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Acid-Base Strength in Dimethyl Sulfoxide

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Dimethyl sulfoxide (DMSO) has an autoprolysis constant of the order of 5×10^{-18} . Its basic strength is comparable to that of water; hydrochloric and sulfuric acids are completely dissociated in this solvent, whereas the acid di-*n*-butylammonium ion has a dissociation constant about ten times as large as that in water. Water is an extremely weak base in DMSO. The degree of dissociation of several uncharged acids is quite abnormal. The dissociation constant of picric acid is of the order of 500 times greater than that in water, while that of 2,6-dinitro-4-chlorophenol is of the same order of magnitude in both solvents. Extremely large stabilization of the nitrophenolate ions in DMSO is indicated. On the other hand, acetic acid has a constant which is about 10^{-7} as large in DMSO as in water, while that of benzoic acid is 10^{-8} as large. Brom cresol green and brom thymol blue have constants about $1/250$ as large in DMSO as in water, a value close to that predicted for a univalent negatively charged acid on the basis of the difference in dielectric constant between the two solvents. The univalent bisulfate ion has a constant 10^{-7} as large in DMSO as in water.

Dimethyl sulfoxide (DMSO) is a solvent which is highly associated and moderately viscous¹ and has a dielectric constant of 46.7. The molecule is pyramidal² and highly polar ($\mu = 3.9$ debyes). DMSO contains non-bonded electrons and should exhibit basic properties. This is confirmed in the present study. DMSO is known to form one to one addition compounds with nitric acid³ and Lewis acids.⁴ From polarographic studies^{1,5} it was concluded that perchloric, hydrochloric, and sulfuric (K_1) acids are completely dissociated but that carboxylic acids are very weak, while the second dissociation constant of sulfuric acid is much smaller than that in water. From the fact that amounts of water up to 1% had no effect on the polarographic waves of strong acids, it was concluded that water and DMSO are similar as

far as differentiation of the strength of acids is concerned. This is confirmed in the present work which deals with an exploratory study of the order of strength of several acids. The effect of ionic strength upon acid-base equilibria has been neglected. From the dielectric constant, the limiting Debye-Hückel expression is calculated to be $-\log f_{\pm} = 1.11 z_i^2 \sqrt{\mu}$. The maximum value of the ionic strength at which the expression holds is much smaller than in aqueous solution. Although much time was spent in obtaining solvent free of impurities, it has been impossible to remove traces of acidic and basic impurities. For this reason it was necessary to conduct experiments in well buffered solutions of appreciable ionic strength.

Instead of making inexact corrections for ionic strength effects, equilibria have been expressed in terms of concentration constants.

Dissociation constants were estimated by the indicator method, the concentration ratio of acid to basic form of the indicator being determined spectrophotometrically. E.m.f. measurements

(1) For tabulation of some physical properties, see I. M. Kolthoff and T. B. Reddy, *J. Electrochem. Soc.*, **108**, 980 (1961).

(2) O. Bastiansen and H. Viervoll, *Acta Chem. Scand.*, **2**, 702 (1948).

(3) A. Saytzeff, *Ann. Chem. Liebigs*, **144**, 150 (1867).

(4) F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960).

(5) T. B. Reddy, Ph.D. Thesis, University of Minnesota, 1960.

have been made with a glass electrode to substantiate the results obtained with indicators. In order to estimate the autoprotolysis constant, the dissociation constant of a weak base has been estimated by the conductance method.

Experimental

Solvent.—DMSO (Stepan Chemical Co., Chicago, Ill.) was shaken overnight with activated alumina (Woelm chromatographic grade-activity I) which had been ignited previously to 600°. The solvent then was siphoned into a distillation flask and vacuum fractionated at a pressure of a few millimeters through a 20-in. column packed with porcelain saddles. A first fraction amounting to 10% of the total was rejected and the second fraction of about 80% was collected. This fraction was subjected to the same treatment twice or more until the specific conductance was 2×10^{-8} ohm⁻¹ cm.¹ or less and the water content 0.01% (w/w) or less as determined by the Karl Fischer method.

Solutions of Acids and Bases.—A solution of sulfuric acid in DMSO was obtained by slowly adding concentrated reagent material to DMSO cooled in an ice-bath. Great heat is evolved by the dissolution of the acid, and decomposition of the solvent, probably giving a mercaptan, may result if the temperature of the solution is allowed to rise much above room temperature. Solutions of hydrogen chloride were prepared by scrubbing Matheson hydrogen chloride through concentrated sulfuric acid and slowly bubbling it into the ice-cooled solvent. Only slow decomposition of the hydrogen chloride solution was noted when prepared in this manner. The conductivity of such a solution was constant for at least a week. All organic acids and their sodium salts were reagent grade. Sodium hydrogen sulfate was a Baker and Adamson product. Mallinckrodt reagent grade sodium acetate was dried at 80° before use. Purified glacial acetic acid was supplied by Dr. T. O. Rouse of this Laboratory. Matheson di-*n*-butylamine was distilled at 738 mm. and the fraction boiling at 155–157° collected. A 1 *M* solution of tetraethylammonium hydroxide—polarographic grade (Southwestern Analytical Chemicals)—was used. Reagent grade chemicals were employed elsewhere.

Indicators.—Indicators were obtained from commercial sources and used as obtained except as noted. Eastman Kodak technical grade 2,6-dinitro-4-chlorophenol was recrystallized first from ethanol and then from 75% ethanol-25% 6 *N* hydrochloric acid and dried in a vacuum desiccator; m. p. 78.5–79.5°.

Spectrophotometric Measurements.—Spectrophotometric measurements were made with a Beckman Model B spectrophotometer. For spectra beyond the range of this instrument, a Beckman Model DU was employed. All measurements were made at ambient temperature. The absorption cells were filled with the aid of calibrated pipets and additions of stock solutions of indicators and acids were made with Gilmont ultramicroburets.

E.m.f. Measurements.—A Beckman No. 290 glass electrode containing an inner silver-silver chloride electrode in an aqueous sodium chloride solution was employed. The reference half-cell was an isolated silver-silver chloride (sat.)-sodium chloride (sat.) electrode in DMSO. A silver-plated platinum wire was placed into a solution saturated with respect to both silver chloride and sodium

chloride. The solubility of silver chloride in DMSO increases in the presence of sodium chloride by the formation of a soluble complex. The glass electrode was stored in water and wiped dry before use. The glass electrode was assembled using a U-tube with a fritted glass disk isolating the compartments. The tube was filled with test solution and the glass electrode dipped into one compartment. Electrolytic contact between the reference electrode and the other compartment was brought about with the aid of a small capillary tube filled with the solution contained in the reference electrode. The e.m.f. was measured with a Beckman Model H *pH* meter. It was often necessary to use a Weston standard cell as a bucking potential in series with the unknown e.m.f. to bring the observed reading on scale.

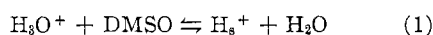
Conductance Measurements.—The conductance cell consisted of lightly platinized electrodes of area 1 cm.² and placed 1 cm. apart. The leads were well separated. The cell constant found by measuring the resistance of an aqueous 1.000×10^{-3} *M* potassium chloride solution was 0.334. All measurements were made at $25.00 \pm 0.05^\circ$. The cell was washed and dried overnight at 50° at a pressure of a few mm. No change of cell constant by drying was observed. The resistance measurements were made with a Leeds and Northrup Jones bridge using an a.c. signal of 1000 c.p.s. and 0.5 volt. A Heathkit oscilloscope was used as a null detector. The cell was filled with a calibrated pipet and addition of solute was made with a Gilmont ultramicroburet. The cell was used for measurement of the conductance of di-*n*-butylamine solutions. The solvent was purged with nitrogen to remove carbon dioxide before adding the base. The solution thus obtained was analyzed by adding a 10-ml. aliquot from the conductance cell to 40 ml. of a 50% ethanol-water mixture and titrating with standard aqueous hydrochloric acid using a *pH* meter with glass and calomel electrodes. The end-point was found by the second derivative method. Because of the large resistance involved, measurements were made with the cell in parallel with a standard resistor. This procedure renders the resistance values less precise.

Results

Indicator Studies.—After extensive testing of many acid-base indicators,⁵ 2,6-dinitro-4-chlorophenol was found suitable for measurement of the ratio of acid to alkaline form in dilute solutions of hydrogen chloride and of sulfuric acid in DMSO. The alkaline form has a yellow color while the acid form is colorless. The concentration of the basic form of the indicator was determined spectrophotometrically at 480 *mμ* and the concentration of the acid form found by difference from the total. Plots of $\log [In^-]/[HIn]$ against *p**cH* gave straight lines of slopes -0.78 and -0.86 for hydrogen chloride and sulfuric acid, respectively, in the concentration range between 5×10^{-5} and 2×10^{-3} *M*. Substitution of concentration with activity would yield slopes closer to one. The *pK* values of the indicator were found to be 3.63 and 3.67, respectively, for the two acids employed.

The results substantiate the conclusion from polarographic work¹ that both hydrogen chloride and sulfuric acid are completely dissociated in DMSO.

Basic Strength of Water.—By spectrophotometric determination of an indicator equilibrium in hydrogen chloride solution containing known amounts of water it is possible to determine the acid dissociation constant $K_{H_3O^+}$ corresponding to the reaction



$$K_{H_3O^+} = \frac{[H_s^+][H_2O]}{[H_3O^+]}$$

in which H_s^+ is the concentration of solvated hydrogen ions in DMSO. It is easily derived⁶ that

$$r = \frac{K_I}{C_a} \left(\frac{C_{H_2O}}{K_{H_3O^+}} + 1 \right) \quad (2)$$

in which r is the ratio of alkaline to acid form of the indicator ($[In^-]/[HIn]$), C_a the analytical concentration of strong acid, and C_{H_2O} the concentration of water. 2,6-Dinitro-4-chlorophenol was used as indicator in $4.41 \times 10^{-4} M$ hydrochloric acid and the value of r determined in the presence of various amounts of water. As demanded by the relation in equation 2, a plot of r vs. C_{H_2O} yielded a straight line which is shown in Fig. 1. The slope of the line K_I/C_a was 0.57, corresponding to $K_I = 2.5 \times 10^{-4}$ or $pK = 3.60$, while the intercept is 0.57, giving $K_{H_3O^+} = 2.2$. Thus in a solution 0.1 M in water $[H_s^+]/[H_3O^+] = 22$, indicating that water in DMSO is a very weak base with a basic strength of the same order of magnitude as that of the solvent. Using a similar

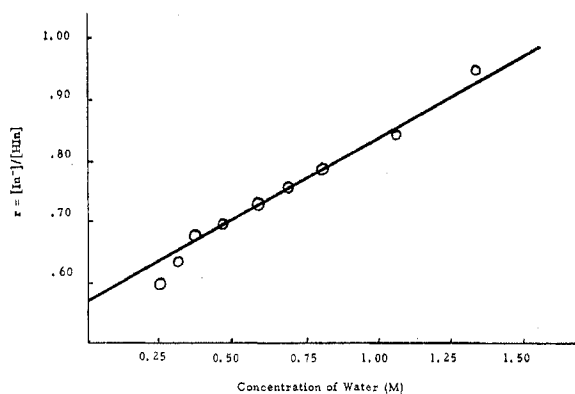


Fig. 1.—Graph of $r = [In^-]/[HIn]$ against concentration of water in a solution which was $4.41 \times 10^{-4} M$ in hydrogen chloride and $3.38 \times 10^{-5} M$ in 2,6-dinitro-4-chlorophenol.

method, Guss and Kolthoff⁶ found a value of $K_{H_3O^+} = 0.23$ in methanol.

Weak Acids.—2,6-Dinitro-4-chlorophenol could be used for the determination of the dissociation constant of salicylic acid but not for weaker acids. For weaker acids, brom cresol green and dibromo-*o*-cresolbenzein were used as indicators. The pK of these indicators was determined in salicylate buffers. The intensity of the color of dibromo-*o*-cresolbenzein in DMSO was found to decrease on standing. For this reason the stock solution was allowed to age for a week before use, after which time there was only little change of color on standing. The pK of benzoic acid was determined in benzoate buffers using dibromo-*o*-cresolbenzein as indicator. The second dissociation constant of sulfuric acid was estimated by preparing a solution $5 \times 10^{-4} M$ in both sodium hydrogen sulfate and sodium sulfate and $2 \times 10^{-5} M$ in dibromo-*o*-cresolbenzein. The ratio of the concentration of the two forms of the indicator was determined and pK_2 calculated in the usual way. The low solubility of sodium sulfate prevented a more extensive study. The pK of brom thymol blue was determined spectrophotometrically in benzoate buffers and this indicator then was employed to estimate the pK of acetic acid in acetate buffers. In general, all graphs of the log of the ratio of the forms of the indicator against pH gave a slope close to 1, except for acetic acid (*v.i.*). The pK of picric acid has been estimated by observing the absorbance by the picrate ion in relatively concentrated solutions of sulfuric acid in DMSO. Spectra were determined⁶ for all indicators in the acid and basic forms except for one-color indicators. Beer's law has been shown to hold for all indicators except picric acid, for which it was not tested. Table I lists the results obtained spectrophotometrically.

Conductance of Di-*n*-butylamine.—In order to estimate the autoprotolysis constant of the solvent, it was necessary to determine the dissociation constant of a weak base in DMSO. Di-*n*-butylamine was selected because it is a rather strong base in water [$pK_{BH^+} = 11.31$]⁷ and is soluble in DMSO. The conductance data for three solutions of the amine are given in Table II.

The dissociation constant of a weak electrolyte normally is obtained from a plot of $1/\Lambda$ against Λc . In this case, such a plot did not give a straight line. For this reason, a value of Λ_0 for the

(6) L. S. Guss and I. M. Kolthoff, *J. Am. Chem. Soc.*, **62**, 1494 (1940).

(7) N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932).

TABLE I
pK VALUES FOR ACIDS AND INDICATORS IN DMSO

Substance	pK (DMSO)	pK (H ₂ O)	ΔpK
Sulfuric acid	Strong	Strong	...
Hydrogen chloride	Strong	Strong	...
Picric acid	-1.9	0.80	-2.7
2,6-Dinitro-4-chloro-phenol	3.65
Salicylic acid	6.9	2.98	3.9
Brom cresol green	7.4	4.90	2.5
Dibromo- <i>o</i> -cresol-benzen	8.6	6.0	2.6
Benzoic acid	10.0	4.20	5.8
Bisulfate ion	9.1	1.92	7.2
Brom thymol blue	10.2	7.30	2.9
Acetic acid	11.4	4.76	6.7
Di- <i>n</i> -butylammonium ion	10.3 ^a	11.31	-1.0

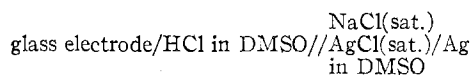
^a From potentiometric measurements.

TABLE II
CONDUCTANCE DATA FOR DI-*n*-BUTYLAMINE IN DMSO

Concn. amine $M \times 10^2$	Specific conduct. due to solvent (ohm ⁻¹ cm. ⁻¹) $\times 10^8$	Specific conduct. due to solute (ohm ⁻¹ cm. ⁻¹) $\times 10^8$	Equivalent conduct. (ohm ⁻¹ cm. ²) $\times 10^2$	$\alpha = \Lambda/\Lambda_0 \times 10^2$	$K = \alpha^2 \times 10^7$
48.6	0.18	7.07	1.41	4.70	1.07
8.36	.25	2.76	3.06	10.0	0.834
0.955	.26	0.88	6.53	21.7	0.450

amine was estimated from conductance data of Sears, Lester, and Dawson.⁸ The value selected was $\Lambda_0 = 30$. The per cent. ionization and dissociation constants then were calculated from simple theory. The value of the dissociation constant varied between 0.5 and 1.1×10^{-7} in the range investigated. A value of $K = 10^{-7}$ was taken as the closest order of magnitude.

E.m.f. Measurements.—Attempts to use a hydrogen electrode in solutions of acids in DMSO failed. Therefore, the glass electrode was employed. The e.m.f. of the system



at varying hydrogen chloride concentrations is given in Table III.

Neglecting activity and liquid junction effects, the theoretical Δe.m.f. upon a tenfold concentration change is 59 mv., while the observed values are greater than this value. However, the liquid junction potential between the reference electrode and test solution may be considerable and cause

(8) P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956).

TABLE III
E.M.F. DATA FOR HYDROGEN CHLORIDE SOLUTIONS

Concn. hydrogen chloride (M)	E.m.f. (v.)	Δe.m.f. (mv.)
4.4×10^{-2}	-0.312	> +71
4.4×10^{-3}	-0.241	
4.4×10^{-4}	-0.173	

some of the deviation from ideal behavior. Since a 0.0441 M hydrogen chloride solution is the closest in ionic composition to that of the reference electrode, the formal potential of the reference, $E^{0'}$, has been calculated from the observed e.m.f. and the concentrations of hydrogen ions from the expression

$$E = E^{0'} - RT/nF \ln [H^+] \quad (3)$$

The calculated value of the formal potential is -0.392 v. The pH of a solution then can be estimated from equation 4.

$$pH = (E - E^{0'})/0.0591 \quad (4)$$

The extent of agreement with the spectrophotometric data was used to judge the validity of equation 4. The electrode system was tested by making e.m.f. measurements on several 1:1 buffers of acids and conjugated bases previously studied. Measurements were made after a steady e.m.f. had been established. The results are given in Table IV.

TABLE IV
E.M.F. MEASUREMENTS ON BUFFER SOLUTIONS OF WEAK ACIDS

Acid	pK (e.m.f.)	pK (spectro.)
Salicylic	6.9	6.9
Benzoic	9.9	10.0
Bisulfate ion	8.8	9.1

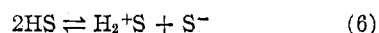
The agreement between the two methods is much better than expected and gives confidence that the values determined with the glass electrode are not much in error.

An estimate was made of the autoprotolysis constant of DMSO by measuring the e.m.f. of the electrode system in a buffer which was 4.82×10^{-2} M in both di-*n*-butylamine and di-*n*-butylammonium chloride and 0.1 M in tetraethylammonium perchlorate. The inert electrolyte was added to increase the conductivity of the solution and to establish a steady e.m.f. rapidly. The observed e.m.f. was +0.213 v. and the pK of

di-*n*-butylammonium ion was calculated to be 10.3. In any solvent

$$pK_s = pK_B + pK_{BH^+} \quad (5)$$

K_s = autoprotolysis constant for an ionization mechanism



in which HS is solvent, H_2S^+ solvated proton, and S^- lyate ion. Using the values obtained for di-*n*-butylamine in DMSO: $pK_s = 7 + 10.3 = 17.3$, or $K_s \sim 5 \times 10^{-18}$. The significance of this result will be discussed later.

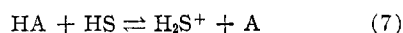
E.m.f. measurements in very dilute solutions of tetraethylammonium hydroxide in DMSO obtained by adding 1 *M* aqueous hydroxide to DMSO gave anomalous results. The solutions eventually turned dark and turbid. Potentiometric titrations of solutions of the hydroxide with hydrogen chloride in DMSO showed that hydroxyl ions slowly react with the solvent to give the lyate ion which apparently attacks the solvent when present in any appreciable amount giving weakly basic products. Details may be found elsewhere.⁵

Discussion

Although this study is of an exploratory nature, some definite conclusions can be drawn regarding abnormal behavior of certain acids in DMSO. A detailed study of each conjugated acid-base system is necessary before a quantitative interpretation can be given.

DMSO has about the same dielectric constant as acetonitrile (AN), but it is a much stronger base. Whereas perchloric, hydrochloric, and sulfuric (K_1) acids are completely dissociated in DMSO, only perchloric acid is strong in AN while hydrochloric and sulfuric acids are weak in AN with dissociation constants of the order of $10^{-8.5}$ and $10^{-7.2}$, respectively.⁹ That DMSO is a relatively strong base as compared to water is substantiated by the fact that water in DMSO behaves like a very weak base while in AN it is a relatively strong base.¹⁰

The dissociation of an acid in an amphiprotic solvent is given by



where HA is the acid, HS is the solvent, H_2S^+ is the solvated proton (lyonium ion), and A is the conjugate base. The equilibrium of an uncharged

acid is greatly affected by two factors: the dielectric constant of the medium and the basic character of the solvent. The effect due to dielectric constant may be estimated from the Born equation.¹¹ If we assume that all species are spheres of radius equal to 2×10^{-8} cm., then the difference in pK of an acid of charge z between water and DMSO is given by

$$\Delta pK = 1.06[1 - z] \quad (8)$$

This expression yields a ΔpK value of 0 for acids with charge +1, of 1.1 with charge type 0, and 2.1 with charge type -1.

We have noted already that DMSO and water are very similar as far as their basic character is concerned and it would be expected therefore that the calculated ΔpK values would give the order of magnitude of the difference of pK in water and DMSO. Values of ΔpK are listed in Table I. The cationic acid di-*n*-butylammonium ion is somewhat stronger in DMSO than in water and exhibits normal behavior. The reported value of pK of di-*n*-butylammonium ion is based on only one measurement. However, potentiometric titration curves of the base with hydrochloric acid in DMSO⁵ were of normal slope and yielded a pK value close to that given in Table I.

Sears, Lester, and Dawson⁸ have pointed out that the Walden product, $\eta\lambda_0$ (η being the viscosity of the solvent), for the picrate ion in DMSO is $0.34 \text{ ohm}^{-1} \text{ cm.}^2 \text{ equiv.}^{-1} \text{ poise}$ and that this value is unusually high. Kraus¹² noted that the Walden product for the picrate ion is unusually high in an electron donor solvent like nitrobenzene ($\eta\lambda_0 = 0.29$) and pyridine ($\eta\lambda_0 = 0.30$). The value in DMSO is considerably higher than in either of these. Apparently the picrate ion possesses unusual stability in DMSO which accounts, at least in part, for the high dissociation constant of picric acid in this solvent. The pK value of 2,6-dinitro-4-chlorophenol in water has not been determined. The pK of 2,6-dinitrophenol in water is 3.70. The addition of a chloro group to the 4-position of this molecule would decrease the electron density in the benzene ring and increase the acidity of the phenolic group. This effect will be small, however, since nitro groups are extremely effective in withdrawing electrons while the halogens do so only weakly. The pK of 2,6-dinitro-4-chlorophenol in water should be slightly less than 3.7 and

(9) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3927 (1961).

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

(11) I. M. Kolthoff and S. Bruckenstein, "Treatise on Analytical Chemistry," Part I, Vol. I, Interscience Publishers, New York, N. Y., 1959, pp. 475-542.

(12) C. A. Kraus, *Ann. N. Y. Acad. Sci.*, **51**, 789 (1949).

is therefore similar to that in DMSO. Apparently the substituted nitrophenolate ions also are quite stable in DMSO and the acid is appreciably dissociated in DMSO.

The ΔpK values of carboxylic acids are all much larger than expected. The largest ΔpK are found with acetic acid (6.7) and benzoic acid (5.8). This cannot be accounted for by conjugate ion formation of the type $A^- + (HA)_n \rightleftharpoons A(HA)_n^-$ because this stabilization of the anions would increase the dissociation of the acid. It has been found⁹ that in acetonitrile $K_{2(HA)}$ of several acids like hydrochloric and sulfuric acid is considerably greater than K_{HA} . $K_{2(HA)}$ corresponds to the reaction: $2HA \rightleftharpoons H^+ + A(HA)^-$. Similar relations have been found in methyl isobutyl ketone,¹³ a solvent of dielectric constant of only 12.92 and of extremely weak basic character.

In the determination of pK of acetic acid, the pH was determined in mixtures in which the ratio of acid to salt was varied greatly. A plot of pH vs. $\log [A^-]/[HA]$ yielded a slope of 0.52 instead of approximately one. This can be explained by assuming a reaction $HA + A^- \rightleftharpoons A^-(HA)$ but this does not explain the extremely small values of the dissociation constant of acetic (and of benzoic) acid in DMSO.

A more detailed study of the degree of association of acids with their anions in DMSO is neces-

sary before the abnormally small dissociation of these acids can be explained.

The univalent indicator acids brom cresol green and brom thymol blue have ΔpK values of the order of 2.6, close to the value of 2.1 predicted from the Born relation.

Considering the relatively strong basic character of DMSO, the ΔpK_2 of 7.2 for sulfuric acid is abnormally large. Quite generally, K_2 of sulfuric acid in non-aqueous solvents is found to be very much smaller than in water. Actually, the second dissociation constant of sulfuric acid in water is unusually large, possibly as a result of pronounced stabilization of the sulfate ion through hydrogen bonding to the solvent.

The autoprotolysis constant of DMSO is of the order of 5×10^{-18} and is slightly less than that of methanol, which has a K_s of 2×10^{-17} . DMSO is a base of comparable strength to water but is a much weaker acid.

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(13) C. E. Gracias, Ph.D. Thesis, University of Minnesota, 1961.