rapid randomization of the chlorine activity in the $POCl_3$ rich systems is consistent with an ion-molecule interaction and may be taken as indicative of the rate with which equilibrium is established in (1) and (2), above, in the ionizing solvent $POCl_3$.[16]

Per contra, the absence of exchange in BCl_3 rich systems may be taken as a reflection of the fact that (a) most of the $POCl_3$ in the system is tied up as the addition compound and thus not available for participation in equilibrium 1; and (b) any free phosphoryl chloride is likely present as the undissociated molecule, since the solvent nature of boron trichloride is such as to repress the self ionization equilibrium on the one hand and to hinder the migration of free chloride ions through the solution (as required by (2)) on the other.

The observed rapid halogen exchange in a reaction system composed of an equimolar mixture of BCl_3 and $POCl_3$ is in consonance with the suggested mechanism, since the decomposition of the addition complex, and resultant evaporation of BCl_3 into the gas phase of the reaction vessel, leaves behind a phase which is rich in $POCl_3$ and in which the exchange then can occur as suggested. This decomposition of the addition compound into its components suggests relatively weak bonding in the coördinate bond, in agreement with the results obtained by Sheldon and Tyree.[7] These workers were able to show that while CCl_4 and $SiCl_4$ formed no addition compounds with $POCl_3$, both $AsCl_3$ and $SnCl_4$ formed "weak" compounds and $TiCl_4$ formed two "strong" compounds. On the basis of electronegativity considerations (C and Si ~2.5, B and As ~2.0, Sn ~1.7 and Ti ~1.6) the formation of a "weak" compound between BCl_3 and $POCl_3$ is thus not unexpected. The experimental observation in the present study that a clean separation between $POCl_3$ and BCl_3 could be obtained by distillation into a liquid nitrogen cooled trap of the volatile material evolved from the addition compound held at −78° is further evidence of this weak compound formation and is in qualitative agreement with the observations of Burg and Ross[4b] who showed that the addition compound dissociation has a ΔF^0_{298} of -4.6 kcal. mole^{-1} and that the vapor is some 89.5 to 91.2% dissociated.

A test of the proposed mechanism lies in the measurement of conductivities of dilute solutions of BCl_3 in $POCl_3$ and of $POCl_3$ in BCl_3. If the present suggestions are correct, the former should show the moderate conductance to be expected from the self ionization of $POCl_3$, *without however any increase due to the presence of the BCl_3 solute.* Any increase in conductivity above this value (aside from possible activity effects) would be at variance with our suggested mechanism and could be taken as an indication of the formation of tetrachloroborate anions. The dilute solutions of $POCl_3$ in BCl_3 solvent, on the other hand, should show essentially zero conductance if the present suggestions are valid. Conductimetric measurements of this type currently are being undertaken[17] and should shed further light on the nature of $POCl_3$ as an ionizing solvent.

The author is indebted to the Hooker Electrochemical Company for their generosity in providing samples of $POCl_3$ and to Professors P. E. Yankwich and A. Kuppermann for illuminating discussions of this work, as well as to Professor R. R. Holmes for preliminary data on possible compound formation in the PCl_3–BCl_3 system.

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[16] NOTE ADDED IN PROOF.—Baaz and Gutmann (*Monatsh.*, **90**, 426 (1959)) have suggested the equilibrium $Cl_5SbOPCl_3 \rightleftarrows SbCl_6^- + POCl_2^+$ to account for observed conductivities in liquid $POCl_3$. While such a step is not ruled out completely in the present instance, it is likely that the Cl^- ion in (2) originates from a solvent molecule dissociation rather than from transfer of a chloride ion from the addition compound $POCl_3$.

[17] In the laboratory of Professor V. Gutmann, Technische Hochschule, Vienna.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Acid Ionization Constants of Alcohols. II. Acidities of Some Substituted Methanols and Related Compounds[1,2]

BY P. BALLINGER AND F. A. LONG

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The acid ionization constants of twelve simple alcohols have been determined by a conductivity procedure for dilute solutions in water at 25°. The values of K_{HA} range from 5.8×10^{-13} for trichloroethanol to 3×10^{-16} for methanol and allyl alcohol. For several of the alcohols comparisons can be made of their relative acidities in water with the relative acidities reported by Hine and Hine for the solvent 2-propanol. The qualitative agreement is good. A plot of pK *versus* σ^* for the aqueous ionization of a set of simple substituted methanols leads to a straight line with slope $\rho^* = 1.4$. The data lead to an extrapolated pK value for ethanol in water of 15.9. Using this, the relative acidities of methanol, water and ethanol are found to be in the ratio 3:2:1 for the solvent water. Data also are given for ionization of two of the alcohols in deuterium oxide. The resulting K^H/K^D values of 4.5 for 2,2,2-trifluoroethanol and 4.9 for 2-chloroethanol fit in well with data for carboxylic acids and phenols.

A previous communication gave details of a conductivity procedure for determining ionization constants for uncharged acids with pH values in the range 10 to 16.[3] The method has been illustrated for ionization of the alcohols 2,2,2-trifluoroethanol and 2-chloroethanol in the solvents H_2O and D_2O.[3,4] The present paper gives results for a number of other alcohols, most of them simple substituted methanols.

In view of the importance of alcohols, it is not

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[1] Work supported by a grant from the Atomic Energy Commission.

[2] Presented in part at Symposium on Electrolytes of the XLVIIth meeting of the Societa Italiana per il Progresso delle Scienze, Trieste, Italy. June 1959.

[3] P. Ballinger and F. A. Long, THIS JOURNAL, **81**, 1050 (1959).

[4] P. Ballinger and F. A. Long, *ibid.*, **81**, 2347 (1959).

surprising that their acidic properties have frequently been estimated and discussed. Hine and Hine[5] measured relative acidities of a large series of alcohols and amides (as well as water) in the solvent 2-propanol using an indicator method. There have also been several quantitative or semiquantitative estimates of acidity of individual alcohols, particularly ethanol and methanol. Caldin and Long[6] used an indicator procedure to measure relative amounts of ethoxide and hydroxide ions in water–ethanol mixtures. They also extrapolated their data to the two pure liquids and discussed relative acidities of ethanol and water in both solvents. Unmack[7] using her own conductivity data and some solubility data of Faurholt[8] concluded that methanol was roughly a three-fold stronger acid than water. However, she also noted that the autoprotolysis constants implied that methanol was actually the weaker acid. In the main ethanol is assumed to be weak relative to water (or methanol),[5,9] but even here there is at least one contrary opinion.[10]

A feature that often complicates this sort of discussion is variation in the reference solvent and one of the objects of the present study was to obtain a consistent set of data for the solvent water. Still another problem is that of standard state. The reaction that enters when a weakly acidic alcohol is added to an aqueous solution of base is

$$\mathrm{OH^- + ROH = RO^- + H_2O} \qquad (1)$$

Unmack and Caldin and Long utilized an equilibrium constant K' defined as

$$K' = \frac{C_{\mathrm{OH^-}}\, a_{\mathrm{ROH}}}{C_{\mathrm{OR^-}}\, a_{\mathrm{H_2O}}} \qquad (2)$$

where C_{OH^-} and C_{OR^-} refer to concentrations and where the activities for alcohol and water are each referred to unity for the pure component and hence are given for mixtures by the relative vapor pressures. We shall discuss a conventional ionization constant defined as

$$K_{\mathrm{HA}} = \frac{C_{\mathrm{H^+}}\, C_{\mathrm{OR^-}}}{C_{\mathrm{HOR}}}\; \frac{y_{\mathrm{H^+}}\, y_{\mathrm{OR^-}}}{y_{\mathrm{HOR}}} \qquad (3)$$

where C_{H^+}, etc., are molar concentrations and where the activity coefficients y_{H^+}, etc., are referred to the infinitely dilute aqueous solution. Put another way, equation 3 has for its standard state a hypothetical one molar concentration (with unit activity coefficient) for each of the species. Numerical values from these two treatments must evidently be compared with caution.

Experimental

Materials.—The best available samples of the alcohols were treated with anhydrous sodium carbonate to remove traces of mineral or carboxylic acids, then treated with a suitable drying agent and fractionated. Vapor phase chromatography was used wherever possible to establish the purity of the alcohols. Since even a minute trace of an acid appreciably stronger than the alcohol studied would lead to a spurious value for the pK of the latter, especially for pK's above about 14, it was essential to purify the materials with the greatest rigor. It was also essential to make sure that the alcohols were free from electrolyte. Accordingly, the electrical conductivity of a solution of the alcohol (of a concentration equal to or greater than the highest used in the subsequent pK determination) was measured and compared with the conductivity (*ca.* 1–2 $\times 10^{-6}$ ohm^{-1} cm.$^{-1}$) of the water itself. In a typical experiment of this kind, using a cell constant of 0.5083 cm.$^{-1}$, trichloroethanol (0.2 M) had a conductivity of 4.261 $\times 10^{-6}$ ohm^{-1} compared with 3.797 $\times 10^{-6}$ ohm^{-1} for the water alone. Calculation of the effective parallel conductance due to the organic compound (4.64 $\times 10^{-7}$ ohm^{-1}) showed that hydrogen ion, if responsible, can be present only in negligible (*ca.* 10^{-6} N) concentration compared with that (3.75 $\times 10^{-3}$ N) of the alkali used for the pK measurements. Frequently the specific conductivity of the pure material itself was measured. For example, methanol had a specific conductivity of *ca.* 10^{-6} ohm^{-1} cm.$^{-1}$ which compares favorably with the literature value[11] of 3 $\times 10^{-7}$ ohm^{-1} cm.$^{-1}$.

The preparation of reagents and solutions has been described previously.[3] The same reference also describes the procedure and calculations employed to determine the pK of an alcohol such as trifluoroethanol which does not react irreversibly with hydroxide ion.

The procedure for those alcohols (for example, 2-chloroethanol[4]) which are hydrolyzed irreversibly was as follows. Known volumes (usually 10 ml.) of solutions of the alcohol and of sodium hydroxide at thermostat temperature were mixed rapidly at zero time in a cell of special design.[4] At measured intervals, the resistance of the mixture was determined and plotted against time. The graph thus obtained was linear for 10–15 minutes and gave a good extrapolation to the resistance at zero time. Even this refinement was insufficient when using 2,2-dichloroethanol, which underwent slight but appreciable hydrolysis in neutral solution. Here, the pure material was added to sodium hydroxide solution at zero time and the mixture shaken and quickly transferred to the cell. After obtaining sufficient resistance measurements for the extrapolation, an aliquot of the solution was removed and the total chloride ion (and therefore the concentration of the alcohol) estimated by the Volhard method after complete hydrolysis with strong alkali.

Values of the equilibrium constant K for the reaction $\underset{}{\mathrm{SH}} + \underset{(1-\alpha)}{\mathrm{OH^-}} \overset{K}{\rightleftharpoons} \underset{(\alpha)}{\mathrm{S^-}} + \mathrm{H_2O}$, where SH and $\mathrm{S^-}$ represent the alcohol and its anion, respectively, were calculated as described previously.[3,4] For dilute solutions the activity coefficient correction factor for this reaction $y_{\mathrm{S^-}} a_{\mathrm{H_2O}} / y_{\mathrm{SH}} y_{\mathrm{OH^-}}$, will to a first approximation be unity. Hence to the same approximation multiplication of the observed K values by the ion product for pure water leads to the thermodynamic ionization constant for the acid SH. Table I gives illustrative data. The two examples are the relatively strong acid trichloroethanol and methanol, the weakest acid studied.

Results and Discussion

Table II gives values of the ionization constants for several carbon, hydrogen, oxygen alcohols in water. Most of these alcohols also were studied by Hine and Hine in 2-propanol and we have included these authors' values of relative acidities in the latter solvent. The agreement in the qualitative order of acidity for the two solvents is excellent. There are slight differences in the relative quantitative values but this is not at all surprising considering that both the solvent and the procedures for measurement were different. In fact the comparison of Table II can be taken as another illustration of the rule that relative protonic acidities are roughly independent of solvent.

Table III lists pK_{HA} values for a series of simple alcohols, all of which can be considered to be monosubstituted methanols. A question of interest is

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[5] J. Hine and M. Hine, This Journal, **74**, 5266 (1952).

[6] E. F. Caldin and G. Long, *J. Chem. Soc.*, 3737 (1954).

[7] A. Unmack, *Z. physik. Chem.*, **129**, 349 (1927); **131**, 371 (1928); **133**, 45 (1928).

[8] C. Faurholt, *ibid.*, **126**, 85 (1927).

[9] W. K. McEwen, This Journal, **58**, 1124 (1936).

[10] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 260.

[11] P. Walden, H. Ulich and G. Busch, *Z. physik. Chem.*, **153(A)**, 1 (1931).

TABLE I

EQUILIBRIUM CONSTANTS FOR THE REACTION OF ALCOHOLS WITH 0.0375 M HYDROXIDE ION IN WATER AT 25.0°

Alcohol	Concn. (M)	Resist. (ohm)	Viscos. (corr.)	Resist. (corr.)	λ_{S^-}	α	K (l./mole)
CCl_3CH_2OH	0.0	578.1 = R	.....	(578.1)			
	.01068	759.1[a]	1.00238	757.1		0.350	57.5
	.02136	905.3[a]	1.00476	901.0		.530	58.3
	.03204	1018.2[a]	1.00715	1011	28.0[b]	.634	58.3
	.05340	1181.3[a]	1.0119	1167		.747	58.4
	.1068	1406.1[a]	1.0238	1373		.857	57.9
	.0[c]	706.9	1.0000	(706.9)		Mean =	58.1
	.1068[c]	723.7	1.0238	706.9			
CH_3OH	.0	568.5 = R		(568.5)			
	.989	623.9	1.075	580		0.0294	0.031
	1.98	682.5	1.162	588		.0494	.026
	2.97	745.8	1.247	598	30[d]	.0733	.027
	3.96	812.4	1.336	608		.0967	.029
	4.95	877.5	1.427	616		.112	.026
	0.0[c]	708.0		(708)		Mean =	.03
	0.989[c]	761.6	1.075	708			
	1.98[c]	822.5	1.162	708			
	4.95[c]	1010.3	1.427	708			

[a] Extrapolated to instant of mixing. [b] Calculated by method of ref. 2. [c] 0.005 M potassium chloride solution. [d] Estimated value.

TABLE II

IONIZATION CONSTANTS OF SOME ALCOHOLS IN WATER

Alcohol	$10^{16}K_{HA}$	K_e[a]
$CH{\equiv}CCH_2OH$	280	....
$C(CH_2OH)_4$	79	440
$CH_2OHCHOHCH_2OH$	40	60
CH_2OHCH_2OH	17	43
CH_3OCH_2OH	15	8
CH_3OH	2.9	4.0
$CH_2{=}CHCH_2OH$	~3	2.7
H_2O	1.8[b]	1.20
CH_3CH_2OH	~1[c]	0.95

[a] Relative acidities in the solvent 2-propanol from ref. 5. [b] Ion product referred to hypothetical one molar solution. [c] Estimated from extrapolation of Fig. 1.

TABLE III

SUBSTITUENT EFFECTS FOR IONIZATION OF RCH_2OH

R group	σ^*	pK_{HA}
CCl_3–	2.65	12.24
CF_3–	..	12.37
CHF_2CF_2–	..	12.74
$CHCl_2$–	1.94	12.89
$CH{\equiv}C$–	1.7[a]	13.55
CH_2Cl–	1.05	14.31
CH_3OCH_2–	0.64[b]	14.8
$HOCH_2$–	0.56	15.1[c]
H–	0.49	15.5
$CH_2{=}CH$–	..	15.5
CH_3– (extrap.)	0	(15.9)

[a] This σ^* value is an approximate one estimated by R. W. Taft (personal communication) from two rather disparate sets of experiments. [b] Taft (personal communication) states that this σ^* value is the preferred one for studies in aqueous solutions rather than the published value (ref. 12) of 0.52. See also H. K. Hall, THIS JOURNAL, 79, 5441 (1957). [c] The observed pK for ethylene glycol is 15.4. For the present comparison the statistical factor, log 2, has been subtracted from it.

whether the acidities fall in the order predicted by simple polar inductive effects. In a rough sense it is evident that they do. Strongly electron attracting groups like CCl_3 and CF_3 lead to the strongest acids and there is clearly a decrease in acidity for the less strongly electron attracting groups. However it is obviously desirable to discuss such correlations in more quantitative terms and this can be done by use of the Taft $\rho^*\sigma^*$ development.[12] Taft has shown that when steric effects and resonance effects are negligible, one can expect a correlation of rates and equilibria with substituent parameters as indicated in equation 4

$$\log k_i = \rho^*\sigma_i^* + \text{constant} \qquad (4)$$

which can be thought of as a generalization of the Hammett $\rho\sigma$ equation. Here k_i refers to the measured rate or equilibrium constant when the substrate contains the group i and σ_i^* is the polar substituent parameter for the ith group. ρ^* is a constant which measures the susceptibility of the particular reaction to polar substituent. The ionization of the simple alcohol RCH_2OH would *a priori* be expected to be an excellent case for application of equation 4. Resonance effects should contribute little to the relative stability of either the molecule or anion and it is well known that steric requirements for proton transfer reactions are small.[13] Values of σ^* are available for most of the substituents of interest and are listed in Table III. Fig. 1 gives a plot of the pK values (corrected for statistical factors) against the σ^* values and it is apparent that the correlation of pK with σ^* is excellent.[14] The value of ρ^* which results from the solid line of Fig. 1 is +1.42. This is of about the expected

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(12) R. W. Taft, THIS JOURNAL, **74**, 3120 (1952); **75**, 4231 (1953). For a complete discussion see R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(13) For a discussion, see G. S. Hammond, "Steric Effects in Organic Chemistry," M. S. Newman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 9.

(14) We attempted to make pK measurements for CHF_2CH_2OH but we were unable to prepare a sample of sufficient purity to permit us to obtain a trustworthy value. However, a roughly 90% pure sample, from which acidic impurities had been removed rigorously, did yield an approximate pK of 13.3 in reasonable agreement with that predicted from the σ^* value of 2.05 for the CHF_2 group.

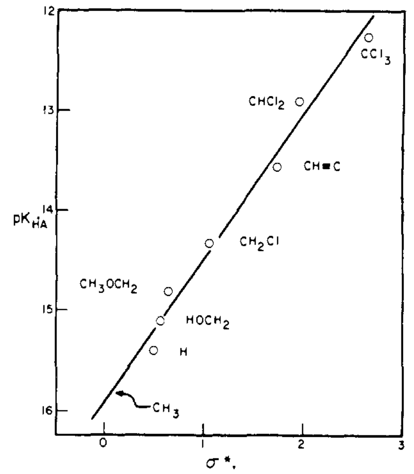

Fig. 1.—Plot of pK_{HA} *vs.* σ^* for ionization of substituted methanols in water.

size for for ionization of these acids and in fact is very close to the ρ^* value 1.36 which Taft[12] calculated from the data of Hine and Hine for acidity of alcohols in 2-propanol. Clearly the assumption that steric and resonance effects are negligible is well justified.[15]

Extrapolation of Fig. 1 to the σ^* value of zero for the CH_3 group leads to a predicted pK value for ethanol in water of 15.9 with an estimated error of ± 0.2.[16] The implications thus are that ethanol in water is only a slightly weaker acid than methanol and that methanol, water and ethanol are all of comparable acid strength. More specifically if we consider as standard state a one molar solution in water, the relative acidities of these three substances are in the approximate ratio 3:2:1 (Table II). The close similarity of the acidity in water of methanol and ethanol is of some interest in view of the frequent use of the McEwen values of $pK = 16$ for methanol and 18 for ethanol.[17]

The equilibrium constants for the reactions of methanol and ethanol with hydroxide ion can be converted to values which refer to the pure liquids as standard states by use of the vapor pressure data of Butler, *et al.*[18,19] These investigators define an activity coefficient f_2 for the alcohols by the relation $p_2/p_2^0 = N_2f_2$ where p_2/p_2^0 is relative vapor pressure of the alcohol in water and N_2 is its mole fraction. By extrapolating their data to infinite dilution in water, they obtain $f_2^0 = 1.507$ for methanol and $f_2^0 = 3.48$ for ethanol. A molar solution of an alcohol in water corresponds at 25° to a mole fraction N_2 of 0.0184 for methanol and 0.0188 for ethanol. These figures and the data for the ionization constants of the alcohols in water permit calculation of the constants K' as defined in equation 2 for the particular case of an infinitely dilute solution of the alcohol and of the ionic species in water. The results are

$$K' = 0.96 \text{ for methanol}$$
$$K' = 5. \text{ for ethanol}$$

The value of K' for ethanol agrees very well with the figure of 4.5 which is stated by Caldin and Long to result from kinetic studies in dilute solutions of alcohol in water. The value of $K' = 0.96$ for methanol in water is also in reasonable agreement with an average of the several values listed by Unmack. The roughly 6-fold difference between the values of K' for the two alcohols is about equally due to the higher acidity of methanol in water on a molar concentration basis (Table II) and to the different magnitudes of f_2^0 for the two alcohols.[20]

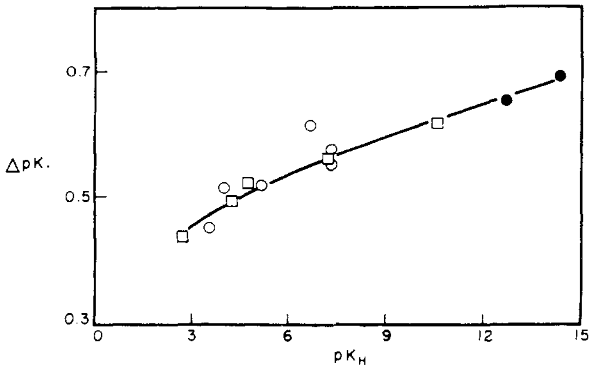

Fig. 2.—Values of $(pK^D - pK^H)$ *vs.* pK^H for relative ionization in H_2O and D_2O: □ chloroacetic, acetic and benzoic acids, hydroquinone and dihydrogenphosphate ion (Rule and LaMer); ○ substituted phenols (Martin and Butler); ● aliphatic alcohols.

The pK values for two of the alcohols of Table III have been measured in the solvent deuterium oxide (99.5 atom % D).[3,4] The results are CF_3CH_2OD, $pK_{DA} = 13.02$, $K^H/K^D = 4.5$; CH_2ClCH_2OD, $pK_{DA} = 14.99$, $K^H/K^D = 4.9$. These values are compared in Fig. 2 with the K^H/K^D data of Rule and LaMer[21] and also with the less precise ratios of Martin and Butler for several substituted phenols.[22] The ΔpK values for the very weak acids fall nicely on an extension of the Rule and LaMer curve which also agrees well with the values for the phenols. This extended plot offers further support for the proposal that ΔpK values increase with increasing pK^H. But even though this proposal does appear to be valid, it should be noted that there is a good deal of evidence that the values of ΔpK vary with acid type with the result that the curve of Fig. 2 is by no means universally applicable.[23]

Ithaca, N. Y.

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[15] One can combine the curve of Fig. 1 and the data of Table III to arrive at estimates of σ^* values for a few additional substituent groups. The groups and estimated σ^* values are: CF_3, 2.5; CHF_2CF_2, 2.2; $CH_2{=}CH$, 0.3.

[16] We have made a few measurements of the effect of ethanol on the conductivity of aqueous solutions of sodium hydroxide. No effects were observed beyond those expected from viscosity changes. This indicates that K for reaction 1 is not larger than about 0.02, in rough agreement with the above extrapolated value for pK.

[17] See, for example, S. Winstein and E. Grunwald, This Journal, **70**, 828 (1948), who start from the McEwen value of $pK = 18$ for ethanol in making estimates of the pK's for some chlorohydrins.

[18] J. A. V. Butler, D. W. Thompson and W. H. Maclennan, *J. Chem. Soc.*, 674 (1933).

[19] R. Shaw and J. A. V. Butler, *Proc. Roy. Soc.* (*London*), **129A**, 519 (1930).

[20] Caldin and Long use the value of $K' \simeq 5$ for ethanol in water to reach the conclusion that for this solvent water is a 5-fold stronger acid than ethanol. The difference between their factor of 5 and the factor of 2 as listed in Table II is of course entirely due to a different choice of standard states for the comparison.

[21] C. K. Rule and V. K. LaMer, This Journal, **60**, 1981 (1938).

[22] D. C. Martin and J. A. V. Butler, *J. Chem. Soc.*, 1366 (1939).

[23] See, for example, the recent discussion of E. Högfeldt and J. Bigeleisen, This Journal, **82**, 15 (1960).