17.7, $Q_{OC}{}^{C} = -27.1$, and $Q_{NC}{}^{C} = -20.5$. Spin densities as calculated by the McLachlan method (Table IV) were used. The calculated C^{13} splittings were -5.9, 2.0, and 0.1 gauss for positions 7, 8, and 1, respectively. The largest splitting is predicted for position 7 and this was confirmed experimentally; however, the calculated value was twice as big as the observed one. These results therefore suggest that the splitting constant of 1.89 gauss is associated with position 8 rather than 1. The results of these calculations, although in qualitative agreement with the experimental data, should be treated with some reserve, since it has been pointed out by Karplus and Fraenkel[22] that the calculated C^{13} splittings are very sensitive functions of the spin density of a central atom and of its neighbors, and cancellations can occur among different contributions to the splitting. In addition, Das and Fraenkel[29] showed that calculated spin densities adjusted to fit the proton splittings are not always accurate enough for "blank positions" where no proton is attached.

Acknowledgment. We wish to acknowledge our appreciation to Professor G. K. Fraenkel for bringing Dr. Rieger's thesis to our attention and to Professor Rieger for permission to quote some of his results. We also thank Professor A. H. Maki for a copy of his SESRS computer program and Mr. D. Saperstein for his help in preparation of some of the computations.

Basicities of Methanol and 2-Propanol as Determined by Raman Spectrophotometry[1]

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Abstract: Raman intensity measurements have been used to determine the concentration of unprotonated alcohol in solutions of methanol in aqueous hydrochloric acid and 2-propanol in aqueous perchloric and hydrochloric acids. This technique leads to the following values of H_0 for 50% protonation: methanol in HCl, -4.86 ± 0.37; 2-propanol in HCl, -4.72 ± 0.95; 2-propanol in $HClO_4$, -5.16 ± 0.45.

It has always been difficult to determine the basicities of aliphatic alcohols; they are too weakly basic for the techniques used in dilute aqueous solutions, and they do not have the usual spectral properties which have been used to measure base strengths of other compounds in concentrated acid solutions.[3] Moreover, the study of aqueous solutions of alcohol is complicated by the similarity in chemical and physical properties of the solute and solvent.

It is not surprising, then, that the first quantitative evidence for protonation of a simple alcohol appears to have been obtained indirectly from a kinetic study primarily concerned with another reaction.[4] In their studies of the rate of hydride transfer from 2-propanol to the triphenylcarbonium ion, Bartlett and McCollum[4] attributed the decrease in rate produced by increasing acid concentration to the formation of an oxonium ion. Their results indicated a value of -3.2 for the pK_{BH^+} of 2-propanol. (The pK_{BH^+} is defined as the value of H_0 for which the ratio $(BH^+)/(B) = (ROH_2{}^+)/(ROH)$ is unity.) Similar kinetic evidence has been obtained for 2-propanol in the oxidation by chromium(VI) oxide[5] ($pK_{BH^+} = -3.8$) for ethanol in a hydride-transfer reaction[6] ($pK_{BH^+} = -2.3$), and for *t*-butyl alcohol in the alkylation of acrylonitrile[7] ($pK_{BH^+} = -3.8$). All these systems were studied as relatively dilute solutions of alcohol in concentrated acid, as is evident from the p*K* values. (For example, 50% sulfuric acid has an H_0 of -3.4.)

In addition to measurements based on kinetic techniques, more direct equilibrium studies have been carried out, using the phase distribution of alcohol between aqueous acids and organic solvents or pure alcohol. These methods indicated that 2-propanol had a pK_{BH^+} of around -1.2,[6] in contradiction to the result from the kinetic method. On the other hand, similar experiments by Arnett and his group[8] and by Deno and co-workers[9] tended to confirm the original estimates of Bartlett and McCollum for the basicity of simple alcohols. Further conflicting evidence was offered by an nmr study of ethanol,[10] which indicated 50% protonation at an H_0 value of -4.8, but did not give the expected dependence of the chemical shift on the acidity function.

In view of the difficulties of measuring the basicity of alcohols, and the contradictory data for them, a new technique proposed by Deno and Wisotsky[11] is of great interest. They measured the Raman intensity of

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

[2] Max-Planck-Institut für Chemie, 6500 Mainz, Germany.

[3] *Cf.*, for example, E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

[4] P. D. Bartlett and J. D. McCollum, *J. Am. Chem. Soc.*, **78**, 1441 (1956).

[5] J. Roček and J. Krupička, *Collection Czech. Chem. Commun.*, **23**, 2068 (1958).

[6] W. F. Smith, Ph.D. Thesis, Harvard University, 1960.

[7] N. Deno, T. Edwards, and C. Perizzolo, *J. Am. Chem. Soc.*, **79**, 2108 (1957).

[8] E. M. Arnett and J. A. Anderson, *ibid.*, **85**, 1542 (1963).

[9] N. C. Deno and J. O. Turner, *J. Org. Chem.*, **31**, 1969 (1966).

[10] J. T. Edward, J. B. Leane, and I. C. Wang, *Can. J. Chem.*, 40, 1521 (1962).

[11] N. C. Deno and M. J. Wisotsky, *J. Am. Chem. Soc.*, **85**, 1735 (1963).

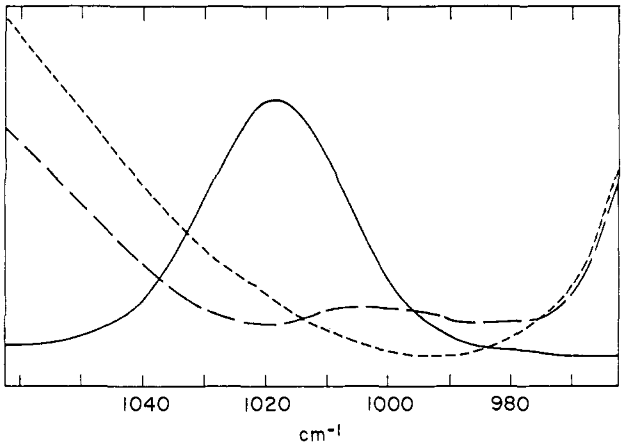

Figure 1. Raman spectra in the region of the methanol C–O stretching vibration: ———, 10% methanol in water; - - - -, 7.5 M HClO$_4$; — —, 10% methanol in 7.5 M HClO$_4$.

the C–O stretching band of methanol (at 1021 cm^{-1}), which disappears upon formation of the oxonium ion. Their data indicate that methanol is half-protonated in 39% sulfuric acid, which leads to a pK_{BH^+} of -2.2. Their similar spectroscopic determinations for methylamine, acetamide, dioxane, and acetone gave pK values in good agreement with those obtained by other methods.

However, in examining their published spectra for the alcohol systems, one notes that the 1020-cm^{-1} band is almost coincident with a strong band of the sulfate ion. This necessitates a large background correction which may lead to large errors in intensity. We hoped to improve upon these measurements by studying methanol in acids which do not have a Raman band in this region, and also, to extend the method to other alcohols, if possible. In this communication we report our results for methanol in hydrochloric acid and 2-propanol in hydrochloric and perchloric acids.

Experimental Section

Methanol (Baker and Adamson reagent grade) and 2-propanol (Baker Analyzed reagent) were used without further purification. Solutions in water and in aqueous hydrochloric and perchloric acids (both Baker Analyzed reagents) were made up volumetrically. Acid concentrations in the alcohol solutions were determined by titration of aliquot portions with standardized sodium hydroxide solutions, bromthymol blue being used as indicator. Acidity functions were obtained from the compilation of Paul and Long.[12]

The measurements were made with a Cary Model 81 Raman spectrophotometer (Applied Physics Corp.). The 4358-A exciting line of the Toronto arc was isolated by means of a circulating filter solution of ethyl violet and Cyasorb UV24 (American Cyanamid Corp.). Most of the work was done with Pyrex sample cells 19 mm in diameter and with a volume of 65 ml; a few measurements were also made with 5-ml cells 7 mm in diameter. It has been shown previously[13] that the temperature within these sample cells while in the spectrometer is 33 ± 5°.

Spectra were recorded with a spectral slit width of 20 cm^{-1}, at a speed of 0.25 cm^{-1}/sec, and with a scale of 10 cm^{-1}/in. of chart. The sensitivity of the spectrophotometer was set so that the area of the unprotonated alcohol peak was about 50 cm^2, and areas were measured with a planimeter.

Results

In the case of methanol, the band used as a measure of protonation was the one at 1020 cm^{-1} (in aqueous solution) used by Deno and Wisotsky.[11] It was shown that this band has essentially disappeared in concentrated acid solutions (Figure 1). At intermediate concentrations, its position is shifted toward lower frequencies, by as much as 10–20 cm^{-1}, and its breadth is increased. These effects may result from changes in hydrogen bonding of the alcohol as it competes with the hydronium ion for solvent molecules. However, in none of the acid solutions were we able to find any new bands attributable to the oxonium ion form. As a monitor of the lamp intensity (which changes only very slowly with the filter solution we use), the weak band at 1460 cm^{-1} due to the CH$_3$ deformation vibration was used. We found this preferable to the C–H stretching bands at 2850 and 2960 cm^{-1} which Deno and Wisotsky used for this purpose. The latter bands are near the very strong O–H stretching band of water; hence, the base line is very steep, making it difficult for us to obtain precise intensity measurements. Some measurements were made at alcohol concentrations of 5–20% (by volume), but only a 5% solution was used for the complete range of acid concentrations. The intensity measurements on the aqueous solutions showed that the scattered light intensity of the 1020-cm^{-1} band was indeed proportional to the methanol concentration. Perchloric acid solutions were not suitable for quantitative intensity measurements. The 1020-cm^{-1} region lies between two strong ClO$_4^-$ peaks, and it is difficult to correct for the resulting curvature of the base line. Therefore, we used hydrochloric acid, which has no peak in this region, but which limits the experiments to a region where H_0 is greater than -4.2.

The experiments on 2-propanol were all carried out with 5% (by volume) solutions of alcohol in aqueous perchloric and hydrochloric acids. The spectral region where the C–O stretching band is expected to appear does not exhibit a single peak at 1020 cm^{-1}, but rather a sharp peak at 950 cm^{-1} and a doublet at 1125 and 1160 cm^{-1}; the intensities of all of these decrease in acid solutions (Figure 2). To avoid the strong ClO$_4^-$ bands in this region, we utilized instead a band at 815 cm^{-1}. This is probably an O–H deformation vibration; in any case, the band was found to disappear almost completely in strong acid (Figures 2 and 3). Again, the band was observed to broaden and to shift to lower frequencies in acid solutions.

Since we had found no particular advantage in the procedure of using an internal intensity standard (see below), this method was abandoned in favor of a simpler procedure. At each acid concentration, we made two series of three measurements for the acid solution A and the aqueous solution W, each containing the same concentration of alcohol. In the first series, cell 1 contained A and cell 2 contained W, and intensities were measured in the sequence A1, W2, A1′, W2′, A1″, W2″. To partially eliminate any time-dependent variables, the ratios R = A1/W2, R' = A1′/W2′, etc., were taken. For the second series, the solutions were interchanged in the two cells, and the sequence of measurements was repeated to give R = A2/W1, etc. Finally, since there may be small differences in the optical efficiency of the two cells, the preceding ratios

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

[13] K. Heinzinger and R. E. Weston, Jr., *J. Chem. Phys.*, 42, 272 (1965).

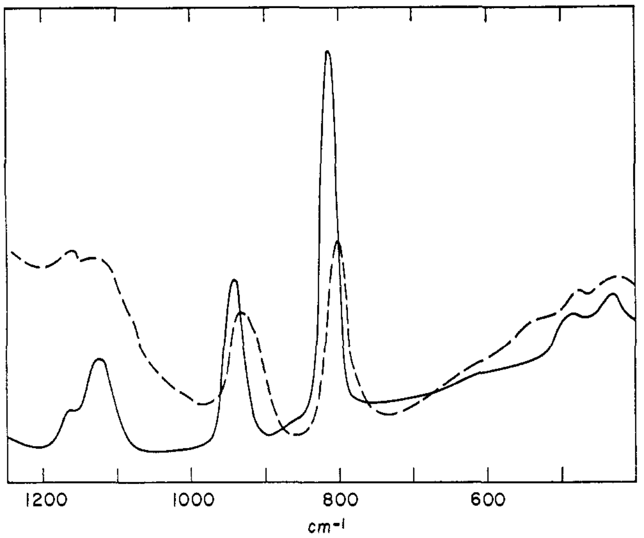

Figure 2. Raman spectra of 5% 2-propanol solutions: ———, in water; - - - -, in 11 M HCl.

were averaged geometrically, so that the final ratio is given by $R = (\mathrm{A1A2/W1W2})^{1/2}$, etc. The particular method of averaging was shown to be relatively unimportant. The same ratios, within the limits of experimental error, were obtained by the method just described, by the averaging method used previously,[13] or by forming the simple mean ratio, $\Sigma\mathrm{A}/\Sigma\mathrm{W}$.

Table I. Raman Intensities of 1020- and 1460-Cm^{-1} Bands of 5% Methanol Solutions

	Peak area		$(\mathrm{ROH})_\mathrm{A}/(\mathrm{ROH})_\mathrm{W}$		$(\mathrm{ROH_2^+})/(\mathrm{ROH})$	
Solvent[a]	1020	1460	I[b]	II[c]	I	II
Series I, 7.32 M HCl, $H_0 = -2.71$						
A	9.76	6.25	0.830	0.840	0.205	0.190
W	12.23	5.95				
A	9.63	5.93	0.862	0.830	0.160	0.205
A	9.49	5.93	0.851	0.817	0.175	0.224
W	11.02	5.94				
Series II, 7.32 M HCl, $H_0 = -2.71$						
W	11.51	6.95				
W	11.60	5.73				
A	8.76	6.10	0.766	0.776	0.305[d]	0.289
A	8.95	5.59	0.851	0.793	0.175	0.261
A	8.88	5.62	0.840	0.787	0.190	0.271
A	8.79	5.63	0.830	0.779	0.205	0.284
W	10.72	6.02				
Series III, 9.58 M HCl, $H_0 = -3.42$						
W	11.49	6.29				
A	8.11	6.04	0.713	0.712	0.402	0.404
A	8.23	5.88	0.745	0.722	0.342	0.385
W	11.29	6.23				
Series IV, 10.96 M HCl, $H_0 = -3.92$						
A	7.67	5.98	0.680	0.693	0.470	0.443
A	7.63	5.89	0.691	0.690	0.447	0.449
W	10.64	6.08				
W	11.49	5.90				
Series V, 11.44 M HCl, $H_0 = -4.18$						
W	11.55	6.42				
W	11.88	5.75				
A	6.53	5.60	0.622	0.569	0.607	0.757
A	6.63	5.71	0.617	0.578	0.621	0.730
W	11.03	6.20				
W	11.45	5.57				

[a] W = water, A = acid. [b] $(1020/1460)_\mathrm{A}$/mean(1020/1460) of all W solutions = $(1020/1460)_\mathrm{A}/(1.88 \pm 0.12)$. [c] $(1020)_\mathrm{A}$/mean 1020 for W solutions of same series. [d] Excluded from least-squares analysis.

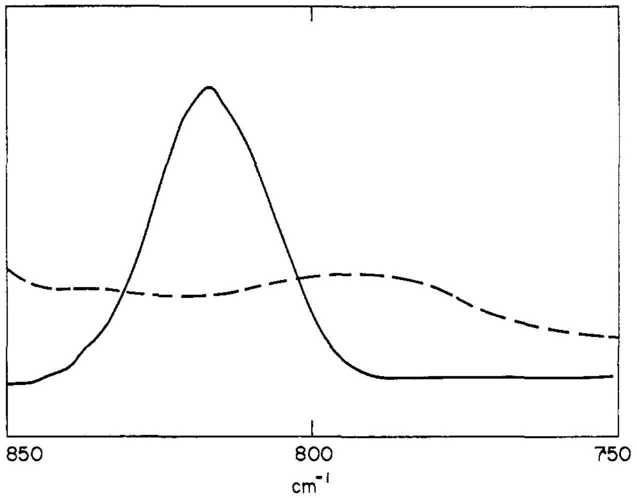

Figure 3. 2-Propanol Raman band used for concentration measurements: ———, 5% solution in water; - - - -, 5% solution in 11 M $HClO_4$.

In principle, the intensity measurements should be corrected by a factor related to optical effects in the spectrophotometer and dependent on the refractive index of the solution.[14] However, in the hydrochloric acid solutions, no consistent trend in the intensity of the 1460-cm^{-1} band with increasing acid concentration was found, so no correction factor was applied. Of course, when the C–H band intensity is used to normalize the C–O band intensity (by taking the ratio of the integrated intensities), any such optical effect will drop out of the final ratio. In the case of perchloric acid solutions, where no internal intensity standard was used, a correction factor was derived from earlier work on perchloric acid.[13]

In the most concentrated hydrochloric acid solutions, it was found necessary to obtain the spectra immediately after preparation of the solutions. Otherwise, a reaction took place which produced a water-insoluble phase, presumably the alkyl chloride corresponding to the alcohol in solution.

The results of these measurements are shown in Tables I–III and Figures 4 and 5. Table I contains the relevant data for solutions of methanol in hydrochloric acid. Ratios $(\mathrm{BH^+})/(\mathrm{B}) = [(\mathrm{B})_\mathrm{aqueous} - (\mathrm{B})_\mathrm{acid}]/(\mathrm{B})_\mathrm{acid}$ were calculated in two ways. Method I uses the 1460-cm^{-1} band as an internal intensity standard for the 1020-cm^{-1} band, while method II simply uses the relative intensities of the 1020-cm^{-1} band in acid and in water. In this method, the intensity used for the aqueous solution was the mean of values obtained during a given series of measurements. Since the two methods led to virtually identical results (*cf.* Figure 4), only method II was applied to 2-propanol solutions, and the data are in Table II.

The conventional treatment of data such as these calls for a linear dependence of the quantity $\log[(\mathrm{BH^+})/(\mathrm{B})]$ on the acidity function, according to the equation

$$\log[(\mathrm{BH^+})/(\mathrm{B})] = \mathrm{p}K_{\mathrm{BH^+}} - H_0 \qquad (1)$$

When the data of Tables I and II are plotted as a function of H_0, a linear relationship is found (Figures 4 and 5), but it is obvious that the slope is much less than

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(14) D. G. Rea, *J. Opt. Soc. Am.*, **49**, 90 (1959).

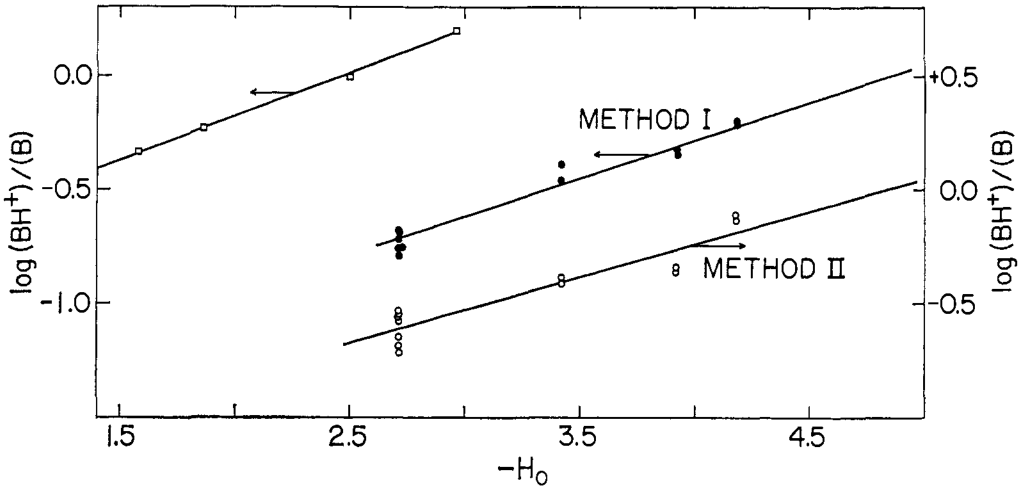

Figure 4. Indicator plot for methanol: ●, 5% methanol in HCl, concentrations calculated according to method I described in text; ○, same solutions, concentrations calculated according to method II; □, 20% methanol in H_2SO_4.[11] The solid lines are drawn with the least-squares parameters of Table III.

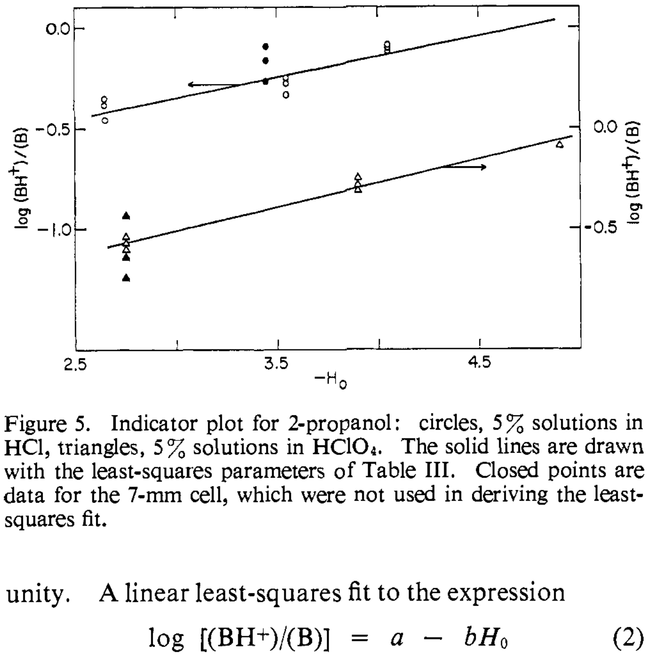

Figure 5. Indicator plot for 2-propanol: circles, 5% solutions in HCl, triangles, 5% solutions in $HClO_4$. The solid lines are drawn with the least-squares parameters of Table III. Closed points are data for the 7-mm cell, which were not used in deriving the least-squares fit.

unity. A linear least-squares fit to the expression

$$\log [(BH^+)/(B)] = a - bH_0 \qquad (2)$$

was carried out, with the results shown in Table III. If we retain the definition of pK_{BH^+} as the value of H_0 when $(BH^+) = (B)$, then

$$pK_{BH^+} = a/b \qquad (3)$$

The pK_{BH^+} values are also included in Table III.

It might be pointed out that in the range of acid concentration used in this work, H_0 is very nearly a linear function of acid concentration in moles/liter, so that we could equally well have used this quantity as the independent variable and obtained a linear dependence of the quantity $\log [(BH^+)/(B)]$.

Discussion

Our work leads to much lower estimates of aliphatic alcohol basicities than does the published interpretation of the Raman measurements of Deno and Wisotsky [11] However, it has been suggested to us by a referee that their spectra may be interpreted in a way which removes this apparent discrepancy. Thus, if their spectrum of methanol in 41% H_2SO_4 (Figure 2 of ref 11) consists of two nearly coincident peaks of comparable intensity, rather than a weak shoulder on a large sulfate peak, the intensity of the methanol peak would be comparable to that found in water. Therefore, the extent of protonation would be small, in agreement with what one would predict from our measurements.

Table II. Raman Intensity of the 815-Cm^{-1} Band of 5% 2-Propanol in Acid Relative to That in Water

Solvent	$-H_0$	(Peak area)$_A$/ (peak area)$_W$	(ROH_2^+)/ (ROH)
7.49 *M* HCl	2.65	0.708	0.412
		0.691	0.447
		0.744	0.344
9.68 *M* HCl[a]	3.45	0.555	0.802
		0.593	0.686
		0.650	0.538
9.87 *M* HCl	3.55	0.682	0.466
		0.639	0.565
		0.653	0.531
11.14 *M* HCl	4.05	0.569	0.757
		0.550	0.818
		0.558	0.792
6.02 *M* $HClO_4$	2.75	0.781	0.280
		0.789	0.268
		0.801	0.248
6.02 *M* $HClO_4$[a]	2.75	0.814	0.228
		0.729	0.372
		0.845	0.183
7.40 *M* $HClO_4$	3.90	0.670	0.494
		0.656	0.525
		0.639	0.565
8.75 *M* $HClO_4$	4.90	0.550	0.819

[a] 5-ml cell used. These data not included in least-squares analysis.

Table III. Least-Squares Parameters of Eq 2

Base	Acid	No. of points	*b*, slope	$\sigma(b)$	$-pK_{BH^+}$	$\sigma(pK)$
Methanol[a]	HCl	12	0.335	0.021	4.86	0.37
Methanol[b]	HCl	13	0.288	0.032	4.85	0.65
2-Propanol	HCl	9	0.202	0.032	4.72	0.95
2-Propanol	$HClO_4$	7	0.235	0.017	5.16	0.45

[a] Method I (*cf.* text). [b] Method II.

The indirect kinetic estimates of base strengths of alcohols give conflicting evidence. For example, Bartlett and McCollum[4] measured rates of reduction of triphenylcarbonium ion and dianisylcarbonium ion by 2-propanol in sulfuric acid. The decrease in the observed second-order rate constant was assumed to be caused by the transformation of a reactive species (the alcohol) into a relatively unreactive one (the oxonium ion). The indicator ratio is then given by the expression

$$(\mathrm{BH}^+)/(\mathrm{B}) = (k_2{}^0 - k_2)/k_2 \qquad (4)$$

where k_2 is the observed rate constant and the superscript denotes the value of this quantity obtained by extrapolation into the region where no protonation occurs. Their data for both carbonium ions may be plotted according to eq 2 to give reasonably good straight lines with a slope of unity and a $\mathrm{p}K_{\mathrm{BH}^+}$ of -3.2. Perhaps significantly they state that it was not possible to find the anticipated dependence of the rate constant on H_0 for alcohol concentrations greater than 0.5 *M*, whereas our solutions were 0.65 *M*.

A similar hydride-transfer mechanism has been proposed by Roček and Krupička[5] for the acid-catalyzed chromate oxidation of 2-propanol in sulfuric acid. Their data, plotted according to eq 2, can be made to fit a line with unit slope and a pK of -3.8 in the H_0 range from -3 to -5, but the deviation from this line is very large at higher H_0 values. The alcohol concentration for these experiments is not specified in their paper, but from other data they give, it appears to be $\leqslant 0.5$ *M*.

On the other hand, Gold and Satchell[15] have found a very different dependence on acidity in their study of the exchange of tritium between aqueous perchloric acid and 2-propanol (concentration, 0.12 *M*). The rate-determining step involves either an oxonium ion or a carbonium ion derived from it. Their experiments show that the logarithm of the rate constant is a linear function of H_0 throughout the range of -1.26 to -4.33. The approach to a limiting value of the rate constant which would be expected if the alcohol were completely protonated was not observed. This indicates an upper limit of about -4.5 for $\mathrm{p}K_{\mathrm{BH}^+}$. Since these experiments were done in perchloric acid, there is again a possiblity that the H_0 scale is not valid for comparing the acidities of perchloric and sulfuric acids relative to alcohols as bases. Also, the temperature of these experiments was 100°, so that a large temperature dependence of the quantity p$K - H_0$ could account for the discrepancy.

Deno, *et al.*,[7] have studied the rate of alkylation of acrylonitrile by *t*-butyl alcohol in sulfuric acid, and from their kinetic results they report that $\mathrm{p}K_{\mathrm{BH}^+} = -3.8 \pm 0.4$. The alcohol concentration was $\leqslant 0.4$ *M*, usually 0.21 *M*. Their value of the pK was obtained by using it to calculate the concentration of oxonium ion from the stoichiometric concentration of butanol, and then searching for the pK value which minimized the dependence of the second-order rate constant on acid concentration. If their data are analyzed by a method analogous to that of Roček and Krupička, the pK would be somewhat less negative.

However, conflicting data were obtained by Gold and Riley,[16] who determined rates of *t*-butylation of anisole in aqueous perchloric acid. No leveling-off in the rate constant at high acidities was observed, although the H_0 range extended to -4.53. This sets an upper limit of about -5 for the $\mathrm{p}K_{\mathrm{BH}^+}$ of *t*-butyl alcohol.

It has also been reported[6] that a kinetic method for ethanol gives a pK of -2.3. Thus, the kinetic determinations for the various alcohols do not give a self-consistent set of values, and one can only assume that there are mechanistic differences which have not yet been completely revealed. In this connection, it is interesting to note that the experiments in which the rate is determined by the concentration of unprotonated alcohol[4–6] generally indicate pK's which are more positive than those in which the rate depends on the oxonium ion concentration.[7,15,16]

In general, the kinetic methods suffer from the disadvantage of indirectness. The dependence of the rate constant on acid concentration is assumed to arise from a change in oxonium ion concentration, but medium effects which are concentration dependent may also contribute. One might expect these medium effects to be larger for the kinetic than for the equilibrium measurements, since there is a considerable difference between the positively charged reactant and the transition state. In equilibrium measurements, however, the positively charged species are $\mathrm{H_3O^+}$ and $\mathrm{ROH_2^+}$, which are probably quite similar.

Information about alcohol protonation is also available from methods which do not depend on kinetic measurements and are probably more straightforward. Arnett and Anderson[8] have applied a solvent extraction method to *n*-butyl, *sec*-butyl, *t*-butyl, and *t*-amyl alcohols in sulfuric acid. The pK values all lie in the narrow range of -2.16 to -2.56.

Related to this method are the solubility measurements of Deno and Turner,[9] where the concentrations in the aqueous sulfuric acid phase were determined spectrophotometrically. The alcohols contained a phenyl group at some distance from the site of protonation to produce optical absorption in the 260–270-mμ region. For 8-phenyloctanol, 11-phenyl-2-undecanol, and 2-methyl-11-phenyl-2-undecanol, they obtained pK's ranging from -2.3 to -2.5.

The possible sources of error in these techniques have been discussed previously.[8] The major assumption in the solvent extraction method is that the distribution coefficient of the unprotonated base is independent of acid concentration, while a similar independence is required of its solubility in the work of Deno and Turner. Furthermore, the oxonium ion is assumed to be insoluble in the organic phase, which may not be true, especially if this phase contains a substantial amount of alcohol.

An attempt to use the chemical shift in proton magnetic resonance spectra of ethanol[10] in sulfuric acid does not appear to give a valid estimate of the pK, probably because of solvent effects.

Mention should be made of some surprising results obtained in relatively dilute (0.1–1.0 *M*) acid solutions of methanol and 2-propanol. Using a method in which there is competition for protons between the alcohol and a basic indicator, Wells[17] obtains very high $\mathrm{p}K_{\mathrm{BH}^+}$ values of about -1. Earlier determina-

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(15) V. Gold and R. S. Satchell, *J. Chem. Soc.*, 1930 (1963).

(16) V. Gold and T. Riley, *ibid.*, 4183 (1962).

(17) C. F. Wells, *Trans. Faraday Soc.*, **61**, 2194 (1965).

tions[18] which depend on the kinetics of the photosensitized autoxidation of 2-propanol gave even higher values. Wells attributes the large differences between these results and those in more concentrated acid solutions to differences in the acidity of the proton at various stages of hydration.

In conclusion, the following statements about the basicities of aliphatic alcohols can be made.

1. Several kinetic and equilibrium measurements have been reported previously which indicate a pK range of -2.2 to -3.8 in sulfuric acid, in agreement with the Raman work of Deno and Wisotsky.
2. Our results, in contrast to these, suggest a pK of almost -5, in agreement with kinetic results obtained by Gold and co-workers.
3. The earlier Raman results of Deno and Wisotsky can be reinterpreted to indicate that the extent of methanol protonation in all of their solutions was very small.
4. Contrary to optimistic statements by Arnett,[3] who describes the Raman method as producing "unequivocal" results, it seems quite clear that estimates of alcohol protonation obtained by this method differ significantly from several of those obtained by other methods. The Raman method, in principle a very direct one, may still reflect effects other than protonation, such as changes in hydrogen bonding.

The problem of hydrogen bonding, or more generally, of solvent–solute interaction, may well be the key to the lack of agreement between the various experimental measures of alcohol basicity. By their nature, these solutes will be strongly hydrogen-bonded to water molecules. In concentrated acid solutions, when the water concentration is low, there will be a competition between hydrogen bond formation (water–water and water–alcohol) and solvation (ion–water and ion–alcohol). Hence, one might anticipate complex medium effects which need not produce the same dependence on acid concentration for different methods of determining the alcohol basicity.

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Solvation of Extracted Complex Metal Acids. III. The $HFeCl_4$–Diethyl Ether System[1]

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Abstract: In an attempt to learn more about the solvation of extracted halometallic acids of the type HMX_4, the effects of acidity, Cl^- concentration, and ether concentration on the distribution of Fe(III) between aqueous HCl or acidified LiCl and diethyl ether–benzene mixtures were studied. The solvation number of the extracted ion pairs is near 4. A comparison of these results with nitrobenzene solvation studies has tempted us to suggest that with very weakly basic extractants one may not, on the basis of available data, definitely reject the possibility that anion (or dipole) solvation might play a significant role in the extraction of acids.

It is well known that many trivalent metals including Fe(III) are extracted from aqueous acid halide solutions by weakly basic solvents, *e.g.*, diethyl ether, as the halometallic acids, HMX_4.[2–7] It is also generally accepted that there is no primary solvation of the metal anion which is tetrahedrally surrounded by halides and assumed to be saturated.[3]

The common method of studying solvation in extraction systems is the so-called dilution technique. This essentially involves following the change in the distribution coefficient as the extractant is diluted with a second inert solvent, all other parameters being held effectively constant. Dilution studies involving strong acids and strongly basic extractants have generally been interpreted in terms of the concept that one may assign all of the observed (coordinately solvating) extractant molecules to the hydrated proton. This, of course, implies that any additional solvation of either ion which might occur is unobservable by the dilution technique. This concept has been used extensively by Diamond and co-workers[8–11] in the interpretation of their studies of strong acid extraction by the more basic (than the ethers) trialkylphosphine oxides and trialkyl phosphates. Recent work with the extremely weakly basic substance nitrobenzene,[12,13]

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