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Author

Jolly, William L.

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University of California

Ernest O. Lawrence Radiation Laboratory

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William L. Jolly

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The Intrinsic Basicity of the Hydroxide Ion

By William L. Jolly

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Liquid ammonia is a much more basic solvent than water, and therefore one expects protonic acids to be more completely ionized ("stronger") in ammonia than in water. In fact, it may be shown that normal protonic acids have ionization constants in liquid ammonia which are about 10^{10} times larger than the ionization constants in water.[1] Now water itself is not exactly a "normal" acid, and one might not expect it to obey this rule exactly. But it is rather surprising to learn the extent to which it disobeys the rule. The pK of water in liquid ammonia is 18, and the pK of water in water is 16. (1) Thus, in liquid ammonia, the ionization constant of water is 100 times smaller than it is in water. The explanation which has been offered for this behavior is that the hydroxide ion is abnormally strongly stabilized in water by hydrogen bonding, and that consequently water in water is an abnormally strong acid. (1) If it were not for the unusual stabilization of the hydroxide ion in water, the pK of water in water would be

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[1] The justification for this rule is discussed in Appendix I.

expected to be about 28! It has recently been shown that the n.m.r. chemical shift for the hydroxide ion in ammonia lies 13 p.p.m. to higher field of that for the hydroxide ion in water. (2) Again the explanation was given in terms of hydrogen bonding in water. Other acids whose anions are strongly hydrogen-bonded in water show anomalous differences in their pK values in water and ammonia, but the anomalies are not as great as they are in the case of water.[2]

It has been shown that dimethyl sulfoxide (DMSO) and water have about the same basicities, and so one would expect normal acids to have similar ionization constants in these two solvents. (3) However the ionization constants of carboxylic acids and the bisulfate ion are $10^6 - 10^7$ times smaller in DMSO than in water. These anomalies can be explained in terms of pronounced stabilization of the anions in water through hydrogen bonding.

It is clear that the acidities of hydroxylic acids and normal acids can be meaningfully compared only when all the acidities are those applicable to the *same non-hydroxylic solvent. In most tables of acid* pK values (such as Table 1) the applicable solvent is water. Thus one gets the impression that an alcohol such as ethanol (aqueous pK ≈ 17) is intrinsically more acidic than acids such as indene (aqueous pK ≈ 20) and diphenylamine (aqueous pK ≈ 23). However in a non-hydroxylic solvent such as an ether or DMSO, the reverse is true — that is, indene and

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[2] See Appendix II.

Table 1.

Rough pK Scale for Weak Acids in Aqueous Solutions

Acid	pK
H_2S	7
CH_3NO_2	10
H_2O	16
C_5H_6, cyclopentadiene	16
C_2H_5OH	17
9-Phenylfluorene	19
C_9H_8, Indene	20
$(C_6H_5)_2NH$	23
Fluorene	23
CH_3CN	25
GeH_4	25
$C_6H_5NH_2$	27
PH_3	27
$C_2H_5GeH_3$	28
$(C_6H_5)_3CH$	32
NH_3	39
$C_6H_5CH_3$	40

diphenylamine are more acidic than ethanol. Steiner and Gilbert (4) have shown that it is possible to have comparable amounts of the four species, triphenylmethane (pK $\approx$ 32), triphenylmethide ion, ethanol, and ethoxide ion, together in DMSO. This shows that triphenylmethane and ethanol have similar acidities in this solvent.

The intrinsic basicity of the hydroxide ion is much greater than that which can be achieved in a solvent such as water or alcohol. Unfortunately, hydroxides are not appreciably soluble in non-hydroxylic solvents. This difficulty has been overcome in many cases by the use of potassium t-butoxide, which has a greater solubility in solvents such as DMSO. (5) It has been shown that synthetically important base-catalyzed reactions such as the Wolff-Kishner reduction and Cope elimination proceed much more rapidly in DMSO-butoxide solutions than in hydroxylic solvents. (6) However, it has not been generally recognized that alkali metal hydroxides need not be dissolved to bring about the ionization of weak acids. Solid sodium hydroxide and potassium hydroxide are very effective in the preparation of salts. From readily available thermodynamic data[3] we calculate the following equilibrium constants.

$$2KOH_{(s)} + H^+_{aq} = K^+_{aq} + KOH\cdot H_2O_{(s)} \qquad K = 10^{31}$$

$$2NaOH_{(s)} + H^+_{aq} = Na^+_{aq} + NaOH\cdot H_2O_{(s)} \qquad K = 10^{23}$$

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[3] Most of the data were taken from the N.B.S. Circular 500 (7), but it was necessary to estimate the entropies of KOH and $KOH\cdot H_2O$ using the methods outlined by Latimer. (8)

We see that any acid with an aqueous pK less than 31 should react with potassium hydroxide to form the potassium salt, and any acid with an aqueous pK less than 23 should react similarly with sodium hydroxide. Of course these reactions only have meaning for nonaqueous solvents, because it is not possible, for example, to have both KOH and $KOH{\cdot}H_2O$ in equilibrium with a solution which in the usual sense is aqueous. The free energy of transfer of a salt or a neutral species from water to another solvent is rather small, and so we can consider these reactions and their calculated equilibrium constants to be valid for any solvent

$$2KOH_{(s)} + HA = K^+ + A^- + KOH{\cdot}H_2O \qquad K = 10^{31-pK_{HA}}$$

$$2NaOH_{(s)} + HA = Na^+ + A^- + NaOH{\cdot}H_2O \qquad K = 10^{23-pK_{HA}}$$

The aqueous pK values for a few acids are presented in Table 1. From this table we can get an idea as to the kinds of acids which will react with KOH and NaOH. We have found several of these reactions to be synthetically useful. By simply stirring powdered reagent grade KOH with solutions of the appropriate acids in 1,2-dimethoxyethane, we have prepared, in quantitative yield, solutions of the potassium salts of germane, ethylgermane, cyclopentadiene, indene, and fluorene. The reactions are much easier and safer to carry out than the usual reactions of dispersed metal suspensions with weak acids. Using the solutions prepared from KOH as intermediates, a variety of derivatives, such as CH_3GeH_3, $CH_3GeH_2C_2H_5$, ferrocene, nickelocene, and bis-indenyliron(II), have been prepared. (9)

$$CH_3Cl + K^+ + GeH_3^- \rightarrow CH_3GeH_3 + KCl$$

$$CH_3Cl + K^+ + C_2H_5GeH_2^- \rightarrow CH_3GeH_2C_2H_5 + KCl$$

$$FeCl_2 + 2K^+ + 2C_5H_5^- \rightarrow Fe(C_5H_5)_2 + 2KCl$$

$$NiCl_2 + 2K^+ + 2C_5H_5^- \rightarrow Ni(C_5H_5)_2 + 2KCl$$

$$FeCl_2 + 2K^+ + 2C_9H_7^- \rightarrow Fe(C_9H_7)_2 + 2KCl$$

Undoubtedly many more applications of the reactions of potassium hydroxide with weak acids in non-hydroxylic solvents can be found.

Appendix I. -

From a comparison of the free energies of transferring various salts and acids from water to ammonia, it was concluded that acid pK values generally should be 12 units greater in water than in ammonia. (1) There are very few acids (whose anions do not strongly hydrogen bond with water) for which acidity data in both solvents are available. However, the data for four different acids are discussed in the following paragraphs, and it can be seen that these data indicate $\Delta pK \approx 10$ rather than $\Delta pK \approx 12$.

By convention, the ammonium ion has a pK value of 0 in liquid ammonia.

$$NH_4^+ + NH_3 = NH_4^+ + NH_3 \qquad K = 1$$

In water, the pK value is 9.3 (8), corresponding to ΔpK = 9.3.

$$NH_4^+ + H_2O = H_3O^+ + NH_3 \qquad K = 5 \times 10^{-10}$$

Wilmarth et al (10) measured the rate constant for the aqueous reaction

$$H_2 + OH^- \rightarrow H^- + H_2O$$

in the temperature range 80-110°. From their data, we calculate $k = 2.8 \times 10^{-6}$ l. mole^{-1} sec^{-1} at 25°. Bar-Eli and Klein (11) measured the rate constant for the liquid ammonia reaction

$$H_2 + NH_2^- \rightarrow H^- + NH_3$$

in the temperature range -50 to -70°. From their data, we calculate $k = 6.1 \times 10^{3}$ l. mole^{-1} sec^{-1} at 25°. By assuming that the rate constants for the reverse reactions are equal (diffusion controlled), we calculate, for the ratio of the ionization constants for hydrogen, $6.1 \times 10^3/(2.8 \times 10^{-6}) = 2.2 \times 10^9$, or $\Delta pK \approx 9.3$.

From the conductivity data of Smith (12), it is clear that cyanamide is on the borderline between strong and weak acids in liquid ammonia. We shall assume pK ≈ 0 in ammonia. In water, the pK is 10.4 (13), yielding ΔpK ≈ 10.4.

Birchall and Jolly (14) reported that phosphine reacts with solid NaOH and ammonia to give a very pale yellow solution.

$$NaOH + PH_3 = PH_2{}^-{}_{am} + Na^+{}_{am} + H_2O_{am}$$

If we assume $(PH_2^-) = (Na^+) = (H_2O) \approx 10^{-2}$ and $(PH_3) \approx 0.5$, and estimate $\gamma_\pm = 0.4$, we calculate $K = 3 \times 10^{-7}$. By combining this result with available thermodynamic data (1, 7, 15), we calculate, for PH_3 in ammonia, pK = 16. From the kinetic data of Weston and Bigeleisen on the exchange of hydrogen between phosphine and water (16), one calculates, using the usual standard states for water and phosphine, a value of 27 for the pK of phosphine. Thus we find that the data are consistent with ΔpK ≈ 11.

Appendix II. -

The pK of p-nitroacetanilide in liquid ammonia at -55.6° is 5.1. (17) Using an estimated ΔS° of ionization of -60 e.u., this is corrected to pK = 7.2 at 25°. The pK of p-nitroacetanilide in water is unknown, but from data of Bowden and Stewart (18) and the application of the Hammett $\sigma\rho$ function, we estimate 12.5 for the aqueous pK. Thus we obtain ΔpK ≈ 5.

From kinetic data of Kelley et al (19) we conclude that the rate constant for the ionization of ethanol in liquid ammonia at -33.4° is equal to or less than ~ 0.01 sec^{-1}. The value is only an upper limit because it is possible that, to a certain extent, the rate measured was that for a faster reaction such as

$$2EtOH + NH_3 \rightarrow NH_4^+ + EtOHOEt^-$$

If we assume that the reverse reaction is diffusion controlled ($k = 10^{11}$ l. mole^{-1} sec^{-1}), we calculate $pK \geqslant 13$ for EtOH in liquid ammonia at -33.4°. By using a $\Delta S°$ of ionization of -60 e.u., this value remains unchanged at 25°. From the aqueous pK of 17, we then obtain $\Delta pK \leqslant 4$.

The ΔpK values for the above two acids are considerably less than 10, the average value found in Appendix I. The discrepancies may be accounted for in terms of the hydrogen bonding of the anions in water.

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