm{p}K^{d}_{\mathrm{HA}}$ in AN of *p*-nitrophenol is 20.7 and of *o*-nitrophenol 22.0, while in DMSO the values are 11.0 and 11.0, respectively. Also, in the hydrogen-bond acceptor water, both acids have about the same dissociation constant.

As in previous work[2] picric acid is found to be quite strong in DMSO, but the presently estimated value of $\mathrm{p}K^{d}_{\mathrm{HA}}$ of the order of −1.0 seems more reasonable than the previous value of −1.9.[2] It is of interest to note that for salicylic and 2,6-dihydroxybenzoic acids $\Delta\mathrm{p}K^{d}_{\mathrm{HA}}$ is 9.9 and 9.5, respectively, and similar to that of benzoic and acetic acids ($\Delta\mathrm{p}K^{d}_{\mathrm{HA}} = 9.7$). This would tend to indicate that the above two substituted benzoic acids do not have intramolecular hydrogen bonding in AN. In this respect we also refer to $K^{f}_{\mathrm{HA_2^-}}$ values of these two acids in AN (Table III).

Parker, *et al.*,[5] concluded that, with the exception of picric acid, acidities of uncharged acids in N,N-dimethylformamide (DMF) correlate roughly with those in DMSO. If more precise values than we have at present of $\mathrm{p}K^{d}_{\mathrm{HA}}$ in DMF were available, a close correlation of acidities in both solvents may be expected, since DMF and DMSO are both protophylic aprotic solvents, the hydrogen-bond-donating properties of DMF being very weak. As has been stated by Parker,[5] no close correlation between acidities in aprotic and protic dipolar solvents, like water or methanol, is found. In protic dipolar solvents, anions of different acids are hydrogen bonded to different extents. From Table III it is clear that there is a distinct "resolution" of acid strength in DMSO with reference to water. For example, $\Delta\mathrm{p}K^{d}_{\mathrm{HA}}$ of salicylic and benzoic acids in water is 1.2 while in DMSO it is 4.3. For acids, the anions of which have a delocalized charge, the difference in acidity between water and DMSO is much less than for acids with anions with a localized charge. For example, $\Delta\mathrm{p}K^{d}_{\mathrm{HA}}$ for 4-chloro-2,6-dinitrophenol between water and DMSO is 0.5, while for 3,5-dinitrobenzoic acid, which has almost the same $\mathrm{p}K^{d}_{\mathrm{HA}}$ of 2.8 in water as the above phenol ($\mathrm{p}K_{\mathrm{w}} = 3.0$), $\Delta\mathrm{p}K^{d}_{\mathrm{HA}}$ is 3.85. Evidently, the 3,5-dinitrobenzoate ion is strongly hydrogen bonded in water.

For cation acids the relation between $\mathrm{p}K^{d}_{\mathrm{BH^+}}$ in AN and DMSO is much less simple than for uncharged acids. From Table VI we see that $\mathrm{p}K^{d}_{\mathrm{BH^+}}$ of ammonium is only 6 units smaller in DMSO than in AN, whereas for tributylammonium the difference is 9.7 units. More puzzling even is that $\Delta\mathrm{p}K^{d}_{\mathrm{BH^+}}$ between AN and water for ammonium and the aliphatic ammonium ions is almost constant, 7.5 ± 0.3,[4] whereas ammonium in DMSO is a weaker acid by 1.3 units and tributylammonium a stronger acid by 2.45 units than in water. Both DMSO and water hydrogen bond the cation acids, while water as a hydrogen bond donor can also hydrogen bond the undissociated base, the latter effect tending to increase the acid strength of $\mathrm{BH^+}$ in water. The effect of the number of alkyl groups on $\mathrm{p}K^{d}_{\mathrm{BH^+}}$ of aliphatic ammonium ions in water is not well understood.[14] In DMSO the effect is still more puzzling. Whereas in water diethylamine is a stronger base by 1.8 units than ammonia, we find both to be of the same strength in DMSO. Still more striking is the difference between ammonium and tributylammonium (or triethylammonium) in both solvents. In water tributylamine is a stronger base by 1.7 units than ammonia, whereas in DMSO it is a weaker base by 2.1 units.

There is little doubt that DMSO is a considerably stronger base than water. Values of $\mathrm{p}K^{d}_{\mathrm{BH^+}}$ of water[15] and of DMSO in AN have been reported and found equal to 2.5 and 5.8, respectively, corresponding to a difference of 3.3 units. In unpublished work (M. K.

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(14) See R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N.Y., 1959: see especially p 177.

(15) I. M. Kolthoff and S. Ikeda, *J. Phys. Chem.*, **65**, 1020 (1961).

C., Jr.) the p$K^d_{H^+(H_2O)_4}$ in AN was found to be of the order of 4, thus making the difference in basicity between DMSO and water of the order of 1.8. It is a coincidence that from H_0 values it has been concluded[13,16] that DMSO is 1.8 units more basic than water; we find from H_0 measurements with *p*-dimethylaminoazobenzene a value of 2.65. This large value may be partly accounted for by the slight solubility of the indicator in water and its much greater solubility in DMSO.

Taking into account the relative concentrations of water in water and of DMSO in DMSO, it seems reasonable to conclude that DMSO is some 1.5 ± 0.5 units more basic than water, corresponding to a logarithm of the medium activity coefficient, log γ_{H^+} of -1.5 ± 0.5 in DMSO with reference to water.

In earlier work[6] we have determined H_0 with Hammett indicators in AN and found a value of +5. On the other hand, if the difference in basicity between AN and water were based on the $\Delta pK^d_{BH^+}$ of ammonium and substituted aliphatic ammonium ions, a value of 7.5 ± 0.3 units would be found. It is interesting that we find a similar value of 7.9 from the difference of 9.4 in pK^d_{HA} of uncharged acids in AN and DMSO (corrected for dielectric constant effect) and the basicity of DMSO of 1.5 units as referred to water.

Taking the log γ_{H^+} of the proton in AN as referred to water equal to $+7.7 \pm 0.5$, we can calculate in AN the medium activity coefficient of anions of acids, provided the distribution coefficient between water and AN of the uncharged acids is known. From the solubility in water of picric acid equal to 5.7×10^{-2} M[17] and its dissociation constant of $10^{-0.33}$,[18] we calculate a solubility in water of undissociated picric acid of 6×10^{-3} M. In AN we have determined the solubility and found it equal to 3.0 M, corresponding to log γ_{HPi} of -2.7 assuming the molarity in AN is equal to the activity. Considering the uncertainty in the value of log γ_{H^+} no correction has been made for the difference between molarity and molality. From the value of pK^d_{HPi} of 0.35 in water and 11.0 in AN, we then find the logarithm of the medium activity coefficient of the picrate ion log $\gamma_{Pi^-} = 10.65 - 7.7 - 2.7 = +0.25 \pm 0.5$. Hence, it appears that the medium activity coefficient in AN with reference to water of the picrate ion with its delocalized charge is close to 1. If the value of log $\gamma_{H^+} = 5$, as derived from the Hammett acidity function,[6] were taken, a value of the order of log γ_{Pi^-} of +2.4 would have been found, which is highly improbable. From the solubility product of potassium picrate in water, pK_{SP} = 3.2,[19] and in AN, pK_{SP} = 4.55,[3b] we find log γ_{K^+} in AN of $+1.3 \pm 0.5$, no correction being made for the difference between molarity and molality. Using an entirely different approach, Coetzee and Campion[20] arrive at a value of log γ_{K^-} of 2.8, as compared to a value of -1.5 based on Strehlow's approach.[21] Coetzee's value seems more reasonable, as the potassium ion undoubtedly is more solvated in water than in AN.

The difference in pK^d_{HA} yields a better value for the difference in basicity of two isodielectric aprotic solvents than the difference in p$K^d_{BH^+}$. From Table III it is noted that the formation constant of the homoconjugate ion $K^f_{HA_2^-}$ is of the order of 100 times smaller in DMSO than in AN. The reason is that the acid is not hydrogen bonded in AN, while in DMSO there is competition between solvent and A^- to hydrogen bond the acid.

$$A^- + D\cdots HA \rightleftharpoons A^-\cdots HA + D \quad (D = DMSO)$$

The much smaller value of $K^f_{HA_2^-}$ in DMSO than in AN is responsible for a much different shape of conductometric and potentiometric titration curves of several acids in both solvents as we have observed in unpublished work. Contrary to the behavior in AN,[22] but similar to that in water, sulfonephthaleins do not exhibit a color change from yellow to colorless in DMSO. The monoprotic acid dibromothymolbenzein has the same ΔpK of 11 in AN and DMSO as the ΔpK_2 of the sulfonephthaleins in their color change from monovalent yellow anions to the strongly colored divalent anions. Apparently, the charges in these divalent ions are delocalized and separated enough to make their medium activity coefficients of the same order of magnitude as that of their univalent ions. The pK value of thymol blue is somewhat uncertain, because of the uncertainty in pH of the phenolate buffers used in the determination of its pK. Phenolphthalein does not behave like a simple monoprotic acid; the same behavior is found in other solvents.

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