

It is of interest to attempt to fit these radical ionization potentials to the linear relationship between Hammett σ -constants and ionization potential found for other substituted benzyl radicals.³ In Table II are given values of σ predicted from the σ -i.p. relationship,³ together with $\sigma_{\text{exp.}}$ and $\sigma_{\text{calcd.}}$ values for the reactivity of side chains in pyridines given by Jaffé.^{22,23} The latter were derived from standard MO-LCAO theory. It can be seen that although all three sets agree as to the order of reactivity (and ionization potential) of the three species, the actual values of σ differ greatly from set to set.

TABLE II
 σ -CONSTANTS FOR THE REACTIVITY OF SIDE CHAINS IN PYRIDINES

Position	σ -Constants		
	Predicted from ionization potentials	Experimental ^a	Calculated ^a
2	0.39	0.81, 0.40	0.46
3	.18	.62 ..	0.35
4	.58	.93 ..	1.07

^a Ref. 22.

The appearance potentials of the radical ions from 2-, 3- and 4-picoline were also measured (Table III). From these, the ionization potentials of the radicals and the relationship

$$A(R^+) - I(R) \geq D(R-H)$$

we get values for $D(R-H)$ which are some 20 kcal./mole higher than those found by Roberts and Szwarc⁴ in their pyrolytic work. It is evident, therefore, that the threshold for loss of an H-atom from the picolines by dissociative ionization does not correspond to formation of pyridylmethyl ions with little or no excitation. The situation may have some parallels with the dissociative ionization of toluene, for which a discrepancy of about the same magnitude was found.² Later work on the formation of the "benzyl" ion in the dissociative ionization of benzyl derivatives led to the conclusion that an isomerization occurs in this process, with the formation of a symmetrical tropylium ion.²⁴ One may speculate, therefore, concerning the formation (from dissociative ionization of picolines) of the analogous 7-membered ring with a N-atom, the azepinyl ion

(22) H. H. Jaffé, *J. Chem. Phys.*, **20**, 1554 (1952).

(23) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(24) P. N. Rylander, S. Meyerson and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957); S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957); S. Meyerson, P. N. Rylander, E. Eliel and J. D. McCollum, *J. Am. Chem. Soc.*, **81**, 2606 (1959).



Recently Harrison, *et al.*,²⁵ have pointed out that differences in the ionization potentials of *m*- and *p*-substituted benzyl radicals should be paralleled by differences in the appearance potentials of these radical ions in the dissociative ionization of the *m*- and *p*-derivatives. The absence of such differences can on this basis be taken as evidence of a loss of ring orientation in the ion and consequently of the formation of ions with the tropylium structure. Following this reasoning, the observation that there is no appreciable difference in appearance potentials of the parent-minus-one ions in the three picolines (Table III) would suggest formation of the azepinyl ion. This rearrangement is of course highly conjectural, in the absence of other evidence for an ion of this type. The mass spectra of picolines,²⁶ for instance, do not show any metastable peaks arising from dissociation of an ion of mass 92 comparable to the well known loss of neutral C_2H_2 from $C_7H_7^+$.²⁴ The intensity of the $C_6NH_6^+$ peak in the mass spectra of picolines is in fact much lower than that of $C_7H_7^+$ in toluene. The possibility of the formation of a symmetrical $C_6NH_7^+$ parent ion in the ionization of D- and N¹⁵-labeled anilines has been examined.²⁷ Although there is some evidence for symmetrical ion formation, it is only for certain minor dissociation paths. In aniline, and probably also in picolines, the dissociation pattern does not seem to be dominated by formation of a symmetrical precursor ion as it is in alkylbenzenes. It seems, therefore, that at present one can say only that formation of $C_6NH_6^+$ ion from picolines proceeds from dissociation of an excited state or states of the molecular ions in which orientational energy differences are small.

TABLE III
APPEARANCE POTENTIALS OF RADICAL IONS

Ion	Source	Appearance potential, v.
$C_6NH_6^+$	2-Picoline	12.38 \pm 0.1
	3-Picoline	12.31 \pm .1
	4-Picoline	12.22 \pm .1
	Aniline	See text

The ionization efficiency curve for $C_6NH_6^+$ ion from aniline was found to have a long tail extending over several volts. No meaningful value for the appearance potential could be assigned using the present technique.

(25) J. M. S. Tait, T. W. Shannon and A. G. Harrison, *ibid.*, **84**, 4 (1962).

(26) See for example the spectrum of 2-methylpyridine, No. 1535 in the A.P.I. Project 44 catalog of mass spectra.

(27) P. N. Rylander, S. Meyerson, R. Eliel and J. D. McCollum, presented before A.S.T.M. Committee E-14 on Mass Spectrometry, Los Angeles, Calif., May, 1959.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

Quantitative Raman Spectroscopy for the Determination of Base Strengths of Weak Organic Bases¹

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RECEIVED JANUARY 18, 1963

The protonation equilibria and base strengths of acetamide, methanol, dioxane, acetone and acetonitrile have been studied in aqueous sulfuric acids using a Cary 81 Raman spectrophotometer.

The common organic functional groups such as olefin, alcohol, ether, ketone, amide and nitrile are too

(1) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

weak to be measurable by pH meters and the methods applicable to dilute aqueous solutions. In the aliphatic series, the methods based on ultraviolet spectra that

(2) Recipient of a Fellowship sponsored by Esso Research and Engineering Co.

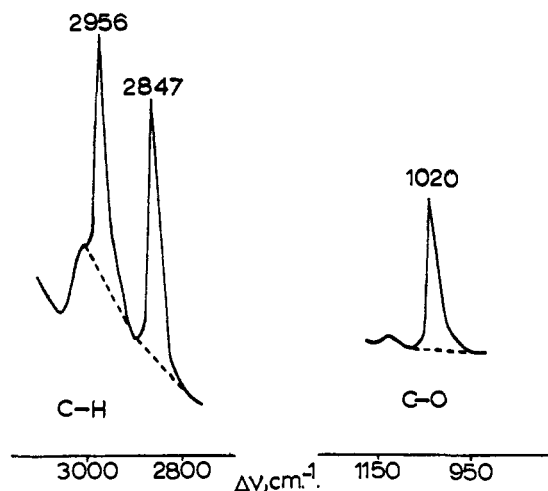


Fig. 1.—Raman spectrum of methanol in water. The sensitivity is 400 for both the C—O and C—H bands. The broken line under the C—O band is the spectrum due to solvent, whereas the broken line under the C—H band is an arbitrary line that was used in computing areas.

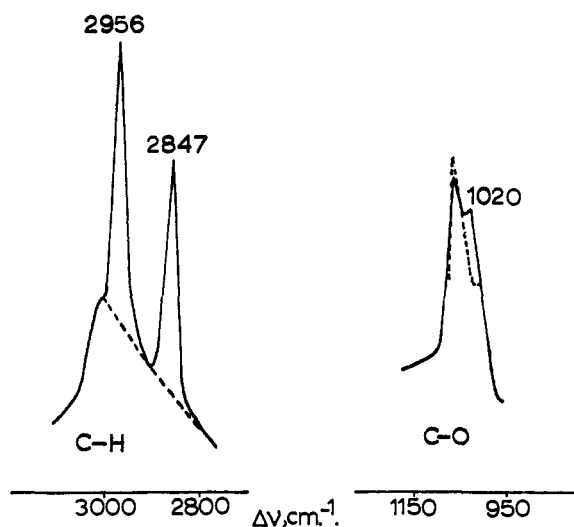


Fig. 2.—Raman spectrum of methanol in 41% H₂SO₄. Sensitivity and meaning of broken lines are the same as in Fig. 1.

have come to be associated with acidity functions and concentrated mineral acids are either not applicable or treacherous because of variation of spectra with solvent. The result was that the basicities of the most common compounds in organic chemistry such as methanol, acetone, acetonitrile, etc., have not been known with confidence.³

In the past several years, Edward and Stewart have done much to establish the base strength of aliphatic amides and ketones.⁴ Although this work was excellent in every way (and we now know it to be correct), there was need for substantiation for two reasons. First was the large discrepancies between the above estimates and those of earlier investigators. Second was the fact that the ultraviolet spectra of the ketones varied with solvent and a possibility existed that this could have caused error.

Also in the past several years, Arnett has estimated base strengths of ethers by examining the variation of distribution coefficient with acid concentration.³ Arnett took every precaution and his results are the

(3) E. M. Arnett, "Advances in Physical-Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963.

(4) J. T. Edward, H. S. Chang, K. Yates and R. Stewart, *Can. J. Chem.*, **38**, 1518 (1960); H. J. Campbell and J. T. Edward, *ibid.*, **38**, 2109 (1960).

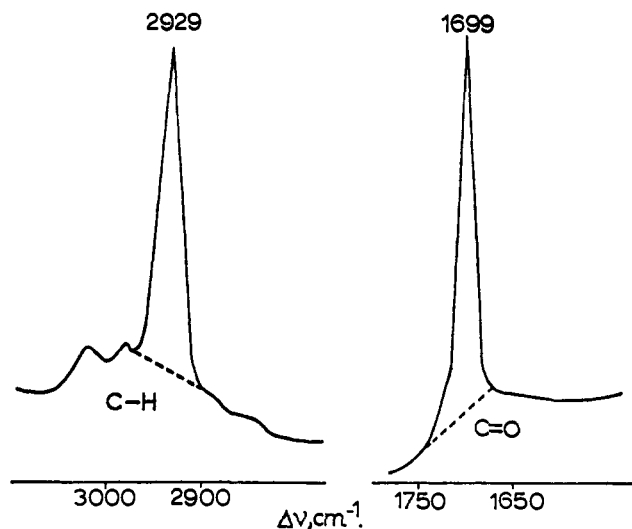


Fig. 3.—Raman spectrum of acetone in water. The sensitivity is 200 for the C=O band and 40 for the C—H band. Broken lines under C=O and C—H are arbitrary and were used in computing areas.

major contribution in this field. However, the method has an indirectness about it and confidence in the results would be added by independent substantiation.

The Raman results, along with additional distribution coefficient studies in progress with both Arnett and ourselves, have established the base strength of the common organic functional groups. The high concentration of base (5–20% by weight) required in the Raman method severely limits its applicability and precision and we do not foresee an extensive development of this method. Nevertheless, the inherent reliability serves to check other estimates.

Experimental

The instrument used was a Cary 81 Raman spectrophotometer utilizing a 3 kilowatt Toronto-type mercury arc source. The 4358 Å. mercury line was used for the exciting radiation. An efficient cooling system maintained the temperature inside the sample compartment at approximately 30°. The sample holder was constructed of glass and had a capacity of 5 ml. All solutions contained 20% by weight of the organic species.

The methylamine–methylammonium chloride system was chosen to test the Raman method because pK_{BH^+} of $CH_3NH_3^+$ is well established at 10.70 and CH_3NH_2 is similar in structure to the other acyclic organic bases studied in this work. The data in Table I demonstrate that the extent of protonation can be determined either from the band at 3323 cm^{-1} ($\Delta\gamma$) or from the band at 3045 cm^{-1} . The former is characteristic of the N—H stretching frequency of unprotonated CH_3NH_2 and the latter is characteristic of the corresponding N—H⁺ stretching frequency of the protonated amine. These band heights or areas were measured relative to those of the C—H stretching frequency at 2980 cm^{-1} , which undergoes relatively little change on protonation.

The band heights or areas of the protonated and unprotonated functional groups were always recorded relative to the C—H bands used as internal standards. Since the Cary 81 spectrophotometer is stable to normal line current fluctuations, in many cases the absolute heights or areas of the bands could have been used for runs made over short periods. However, complete confidence cannot be placed on these absolute heights or areas. Not only is there a gradual decrease in energy transmission of the light filters and output of the source over long periods, but also unusually large changes in line voltage, as can occur during lunch hours or late afternoon, will affect the bands.

Ratios of protonated to unprotonated forms were determined from band areas or band heights. For acetone, methanol and acetamide, the values of % BH^+ were identical by either method. In the case of methylamine, the relative concentrations computed from band areas were in good agreement with the known values, whereas band heights gave poor agreement. For dioxane, band areas gave values of % BH^+ better in accord with those reported by Arnett.³

The shape of the bands and variation with acid concentration are illustrated for several typical spectra in Fig. 1–6. The data are summarized in the tables.

TABLE I

ESTIMATES OF THE POSITION OF PROTONATION EQUILIBRIA FROM INTENSITIES OF BANDS IN THE RAMAN SPECTRA

Methylamine (N-H, 3323 cm.⁻¹; N-H⁺, 3046 cm.⁻¹)

$\Delta\nu$, cm. ⁻¹	N-H				N-H ⁺				BH ⁺
	-NH/CH-		-% BH ⁺		-NH ⁺ /CH-		-% BH ⁺		
Hts.	Areas	Hts.	Areas	Hts.	Areas	Hts.	Areas	BH ⁺ (known)	
2964	0.86	0.36	0	0	0	0	0	0	0
2979	.66	.25	22	31	0.20	0.09	64	34	31
2980	.28	.15	67	58	.28	.18	94	68	62
2983	0	0	100	100	.30	.26	100	100	100

Acetamide (C-H, 2946 cm.⁻¹; C=O, 1688 and 1611-1618 cm.⁻¹)

H ₂ SO ₄ %	C=O/C-H area	BH ⁺ %	H ₂ SO ₄ %	C=O/C-H area	BH ⁺ %
0	0.67	0	0	0.038	0
16	.42	37	21	.034	11
21	.44	34	28	.026	32
28	.36	46	32	.024	37
32	.22	67	41	.019	50
37	.21	69	46	.015	61
46	.13	79			

Dioxane (C-H, 1450 cm.⁻¹; C-O, 1018 cm.⁻¹)^a

H ₂ SO ₄ %	C-O/C-H area	BH ⁺ %	H ₂ SO ₄ %	C=O/C-H area	BH ⁺ %
4	0.58	0	0	0.35	0
12	.58	0	21	.31	0
41	.50	40	46	.29	0
46	.50	40	56	.26	13
50	.49	50	64	.25	17
56	.40	60	74	.22	27
64	.39	70	81	.15	50
			87	.07	76
			96	0	100

Acetonitrile (C-H, 2947 cm.⁻¹)

H ₂ SO ₄ %	$\Delta\nu$, C≡N, cm. ⁻¹	C≡N/C-H, heights
5	2260	0.60
21	2259	.58
46	2262	.51
64	2267	.41
81	2278	.38
96	2284	.33

^a Because of the two oxygens, half protonation is indicated by reduction of the area by 25%, not 50%. The estimates of % BH⁺ are of unusually poor precision because of the small shifts. This ether was included because it was the only ether of several examined in which any estimate was possible.

TABLE II

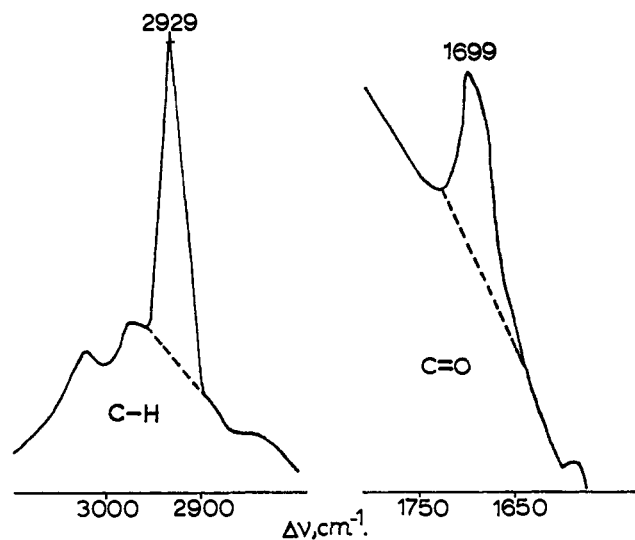
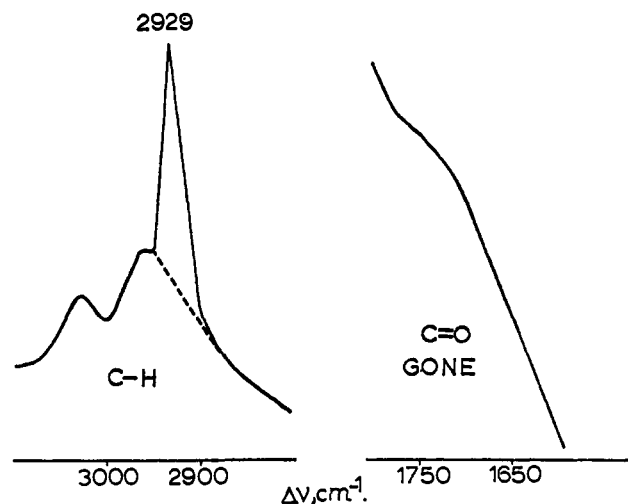
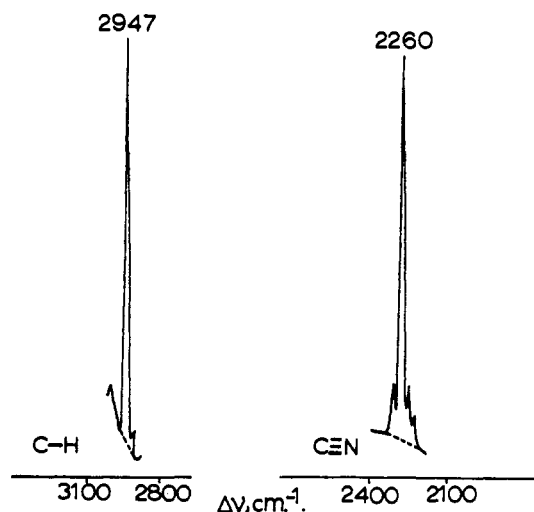
PROTONATION OF ACETONE BY N.M.R. SPECTROSCOPY^a

H ₂ SO ₄ %	Cycles/sec. ^b	H ₂ SO ₄ %	Cycles/sec. ^b	H ₂ SO ₄ %	Cycles/sec. ^b
0	260	76	247	86	213
26	256	79	230	90	212
52	249	85	223	96	211

^a The measurements were made by John J. Houser. ^b This is the position of the n.m.r. band of acetone relative to an external benzene reference contained in the outer jacket of a precision coaxial n.m.r. tube. A correction was made for the difference in bulk susceptibility, but it had little effect on the ultimate conclusion so that the data listed are the uncorrected positions in cycles/sec. A sharp break is evident between 76 and 86% H₂SO₄ which shows that in this region the equilibrium shifts from acetone to protonated acetone. The measurements were made on a Varian A-60 instrument.

Discussion

The calculation of pK_{BH^+} values utilized the familiar Hammett H_0 acidity function and its accompanying equations. Application to the type of base studied in this work is discussed by Arnett.³

Fig. 4.—Raman spectrum of acetone in 74% H₂SO₄; sensitivity and meaning of broken lines are the same as in Fig. 3.Fig. 5.—Raman spectrum of acetone in 96% H₂SO₄; sensitivity and meaning of broken lines are the same as in Fig. 3.Fig. 6.—Raman spectrum of acetonitrile in 5% H₂SO₄. The sensitivity is 400 for the C≡N band and 240 for the C-H band.

Methylamine.—The data in Table I show that the % protonation can be approximately estimated from Raman spectra although the method will never compete with conventional methods.

Acetamide.—The basicity of propionamide has been measured by ultraviolet spectroscopy⁵ and by nuclear magnetic resonance (n.m.r.) spectroscopy.⁶ The respective pK_{BH^+} values of -0.9 and -1.1 are in accord with the value of -1.4 for acetamide which can be calculated from the Raman spectra data in Table I.

Methanol.—The basicity of 2-propanol has been estimated from a study of the variation in rate of hydride abstraction by $(C_6H_5)_3C^+$ as a function of % H_2SO_4 .⁷ The ratio ROH_2^+/ROH was unity in 50% H_2SO_4 and pK_{BH^+} was -3.2 . The analogous values for ethanol were 40% H_2SO_4 and -2.3 .⁸ These values were supported by a study of the kinetics of alkylation of acrylonitrile by *t*-butyl alcohol. The ratio ROH_2^+/ROH for *t*-butyl alcohol was unity in 56% H_2SO_4 and pK_{BH^+} was -3.8 .⁹

Doubt was cast on these results by a study of the distribution of 2-propanol between cyclohexane and aqueous sulfuric acids which seemed to indicate that ROH_2^+/ROH was unity in 20–25% acid.⁸ Further difficulties arose from the n.m.r. spectra of ethanol which exhibits a continuous monotonic change from 20–90% H_2SO_4 .^{6,10} Edward attempted to fit the data to the equation

$$H_0 + pK_{BH^+} + \log c_{BH^+}/c_B \quad (1)$$

and arrived at a pK_{BH^+} value of -4.8 and ROH_2^+/ROH equals unity at 64% H_2SO_4 .

In view of these conflicting reports, the investigations of methanol, ethanol, 2-propanol and *t*-butyl alcohol were attempted by the Raman method. Only methanol gave an acid-sensitive band sufficiently separated from solvent bands. The data in Table I reliably place $CH_3OH_2^+/CH_3OH$ as unity in 39% H_2SO_4 and pK_{BH^+} as -2.2 .

The basicity of alcohols was reinvestigated by the distribution method by both Arnett's group and our own group. Arnett used vapor phase chromatography¹¹ on the simple alcohols. Our group used ultraviolet spectroscopy on a series of $C_6H_5(CH_2)_nOH$ alcohols where n is 4, 6 and 8. Preliminary results of both groups demonstrate that ROH_2^+/ROH ratios are unity for primary alcohols in the 40–50% H_2SO_4 range confirming the original Bartlett–McCullum estimates.

It is our view that the n.m.r. results on ethanol can be reinterpreted to indicate a pK between -2 and -3 . The plot of the difference between CH_3 and CH_2 band positions against % H_2SO_4 begins to rise at H_0 equals -1.5 . The continuous rise of this difference beyond H_0 equals -3.5 (53% H_2SO_4) is not due to shifting protonation equilibrium but is a result of the continuously changing hydrogen bonding energy, $ROH_2^+ - OH_2$, associated with decreasing activity of H_2O .

(5) J. T. Edward and I. C. Wang, *Can. J. Chem.*, **40**, 966 (1962).

(6) J. T. Edward, J. B. Leane and I. C. Wang, *ibid.*, **40**, 1521 (1962).

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

(8) P. D. Bartlett and W. F. Smith, Ph.D. Thesis of W. S. Harvard Univ., 1960.

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

(10) E. M. Arnett (Univ. of Pittsburgh) and A. Bothner-By (Mellon Institute, Pittsburgh) have independently obtained the same result.

(11) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 4999 (1960); **84**, 1684 (1962).

Dioxane.—The n.m.r. spectrum of diethyl ether⁶ can be reinterpreted in a manner identical with our reinterpretation of the ethanol data. A value of pK_{BH^+} of about -3 is indicated in accord with the value -3.61 obtained from distribution studies.¹¹ Attempts to study diethyl ether and tetrahydrofuran by the method failed because the acid-sensitive bands coincided with solvent bands. Data on dioxane were barely interpretable, but it did indicate a pK_{BH^+} of about -3.4 in accord with -3.22 obtained by distribution studies.³

Acetone.—Ultraviolet studies on acetone gave BH^+/B as unity in 80% H_2SO_4 and pK_{BH^+} as -7.2 .⁴ Estimates by the Raman method (Table I) and by the n.m.r. method (Table II) completely confirm these values.

Acetonitrile.—The basicity of nitriles is probably the least known of the common functional groups in organic chemistry. The observation that hydrolysis of acrylonitrile obeyed the equation

$$d \log k = -\lambda H_0$$

from 25 to 85% H_2SO_4 was interpreted to mean that acidities greater than that of 85% acid are required for half protonation of acrylonitrile.⁹ Turning to acetonitrile and the Raman method, the slow change in the $C \equiv N$ stretching band from 0 to 81% acid (Table I) is interpreted as due to increasing the $CH_3C \equiv N - - H_2O^+$ and ultimately the $CH_3C \equiv N - - HOSO_3H$ hydrogen bonding energies. It is concluded that CH_3CN is still predominantly unprotonated in 81% H_2SO_4 . The value for $CH_3C \equiv N$ in 96% H_2SO_4 (Table I) is a value for an effectively much lower acidity because of the large amount of nitrile added.

The cryoscopic work of Hantzsch¹² indicated that $CH_3C \equiv N$ is half protonated in $\sim 99\%$ H_2SO_4 . By eq. 1, pK equals ~ -9.5 . This would make $CH_3C \equiv N$ predominantly unprotonated in 81% H_2SO_4 in accord with the Raman results. A report¹³ that $CH_3C \equiv N$ has a pK of -4.2 is discounted because the authors concede that such a value is on the limit of the method of measurement. The added fact that the solvent used was acetic acid rather than aqueous sulfuric acid cannot account for such a large discrepancy.

Comparison of Raman with Infrared Spectra.—There are a great variety of $-O-H$ bonds in these aqueous mineral acid systems and their energies are nearly a continuum because of variations in hydrogen bonding energies. The Raman bands associated with bending motions of $-O-H$ bonds are weak because bending causes little change in polarizability. Thus background due to solvent is a problem only when stretching bands overlap and such stretching bands are relatively narrow.

Bendings of $-O-H$ bonds are associated with large dipole moment changes and cause strong and virtually continuous absorption in the infrared spectra. We have performed some preliminary experiments using infrared spectra and have concluded, as anticipated, that it is much more difficult to study protonation equilibria in aqueous mineral acids by infrared spectra than by Raman spectra. In these preliminary infrared studies, the aqueous mineral acid solutions were held between films of either polyethylene and/or a copolymer of tetrafluoroethylene and hexafluoropropene

(12) A. Hantzsch, *Z. physik. Chem.*, **65**, 41 (1908).

(13) H. Lemaire and H. J. Lucas, *J. Am. Chem. Soc.*, **73**, 5198 (1951).