for molecular weight, conductivity, and structural studies of the compounds, and for their use as intermediates in preparing other lanthanide complexes difficult to prepare in aqueous solutions. The use of tertiary alcohols, with subsequent heating of the obtained alcoholates, could conceivably result in the synthesis of other organic groups.

Acknowledgments.—The authors express appreciation to The Dow Chemical Co. and in particular to Dr. Ray Rolf for the gift of the 2,2-dimethoxypropane. They are indebted to Professors Harry Eick, Andrew Timnick, and Carl H. Brubaker, Jr., for helpful suggestions. An All-University Research Fund grant assisted the project.

Correspondence

The Deprotonation of Weak Acids

Sir:

Alkali metal salts of very weak protonic acids commonly have been prepared by three methods that do not require a metal salt of the acid as a starting material: (1) reaction with strong bases, (2) direct reaction with alkali metals, and (3) cleavage of halo derivatives with alkali metals. It is the purpose of this communication to show that the thermodynamic limitations of each of these methods may be defined in terms of acid p*K* values.

Reaction with Strong Bases.—In this method the weak acid is treated with an alkali metal salt of a still weaker protonic acid, sometimes using one of the protonic acids as a solvent. The p*K* of the acid whose salt is used as a reactant is an approximate upper limit to the p*K* values of the acids whose salts can be formed in this type reaction. Tables of weak acids and their aqueous p*K* values may be found in various references.[1–3] However these tables must be used with caution, because the p*K* values listed for hydroxylic acids (*e.g.*, water, ethanol, and acetic acid) are valid only in water, where the anions of these acids are abnormally stabilized by hydrogen bonding. In nonhydroxylic solvents such as ammonia, ethers, and dimethyl sulfoxide, the hydroxylic acids are *relatively* much weaker.[4–6] For example, it has been estimated[3] that if the hydroxide ion in water were not stabilized by hydrogen bonding, the p*K* of water would be about 28. This latter p*K* value would be the appropriate one to use when comparing water with nonhydroxylic acids in a nonhydroxylic solvent.

Alkali metal hydroxides are very strong bases, but their base strengths are greatly reduced by dissolving them in hydroxylic solvents such as water or alcohols. The intrinsic basicity of hydroxides can be achieved by using them in the solid form in conjunction with nonhydroxylic solvents, in which they are essentially insoluble.[7,8] In such cases the driving force for the deprotonation of an acid is markedly increased when the solid hydroxide is in excess, because the excess hydroxide can react with the water formed in the reaction to form a stable hydrate. Thus the net reaction in the case of potassium hydroxide is

$$2KOH(s) + HA \longrightarrow K^+ + A^- + KOH\cdot H_2O(s)$$

By making the approximation that the free energies of transfer of $K^+ + A^-$ and HA from water to the nonhydroxylic solvent are negligible,[9–13] we may calculate (using available thermodynamic data)[14,15] that the equilibrium constant for the latter reaction is 10^{31-pK}, where p*K* refers to the aqueous p*K* of the acid HA. We see that anhydrous KOH[16] is capable of deprotonating acids with p*K* values as high as 31. We have found several reactions of this type to have synthetic utility.[17] By simply stirring a suspension of powdered KOH in 1,2-dimethoxyethane with cyclopentadiene (p*K* ≈ 16), indene (p*K* ≈ 20), germane (p*K* ≈ 25), or phosphine (p*K* ≈ 27), we have obtained essentially quantitative yields of the corresponding potassium salts. These potassium salts have been used as intermediates for the preparation of various organometallic compounds such as ferrocene, bisindenyliron, ethylgermane, and methylphosphine. Undoubtedly many

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(1) A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, **3**, 41 (1965).

(2) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.

(3) W. L. Jolly, *J. Chem. Educ.*, in press.

(4) W. L. Jolly, *J. Phys. Chem.*, **58**, 250 (1954).

(5) G. M. Sheldrick, *Chem. Commun.*, 673 (1966).

(6) E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **85**, 3054 (1963).

(7) Many base-catalyzed organic reactions have been effected by the use of heterogeneous solvent–metal hydroxide systems. For example, Wallace, Pobiner, and Schriesheim[8] have autoxidized ketones to carboxylic acids in excellent yields using hexamethylphosphoramide as the solvent in the presence of either KOH or NaOH.

(8) T. J. Wallace, H. Pobiner, and A. Schriesheim, *J. Org. Chem.*, **30**, 3768 (1965).

(9) The absolute values of the free energies and heats of transfer of salts from water to liquid ammonia[4] and the heats of transfer of salts from water to propylene carbonate[10] and formamide[11] are generally less than 6 kcal/mole. However, the heats of transfer of several alkali metal salts from water to dimethyl sulfoxide[12] have been found to be in the neighborhood of −10 kcal/mole. It is likely that the corresponding free energies of transfer to dimethyl sulfoxide are also quite negative. The relative solvating power of a variety of polar nonhydroxylic solvents is discussed by Parker.[13]

(10) Y. C. Wu and H. L. Friedman, *J. Phys. Chem.*, **70**, 501 (1966).

(11) G. Somsen and J. Coops, *Rec. Trav. Chim.*, **84**, 985 (1965).

(12) E. M. Arnett and D. R. McKelvey, *J. Am. Chem. Soc.*, **88**, 2598 (1966).

(13) A. J. Parker, *Advan. Org. Chem.*, **5**, 1 (1965).

(14) U. S. National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties," U. S. Government Printing Office, Washington, D. C. The entropies of KOH and $KOH\cdot H_2O$ were estimated using the methods outlined by Latimer.[15]

(15) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

(16) It may be similarly shown that potassium oxide is potentially capable of deprotonating acids with p*K* values as high as 69. However, the relative unavailability and difficulty of handling K_2O makes it less attractive as a deprotonating agent.

(17) W. L. Jolly, T. Birchall, D. S. Rustad, D. J. Chazan, and D. B. Dowling, unpublished work.

similar applications of KOH in nonhydroxylic solvents will be found. By using dimethyl sulfoxide as the solvent, we have similarly prepared the potassium salt of triphenylmethane (p$K \approx 32$). The discrepancy between this latter result and the above thermodynamic calculation is probably attributable to a particularly high solvation energy in dimethyl sulfoxide.[9,12]

Reaction with Alkali Metals.—In the second method the weak acid is treated with an alkali metal, usually suspended in a finely divided state in a polar solvent. For example, the sodium salt of indene may be prepared by the reaction of indene with a dispersion of sodium in tetrahydrofuran[18]

$$C_9H_8 + Na \longrightarrow Na^+ + C_9H_7^- + 0.5H_2$$

Reactions of this type may be broken into two parts

$$HA = H^+ + A^-$$
$$M + H^+ = 0.5H_2 + M^+$$

If we make the approximation that the free energy of formation of the dissolved salt is the same as that for the salt dissolved in water,[9] then we may readily calculate the pK value of the weakest acids which can react in this way by using the free energy of formation of the appropriate alkali metal ion.[14] Thus we calculate limiting pK values of 51, 46, and 49 for lithium, sodium, and potassium, respectively.

Metal–ammonia solutions are often used to deprotonate acids

$$e_{am}^- + HA_{am} \longrightarrow 0.5H_2 + A_{am}^-$$

By applying the rule that the pK values of normal acids are 10 units higher in water than in ammonia[3] and by using available thermodynamic data,[19] we calculate that acids with aqueous pK values less than 44 should be capable of being deprotonated by metal–ammonia solutions. However, in practice, the limiting pK value is around 37, because anions of acids with aqueous pK values greater than 37 are ammonolyzed in liquid ammonia.

Cleavage by Alkali Metals.—In the third method, the salt of a weak acid is formed by the reaction of an alkali metal with a halo derivative of the weak acid. This method is useful for preparing the salts of extremely weak acids (*e.g.*, benzene) for which the above two methods are inapplicable.[20] For example, sodium phenyl is readily formed by the reaction of finely divided sodium with chlorobenzene[21]

$$2Na + C_6H_5Cl \longrightarrow Na^+C_6H_5^- + NaCl$$

Reactions of this general category (in which a metal M reacts with a halide AX) may be broken into three parts

$$HA = H^+ + A^-$$
$$AX + H = HA + X$$
$$2M + X + H^+ = MX + M^+ + H$$

Obviously, for a given alkali metal and a given halogen, the over-all driving force depends not only on the pK of the acid, but also on the difference in the dissociation energies of the H–A and X–A bonds. Now, almost all of the acids for which this third method is practical are hydrocarbons. Thus we are principally concerned with the differences in the dissociation energies of C–H bonds and the corresponding C–X bonds. To the precision with which we may assume that the latter differences are constant on going from one weak carbon acid to another,[22,23] we may estimate the highest pK for which this type of reaction is thermodynamically possible. By considering the alkali metals lithium, sodium, and potassium and the halogens chlorine, bromine, and iodine, we find that the theoretical limiting pK value varies from 119 (for the cleavage of a chloro compound by potassium) to 102 (for the cleavage of an iodo compound by sodium).[14,15] Obviously it is unlikely that any hydrocarbon will be found whose alkali metal salts cannot be made by this method because of *thermodynamic* limitations.[24]

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[18] R. B. King, "Organometallic Syntheses," Vol. 1, J. J. Eisch and R. B. King, Ed., Academic Press Inc., New York, N. Y., 1965, p 74.

[19] W. L. Jolly, "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, Chapter 3, p 27.

[20] The pK of benzene is about 42 (private communication from A. Streitwieser, Jr.), and thus benzene should be thermodynamically capable of reacting with the alkali metals. However, no reaction takes place. Probably the deprotonation reaction has a high activation energy.

[21] G. E. Coates, "Organo-Metallic Compounds," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1960, p 23.

[22] The data in Table II of the paper by Benson[23] show that the difference between C–H and C–X bond energies is generally constant to about ±3 kcal/mole for a wide variety of organic radicals. For example $D(CH_3–H) = 104$, $D(C_6H_5CH_2–H) = 85$, $D(CH_3–I) = 56$, and $(C_6H_5CH_2–I) = 40$ kcal/mole.

[23] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

[24] This research was supported by the U. S. Atomic Energy Commission.

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The Paramagnetism of $[Cr_4(OH)_6(en)_6]I_6 \cdot 4H_2O$

Sir:

In this laboratory, the paramagnetism of a number of polynuclear ions is being studied, including Pheiffer's $[Cr_4(OH)_6(en)_6]^{6+}$ ion.[1] With $[Cr_4(OH)_6(en)_6]I_6 \cdot 4H_2O$,[2] the effective magnetic moment per metal ion is 3.53 BM at room temperature, a value somewhat less than those previously reported for dimeric hydoxo-bridged chromium(III) complexes.[3] The variation of the effective moment with temperature is shown in Figure 1 along with that of the reciprocal susceptibility. The experimental results can be described by the Curie–Weiss expression

$$\chi_A = \frac{1.93}{T + 76}$$

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[1] P. Pheiffer, *Z. Anorg. Chem.*, **58**, 286 (1908).

[2] Prepared as red-violet crystals by the addition of solid NaI to a hot solution of the chloride. *Anal.* Calcd for $Cr_4C_{12}H_{62}N_{12}O_{10}I_6$: C, 9.58; H, 4.15; N, 11.18. Found: C, 9.55; H, 4.19; N, 11.48.

[3] A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 395 (1961).