[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Acidity Constants of Some Hammett Indicators in Heavy Water. The Hammett Acidity Function, D_0, for DCl and D_2SO_4 Solutions[1]

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Dissociation constants of 14 Hammett indicators with pK values in the range 3.3 to -5.5 have been determined in D_2O solutions of DCl and D_2SO_4. A correlation is made of $pK_{BD^+} - pK_{BH^+}$ as a function of acid strength. The data are used to establish the Hammett acidity function, D_0, for DCl solutions in D_2O in the range 10^{-4}–1 M and for D_2SO_4 solutions in the range 10^{-4}–12 M. D_0 is found to be equal to H_0 for "HCl" solutions and equal to $-\log C_{acid}$. D_0 for D_2SO_4 is found to be the same as H_0 for H_2SO_4 except in the range 10^{-3}–10^{-1} M. The different behavior in this region is a consequence of the differences in the dissociation constants of HSO_4^- and DSO_4^-.

Introduction

Hammett and Deyrup[2] have shown that the study of acid–base equilibria involving a series of structurally related neutral bases can afford a logical basis for the establishment of an acidity scale for strong acids. The acidity scale so determined with neutral bases is referred to as the H_0 scale and the literature on such scales for a number of acids has been reviewed by Paul and Long.[3] Since the Hammett function, H_0, is defined as

$$H_0 \equiv pK_{BH^+} - \log (C_{BH^+}/C_B) \qquad (1)$$

a necessary prerequisite for the establishment of the acidity scale is the determination of pK for the reaction

$$BH^+ = B + H^+ \qquad (2)$$

The Hammett function, H_0, has found widespread application to the correlation of the rates and mechanism of acid-catalyzed reactions. If such reactions are studied in D_2O or in H_2O–D_2O mixtures, it is necessary that the analogous function, which we shall call D_0, be known. It is of interest to compare H_0 and D_0 and to determine $(K_{BH^+})_{H_2O}/(K_{BD^+})_{D_2O}$ as a function of pK_{BH^+}.

Experimental Procedure

The method of determining the thermodynamic ionization constants by spectrophotometric titration has been outlined by Hammett and Deyrup[2] in their pioneer work and reviewed by Paul and Long.[3] Essentially the same method was followed in the present investigation and, as a check on the method, simultaneous measurements were made on solutions in ordinary water.

Materials: D_2O.—The heavy water was nominal 99.8% D_2O obtained from the U.S.A.E.C. and was used without further purification.

Deuterium Sulfate.—D_2SO_4 was synthesized by distilling SO_3 (purified by distillation *in vacuo*) into D_2O under vacuum and cooling with carbon dioxide and acetone. The D_2SO_4 stock solution was about 16 M and was kept in a bottle with glass stopper in a desiccator containing P_2O_5. In spite of reasonable precautions, this acid discolored slowly from reaction with dust particles. When the acid was sufficiently discolored that an appreciable correction had to be made in the spectrophotometric measurements, a new batch was synthesized.

Deuterium Chloride.—DCl was synthesized by adding NaCl (dried in oven 110°) to a concentrated D_2SO_4 solution under vacuum. The DCl evolved was passed through three cooling traps cooled with $CO_{2(s)}$ into a D_2O solution kept at 0° with ice. The proportions were such that the resulting DCl stock solution was 3 M. This acid was analyzed for sulfate by sampling 10 ml., precipitating $BaSO_4$, and weighing the dried precipitate. The amount of sulfate was found to be less than 10^{-6} M, which is negligible.

Indicators.—Following the experience of Hyman, *et al.*,[4] a set of Hammett indicators was obtained from the Aldrich Chemical Company. The indicators *m*-nitroaniline, 2,4-dichloroaniline, diphenylamine and *p*-naphtholbenzein obtained from other sources were purified by recrystallization from alcohol and water until the melting points agreed with the literature values. The Aldrich indicators were checked by melting points only. The substance called *p*-nitroazobenzene was discarded when it was found to have a melting point 10° above the literature value and to be practically insoluble in water and concentrated acids. For a few indicators the acidity constants determined in water deviated by large amounts from those given in the literature. In these cases the indicator was purified by chromatography using Woelm neutral aluminum oxide and anhydrous benzene with about 1% anhydrous methanol. When this was done with benzeneazodiphenylamine the chromatogram split up into one stationary and three moving bands. The same four bands appeared in an Eastman Kodak white label preparation of the same substance. A rough determination of pK for the stationary band (the main component) gave 1.44 in good agreement with the literature.[3] However, thanks to the courtesy of the Aldrich Company, a new preparation of benzeneazodiphenylamine was obtained. This substance was chromatographically pure but gave $pK = 0.99$. According to the Aldrich Company both spectra and *elementary analysis* checked with the composition of benzeneazodiphenylamine. These results indicate that $pK = 0.99$ should be a better value than 1.42 as given by Paul and Long[3] using the data by Hammett and Paul.[5] The value 1.44 obtained in one single instance must thus be regarded as fortuitous. For the other substances chromatographed, this purification step did not change the value of the acidity constant beyond the limits of experimental error.

Solutions.—D_2SO_4 and DCl solutions were prepared from the stock solutions by dilution with D_2O. The molarity of the acid was determined by titration with standard NaOH. Alcoholic solutions of the indicators were prepared by dissolving 50 mg. of indicator in 20 ml. of 95% ethyl alcohol and kept in indicator bottles with calibrated drop tubes.

Experimental Technique.—All measurements were made at room temperature, *i.e.*, 22 ± 2°. The experiments were performed as spectrophotometric titrations. A few drops of indicator solution were added to 10.0 or 20.0 ml. of water or some acid solution in a small bottle. A portion was transferred to a measuring cell and the optical density measured at some suitable wave length. A suitable portion of acid was added from a buret and the operation repeated. Titrations were performed in HCl and DCl up to 1.5 M and in H_2SO_4 and D_2SO_4 up to about 13 M. Measurements were made on two different instruments. First a Cary self-recording spectrophotometer model SX-11 was used with 5-cm. Corex cells. Some of the later measurements were made with a Beckman model DU spectrophotometer and 1 cm. cells.

For each indicator a suitable wave length was determined by scanning the visible or ultraviolet range on the Cary instrument. Then the validity of the Lambert–Beer law was tested. This was found to hold in the range 10^{-5} to 10^{-6} M

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[3] M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

[4] H. Hyman, M. Kilpatrick and J. J. Katz, THIS JOURNAL, **79**, 3668 (1957).

[5] L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934).

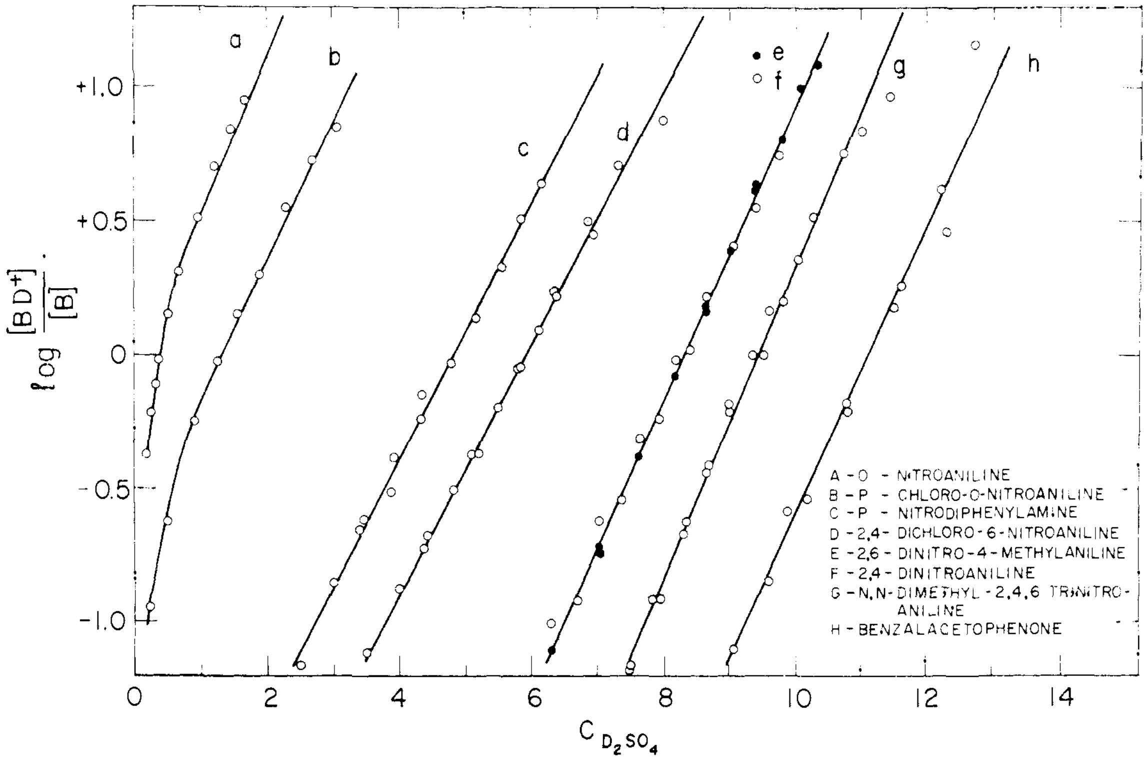

Fig. 1.—Log $(BD^+)/(B)$ plotted against $C_{D_2SO_4}$ for eight Hammett indicators.

(molarity) in indicator concentration, corresponding to a few drops of indicator.

For measurements above 2 *M* in acid concentration, the measurements were performed in small measuring flasks with glass stoppers. This procedure was followed so as to measure the volume change when concentrated acid was added to water or a dilute acid solution.

For the indicator benzalacetophenone, the titration was made with water into the concentrated acid. After the titration, a portion of the solution was titrated with concentrated acid. In this way the reversibility of the reaction was tested and the two titrations gave in heavy water $pK = 5.54$ and 5.51, which is within the limits of experimental error. In heavy water at least duplicate and sometimes triplicate titrations were performed. In light water no duplicate titrations were made if the agreement with the literature was good.

During the course of the measurements no drifts were found with time. Thus if there is any catalyzed exchange of deuterium for protium in the aromatic ring of the indicator it is either slow or fast or of negligible consequence. It is to be expected that substitution of deuterium for protium in the aromatic nucleus will have a negligible effect on *pK* of the indicator.

Experimental Results

A plot of $\log(BD^+)/(B)$ against the concentration of D_2SO_4 solution is given in Fig. 1. We note that the curves are reasonably parallel to one another. The sharp drop off in dilute solution is a consequence of the contribution of hydrogen ions from the dissociation of bisulfate ion.

This test forms the basis of the stepwise procedure of establishing *pK* values and is one experimental criterion of the existence of a D_0 scale. The test in the present case is actually better than for the previous data on protium solutions (*cf.* Fig. 1 ref. 3). The improvement is a result of purification of the indicators and the use of a photoelectric spectrophotometer.

The experimental *pK* values for the different indicators studied are given in Table I. The second column gives best literature values according to Paul and Long.[3] The following four columns contain the values obtained in this investigation together with estimated errors. For the first six indicators *pK* was obtained by extrapolation of pK_c to infinite dilution. In these cases straight lines were drawn parallel to the pK_c line with a displacement such that two-thirds to three-quarters of all the data were situated within these limits. In this simple manner an empirical estimate of the standard deviation of *pK* was made. For the other nine indicators where the *pK*-values were obtained by the stepwise comparison method, the error is given by the standard deviation of the average. The last column gives the difference in *pK* (ΔpK) between the deuterio acid in heavy water solution and the protio acid in H_2O solution.

The agreement between the literature values[2] and the *pK*-values obtained in this investigation is good except for two compounds. Benzeneazodiphenylamine gave $pK = 0.99$ instead of 1.42 as given by Hammett and Paul.[5] However, as mentioned earlier, evidence from the Aldrich Company seems to indicate that the present measurements correspond to benzeneazodiphenylamine. Measurements on the original sample gave the *pK* in HCl of 0.65 and that in DCl of 1.21 with a ΔpK of 0.56 ± 0.02. *p*-Naphtholbenzein was used as indicator by Smith and Elliott[6] and by Kolthoff and Bruckenstein[7] in $HClO_4$-CH_3COOH mixtures. Smith and Elliott determined *pK* to be 0.41. The substance used in the present investigation, purified by chromatography, gave the value -0.99 ± 0.05 in HCl and -1.59 ± 0.05 in H_2SO_4.

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(6) T. L. Smith and J. H. Elliott, This Journal, **75**, 3566 (1953).

(7) I. M. Kolthoff and S. Bruckenstein, *ibid.*, **78**, 1 (1956).

TABLE I

ACIDITY CONSTANTS OF INDICATORS USED FOR DETERMINATION OF THE HAMMETT ACIDITY FUNCTION IN D_2O–D_2SO_4 MIXTURES

Indicator	Best value Paul and Long	*pK* HCl	*pK* H_2SO_4	*pK* DCl	*pK* D_2SO_4	ΔpK
p-Aminoazobenzene	2.77	2.76 ± 0.02	2.79 ± 0.01	3.33 ± 0.02	3.32 ± 0.01	0.55 ± 0.03
m-Nitroaniline	2.50	2.41 ± .02	....	2.97 ± .01	3.00 ± .01	.58 ± .02
2,4-Dichloroaniline	2.00	2.05 ± .01	....	2.55 ± .01	....	.50 ± .01
Benzeneazodiphenylamine[a]	1.42	0.99 ± .02	....	1.55 ± .01[b]	....	.56 ± .02
p-Nitroaniline	0.99	.96 ± .02	....	1.53 ± .01	....	.57 ± .02
Diphenylamine	0.78	.77 ± .01	....	1.31 ± .01	....	.54 ± .01
o-Nitroaniline	−0.29	− .31 ± .01	−0.31 ± .01	0.30 ± .01	0.30 ± .01	.61 ± .01
4-Chloro-2-nitroaniline	−1.03	−1.05 ± .01	−1.02 ± .01	−0.46 ± .01	−0.46 ± .01	.58 ± .02
p-Nitrodiphenylamine	−2.48	....	−2.50 ± .05	....	−2.23 ± .01	.27 ± .05
2,4-Dichloro-6-nitroaniline[a]	−3.32	....	−3.16 ± .01	....	−2.73 ± .01	.43 ± .01
2,6-Dinitro-4-methylaniline	−4.44	....	−4.45 ± .04	....	−4.04 ± .01	.41 ± .04
2,4-Dinitroaniline[a]	−4.53	....	−4.42 ± .01	....	−4.03 ± .01	.39 ± .01
N,N-Dimethyl-2,4,6-trinitroaniline[a]	−4.81	....	−4.98 ± .03	....	−4.67 ± .02	.31 ± .04
Benzalacetophenone	−5.73	....	−5.68 ± .02	....	−5.53 ± .02	.15 ± .03

[a] Indicator subjected to chromatographic purification. [b] Obtained by adding ΔpK from a commercial product to *pK* in HCl of a chromatographed sample.

All measurements with this indicator were performed at 625 mμ in HCl and at 623 mμ in H_2SO_4. Since the difference in *pK* between HCl and H_2SO_4 is much larger than the estimated error, it is obvious that the criterion of *pK* being independent of aqueous solution studied is not fulfilled, and it cannot be used as a Hammett indicator. The difference between HCl and H_2SO_4 may be due to sulfonation in the latter. Further work was not done with this indicator. For the indicators *m*-nitroaniline, 2,4-dichloro-6-nitroaniline, 2,4-dinitroaniline and N,N-dimethyl-2,4,6-trinitroaniline there are appreciable differences between the literature values and those obtained in the present investigation. The *pK* for *m*-nitroaniline agrees with the value 2.43 of Braude and Stern.[8] The three other substances were purified by chromatography and the *pK*-values are given for the chromatographed substance. This purification, however, did not change *pK* beyond the limits of experimental error. No explanation for the discrepancies noted of 0.1 to 0.2 unit can be offered at present. The reproducibility is believed to be better than ±0.05 *pK* unit. Measurements in this investigation were performed at a constant wave length.

For the four cases where the dissociation constants have been determined in HCl and H_2SO_4 or DCl and D_2SO_4, the agreement is excellent. This is a second condition for the applicability of the Hammett method. For *p*-nitrodiphenylamine a rough value of *pK* was obtained from the overlap range and then it was assumed that $H_0 = D_0$, as we shall presently show, and more *pK*-values calculated. These agreed well with the few from the overlap range which justifies the assumption. In this manner a better defined *pK*-value for this indicator was established.

Figure 2 gives a plot of H_0 and D_0 against log C_{acid} for HCl and DCl solutions, respectively. In the range of concentrations studied, 10^{-4} to 1 *M*, H_0 is equal to D_0, and we find empirically

$$H_0 = -\log C_{\text{acid}} \qquad (3)$$

Both of these results are to be expected on theoretical grounds. From equation 1 we can write

$$-H_0 \equiv \log C_{\text{H}^+} + \log \gamma_{\text{H}^+}/\gamma_{\text{BH}^+} + \log \gamma \qquad (4)$$

At a given concentration of acid, the difference between D_0 and H_0 is given by

$$(D_0 - H_0)_{\text{acid}} = \log \frac{\gamma_{\text{H}^+}\,\gamma_{\text{BD}^+}}{\gamma_{\text{D}^+}\,\gamma_{\text{BH}^+}} + \log\,(\gamma_{\text{B}})_{\text{H}_2\text{O}}/(\gamma_{\text{B}})_{\text{D}_2\text{O}} \qquad (5)$$

In solutions of low ionic strength, where the Debye–Hückel limiting law is applicable, $\gamma_{\text{H}^+} = \gamma_{\text{BH}^+}$. Furthermore, in such solutions the activity coefficient of a "neutral" substance is expected to be close to unity. From equations 4 and 5 and the fact that D_2O differs by a negligible amount from H_2O in its dielectric constant, we expect that H_0 will be equal to D_0 and, furthermore,

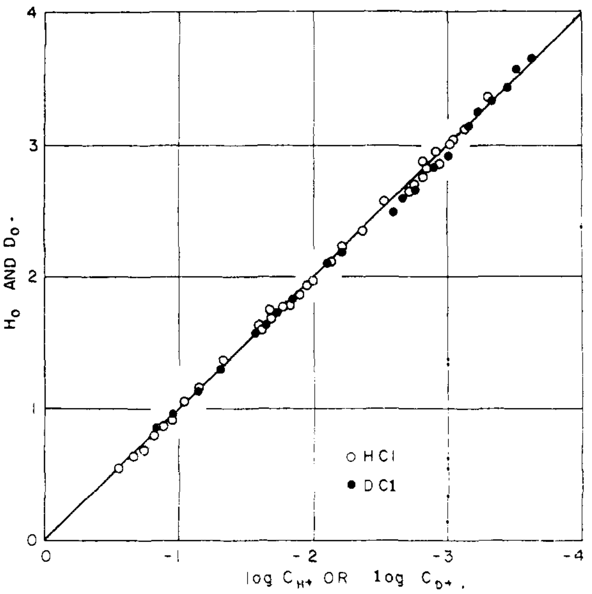

Fig. 2.—H_0 and D_0 plotted against log C_A (C_A = acid concentration) for the range 10^{-4} to 1 *M* hydrochloric acid: O, HCl; ●, DCl.

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(8) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1976 (1948).

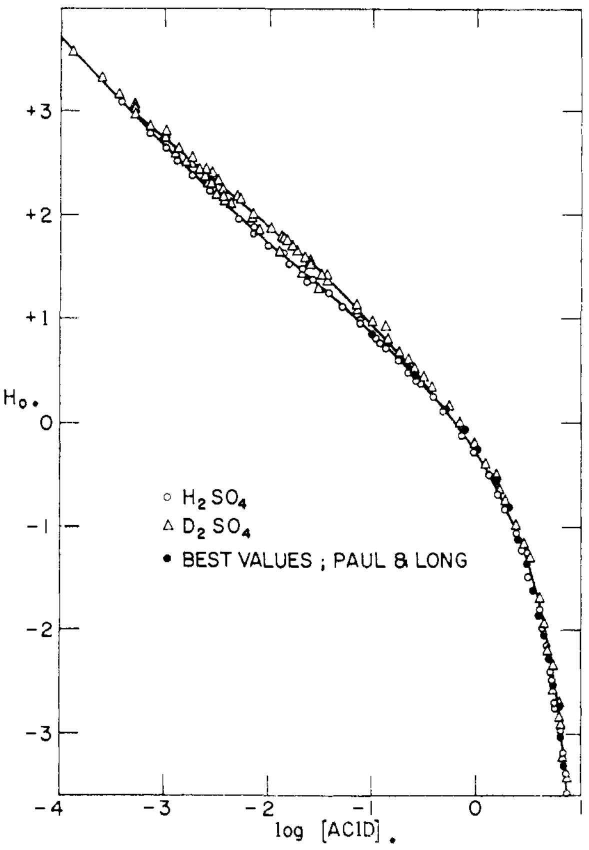

Fig. 3.—H_0 and D_0 plotted against log M for H_2SO_4 and D_2SO_4.

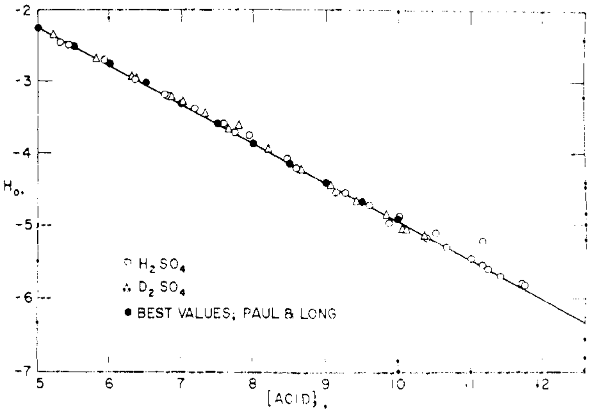

Fig. 4.—H_0 and D_0 plotted against C_A in the range 5–12 M for the acids H_2SO_4 and D_2SO_4: O, H_2SO_4; △, D_2SO_4; ●, best values, Paul and Long.

that H_0 will approach $-\log C_{\text{acid}}$ in dilute solutions.

Figures 3 and 4 give plots of H_0 or D_0 for solutions of H_2SO_4 and D_2SO_4, respectively, against the concentration of acid. In the case of H_2SO_4 solutions good agreement is found with the compilation of Paul and Long.[3] A few isolated measurements of acid-base equilibria in the region of 60–70% D_2SO_4 using aldehydes as indicators have been reported.[9,10] The interpretation given to these measurements by the authors indicated a difference of −0.3 to −0.4 unit between D_0 and H_0 in this concentration range. In this interpretation it was assumed that $pK_{\mathrm{BD^+}}$ equals $pK_{\mathrm{BH^+}}$, whereas the measurements show that this is not the case. Our studies, as well as previous data on the dissociation constants of protio *vs.* deuterio acids, lead one to expect $pK_{\mathrm{BD^+}}$ to be larger than $pK_{\mathrm{BH^+}}$ by just such an amount. We may conclude that the measurements of Schubert and coworkers[9,10] using mesitylaldehyde and 2,4,6-triisopropylbenzaldehyde as indicators are in agreement with our finding that D_0 is equal to H_0 in sulfuric acid solutions at 60% concentration. We note from Fig. 3 that D_0 is equal to H_0 over the entire range studied except for the region between 10^{-3} to $10^{-1}M$ sulfuric acid. In this concentration range the hydrogen ion activity is markedly affected by the incomplete dissociation of bisulfate ion. The difference between D_0 and H_0 is consistent with the fact that DSO_4^- is a weaker acid than HSO_4^-.[11] The present measurements are not sufficiently extensive to obtain improved values for the dissociation constants of HSO_4^- and DSO_4^-. They are consistent with the data presently available. In Table II we give values for D_0 and H_0, respectively, for the concentration range 10^{-4} to 1 M. Above this range, Figs. 3 and 4 show that the tabulation of Paul and Long can be used for either D_0 or H_0. In the range 1–12 M acid, the concentration of hydrogen ion is essentially the stoichiometric concentration. The activity coefficient ratio $\gamma_{\mathrm{H^+}}\gamma_{\mathrm{B}}/\gamma_{\mathrm{HB^+}}$ should have a similar behavior in H_2O and D_2O solutions. In solutions near 100% sulfuric acid we may anticipate a difference between H_0 and D_0.

TABLE II

H_0 AND D_0 AT SELECTED MOLARITIES, 22 ± 2°

log M	H_0 H_2SO_4	D_0 D_2SO_4
−3.80	3.50	3.50
−3.60	3.28	3.28
−3.40	3.08	3.08
−3.20	2.84	2.90
−3.00	2.64	2.73
−2.80	2.45	2.54
−2.60	2.26	2.38
−2.40	2.07	2.20
−2.20	1.89	2.01
−2.00	1.72	1.85
−1.80	1.54	1.71
−1.60	1.38	1.51
−1.40	1.22	1.33
−1.20	1.03	1.13
−1.00	0.83	0.95
−0.80	.65	.72
− .60	.45	.51
− .40	.23	.26
− .20	− .02	− .01
.00	− .30	− .30

The Acidity Constants.—The difference in the acidity constants, $pK_{\mathrm{BD^+}} - pK_{\mathrm{BH^+}}$, are especially interesting since the present measurements deal with a series of strong acids. They provide a

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(9) W. M. Schubert and H. Burkett, THIS JOURNAL, **78**, 64 (1956).

(10) W. M. Schubert and P. C. Myhre, *ibid.*, **80**, 1755 (1958).

(11) C. Drucker, *Trans. Faraday Soc.*, **33**, 660 (1937).

critical test of the Rule and La Mer[12] extrapolation based on the theory given independently by Lewis and Schutz[13] and Halpern.[14] According to this theory ΔpK should increase with pK. We wish to reexamine the basis for this prediction.

In order that the solvation of the proton be specifically considered, we shall write the dissociation equilibrium in the Brönsted form

$$BH^+ + H_2O = B(H_2O) + H_3O^+ \qquad (6)$$

$$BD^+ + D_2O = B(D_2O) + D_3O^+ \qquad (7)$$

For the purposes of the immediate discussion it will suffice to neglect further solvation effects and treat the hypothetical gas phase equilibria. We now introduce the reduced partition functions of Bigeleisen and Mayer[15] and obtain

$$\Delta pK = pK_{BD^+} - pK_{BH^+} = \log f_{BD^+} + \log f_{D_2O} - \log f_{D_3O^+} \qquad (8)$$

To a first approximation ΔpK is proportional to the zero point energy difference between protons and deuterons in the acid, BH^+, plus that in water minus the zero point energy difference of hydrated protons and hydrated deuterons. In the present approximation

$$\Delta pK_1 - \Delta pK_2 = (pK_{BD^+} - pK_{BH^+}) - (pK_{CD^+} - pK_{CH^+}) = \log f_{BD^+} - \log f_{CD^+} \qquad (9)$$

According to the argument of Lewis and Schutz and Halpern, the zero point energy difference between BD^+ and BH^+ will increase with the strength of the B–H bond or the free energy of dissociation of BH^+. From this argument ΔpK will increase with pK.

Rule and La Mer extrapolated the data available to them to the point $\Delta pK = 0$ at $pK_{H_3O^+} = -1.74$. Figure 5, reproduced from their paper, indicates that there is reasonable agreement between experiment and the theory of Lewis and Schutz and of Halpern. The point at $pK = -1.74$ is estimated for acids of the strength of hydronium ion. One must avoid giving any significance to the ratio K_H/K_D from the *defined* standard states of protons and hydronium ions. It is conventional to define the relative standard states of protons and hydronium ions by the reaction

$$H_3O^+ = H_2O + H^+ \qquad (10)$$

$$K_H = \frac{a_{H_2O}a_{H^+}}{a_{H_3O}} = 55.51 \qquad (11)$$

and similarly

$$K_D = \frac{a_{D_2O}a_{D^+}}{a_{D_3O^+}} \cong 55.5 \qquad (12)$$

In order to obtain a meaningful value of $\Delta pK_{H_3O^+} = pK_{D_3O^+} - pK_{H_3O^+}$ it is necessary to measure the fraction of protons and deuterons in the forms of H_3O^+ and H^+ and D_3O^+ and D^+, respectively. It is well known that such information does not exist. The evidence presently available indicates that most of the protons exist as H_3O^+. The use of defined standard states is not applicable to the determination of ΔpK.

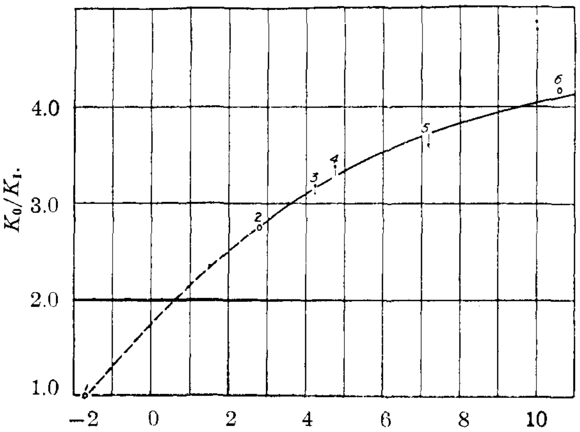

Fig. 5.—Ratios of dissociation constants for protio and deuterio acids from conductimetric and potentiometric measurements.

Inherent in the theory of Lewis and Schutz and of Halpern is the assumption that the zero point energy of the acid is related to its free energy of dissociation. No simple relationship exists between the zero point energy and the dissociation energy of a bond in a polyatomic molecule. For diatomic molecules, the Birge–Sponer method gives[16]

$$D_e = \omega_e^2/4X_e\omega_e \qquad (13)$$

$$D_0 = D_e - 1/2\omega_e + 1/4X_e\omega_e + \ldots \qquad (14)$$

where D_e and D_0 are the dissociation energies from the minimum in the potential and from the ground vibrational state, respectively. The quantities ω_e and $x_e\omega_e$ are defined in terms of the energy of an anharmonic oscillator

$$E/hc = (n + 1/2)\omega_e - (n + 1/2)^2X_e\omega_e + \ldots \qquad (15)$$

In the correlation of vibrational spectra with the structure of polyatomic molecules, it is possible in many cases to find bond or group frequencies which are rather constant from one molecule to another. The requirements for such a constancy are summarized in the literature.[17,18] In particular X–H vibrations are found to be relatively constant from one molecule to another because of the small mass of the proton compared to other atoms and the relative constancy of force constants.

We are, therefore, led to expect that the zero point energy will be primarily a function of the acid type and that ΔpK will depend mainly on the type of acid. In a series of acids of similar type, a small dependence of ΔpK on acid strength as discussed by Lewis and Schutz and Halpern is to be expected. This is the behavior found experimentally and shown in Fig. 6. In compiling this figure we have added 0.10 to the ΔpK values of Schwarzenbach[19] to bring them into agreement with the data of La Mer and coworkers. We note that the point at pK 6.35,

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[12] C. K. Rule and V. K. La Mer, THIS JOURNAL, **60**, 1974 (1938).

[13] G. N. Lewis and P. W. Schutz, *ibid.*, **56**, 1913 (1934).

[14] O. Halpern, *J. Chem. Phys.*, **3**, 456 (1935).

[15] J. Bigeleisen and M. G. Mayer, *ibid.*, **15**, 261 (1947).

[16] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1950, p. 100.

[17] G. Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 194.

[18] E. B. Wilson, J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 74.

[19] G. Schwarzenbach, *Z. Elektrochem.*, **44**, 46 (1938).

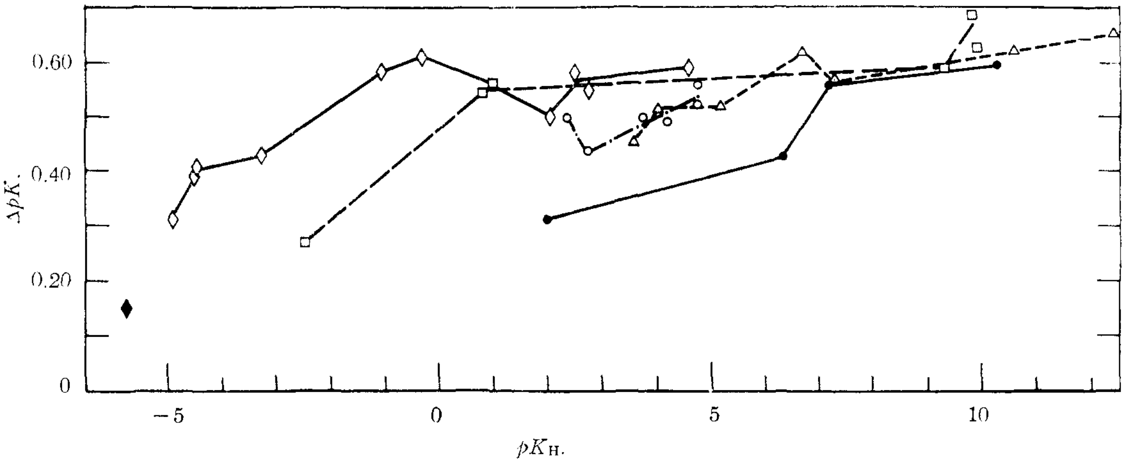

Fig. 6.—ΔpK as a function of acid strength: ◇, substituted anilines; □, amines; ◆, ketones; △, phenols and alcohols (data of D. C. Martin and J. A. V. Butler (*J. Chem. Soc.*, 1366 (1939)), and P. Ballinger and F. A. Long, THIS JOURNAL, 81, 1050, 2347 (1959).); O, carboxylic acids; ●, $MO_x(OH)_y$.

H_2CO_3, is abnormally low. This is due to the fact that an appreciable contribution to the acidity of carbonic acid comes from dissolved CO_2. Our point for *p*-nitrodiphenylamine appears to be somewhat low. The experimental uncertainty in ΔpK is large for this indicator and no conclusions can be drawn at present for ΔpK for amines with pK values less than zero.

In solutions concentrated in sulfuric acid, medium effects on ΔpK are to be expected. These arise in part from the correction necessary to equation 8 from the relative fugacities of H_2O and D_2O in H_2SO_4 and D_2SO_3, respectively. Furthermore reactions of the type

$$BH^+ + H_2SO_4 = B(H_2SO_4) + H_3SO_4^+ \quad (16)$$

become of importance. Even in the approximations used in equation 8 we would find

$$\Delta pK = \log f_{BD^+} + \log f_{D_2SO_4} - \log f_{D_3SO_4^+} \quad (17)$$

These effects may be responsible for the drop in ΔpK for the substituted anilines with negative pK values.

NOTE ADDED IN PROOF.—Bascombe and Bell (*J. Chem. Soc*, 1096 (1959)) have recently reported measurements of pK (H_2O solutions) for some of the indicators studied by us. Their measurements include solutions of H_2SO_4 among a number of different acids. Wherever comparisons can be made, our values of pK and H_0 are in agreement with those of Bascombe and Bell. For the indicator *p*-nitrodiphenylamine they find a medium and wave length effect on pK and H_0. From three different assumptions, pK and H_0 are calculated from measurements at 4100 Å. H_0 is less sensitive to the nature of the assumption than pK. Our values of pK, H_0, and D_0 were obtained from measurements at 4100 Å. The medium effects observed by Bascombe and Bell for this indicator probably explain the fact that our value of ΔpK for this indicator is anomalously low.

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Ion Pairs. I. Isotope Effects Shown by Chloride Solutions in Glacial Acetic Acid[1]

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Appreciable isotopic separation has been obtained in countercurrent columns using the distribution of chlorine between HCl gas and solutions of inorganic chlorides in glacial acetic acid. The isotope effects[3] *vs.* Cl atoms, calculated from the observed enrichments for various species present in the solutions are: HCl (dissolved), 1.0050 ± 0.0002; $HgCl_2$, 1.0061 ± 0.0009; $HCl \cdot H_2O$, 1.0039 ± 0.0003; $SrCl_2$, 1.0042 ± 0.0003; LiCl, 1.0040 ± 0.0003. These results are consistent with a picture involving strong Hg–Cl bonds, but much "looser" interaction between the metal and chlorine atoms in the ion pairs from LiCl and $SrCl_2$.

Introduction

This is the first in a series of papers describing experiments designed to provide a more detailed understanding of the nature of ion pairs in solvents of low dielectric constant. Most previous investigations have been concerned primarily with the dissociation constants of ion pairs. Data on at least three other general aspects of ion pairs should also be available to complete the picture: 1, average vibration frequencies and the stiffness of the bonding present, 2, the lability of various ion pairs as measured by rates of isotopic exchange, and 3, the effects of other salts on the activity coefficients of ion pairs. Such information should prove useful in interpreting kinetic data for organic reactions which apparently involve intermediates with con-

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[3] The isotope effect for a given species is the equilibrium constant, corrected for symmetry, for the isotopic exchange reaction with free atoms. It is numerically equal to the Cl^{37}/Cl^{35} ratio which would be present in the species in equilibrium with equal concentrations of free gaseous Cl^{37} and Cl^{35} atoms.