The Base Strengths and Chemical Behavior of Nitriles in Sulfuric Acid and Oleum Systems

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Protonated nitriles reside long enough in SO_3-H_2O systems to evaluate the basicity of nitriles by nmr spectroscopy. Acetonitrile, propionitrile, and benzonitrile are half-protonated in 98-100% H_2SO_4. Chloroacetonitrile is half-protonated in 30% oleum. The rates of formation of protonated amides from nitriles are reported as well as rates of conversion of protonated amides to acyl cations.

The concentrations of benzoyl cation and protonated benzoic acid are equal in 20% oleum.

Aliphatic Nitriles.—Arnett in his review[1] stated that the basicity of nitriles were the least known among the common functional groups of organic chemistry. From cryoscopic studies, Hantzsch[2] had reported acetonitrile to be half-protonated in 100% H_2SO_4. A more precise value of 99.6% H_2SO_4 was found on the basis of conductimetric work.[3] Using the Hammett H_0 values,[4] pK would be -10.12.

In sharp contrast to the above value is the value of -4.2 reported for acetonitrile[5] and -4.31 for propionitrile.[6] These latter values were obtained by titrating the nitrile with sulfuric acid in a formic acid solvent. The "titrations" were necessarily carried out to only a small per cent conversion of B to BH^+, and we believe that the small changes in acidity appearing with added nitrile were not due to protonation of the nitrile but were due to the presence of free nitrile much as *t*-butyl alcohol has a small effect on acidity in 0-20% even though it does not protonate.[7]

Although the judgement to discount the titration work can rest on the above argument, it is naturally reinforced by the present nmr studies which indicate acetonitrile to be half-protonated in 100% H_2SO_4 and propionitrile to be half-protonated in 98% H_2SO_4. The nmr work thus supports the cryoscopic and conductimetric studies and definitively settles the basicity of aliphatic nitriles.

Chloroacetonitrile was found to be half-protonated in 30 ± 5% oleum. Despite this weaker basicity, its gross rate of hydrolysis to the protonated amide is greater as shown in Table I. This means that protonated chloroacetonitrile hydrates more rapidly than the other protonated nitrile by at least a factor of 3-10. In fact there is an added factor of about 100 because the value of H_0 in 100% H_2SO_4 (where acetonitrile is half-protonated) is -10.8 and the value in 30% oleum (where chloroacetonitrile is half-protonated) is -12.8.[8] It is of course a general principle that the weaker the base, the more reactive (toward nucleophiles) is the protonated form. However, it is of some practical interest that this latter effect overcompensates the lower concentration of protonated chloroacetonitrile.

TABLE I

HALF-TIMES FOR FORMATION OF PROTONATED AMIDE FROM NITRILE AND/OR PROTONATED NITRILE

	Half-time at 35 ± 2°, min					
	% H_2SO_4 (in H_2O)			% SO_3 (in H_2SO_4)		
	70	90	96	15	34	65
Acetonitrile	125	45	25[a]	25	25[b]	*c*
Propionitrile	120	45	30[d]	25	25[b]	..
Benzonitrile	..	40	35	..	*e*	..
Chloroacetonitrile	20	15	5	2	..	<2[f]

[a] A value of 60 min has been reported for 100% H_2SO_4 at 25°.[3] [b] The protonated amide band appears in 4 min and the acyl cation (RCO^+) band in 20 min. The half-time for each process is estimated to be 15-30 min. [c] The protonated nitrile is converted directly to the acetyl cation with a half-time of 6 min. [d] A value of 30 min has been reported for 100% H_2SO_4 at 25°. [e] The acyl cation completely forms within 2 min. [f] The protonated amide was stable for at least an hour.

The nmr band positions are listed in Table II. It is evident that the positions for the several species were sufficiently different to allow ready identification. The nmr spectra of the pure species were not affected by changing acidity. For example the center of the quartet of $CH_3CH_2CONH_3^+$ was 2.76 in 96% H_2SO_4 and 2.78 in 65% oleum. In all cases, equilibria were so rapid that only hybrid bands were observed.

TABLE II

NMR BAND POSITIONS IN PARTS PER MILLION DOWNFIELD FROM TETRAMETHYLSILANE [$(CH_3)_4N^+Cl^-$ INTERNAL STANDARD]

	RCN	$RCNH^+$	$RCONH_3^+$ in		RCO^+
R	in 70% H_2SO_4	in 13% SO_3	96% H_2SO_4	65% SO_3	in 65% SO_3[a]
CH_3	2.10	2.69	2.51	2.61	3.93
CH_3CH_2 α-H[b]	2.42	3.00	2.76	2.78	4.06
$ClCH_2$	4.28	(4.48)[c]	4.57	4.62	...

[a] N. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Am. Chem. Soc.*, **86**, 4370 (1964). [b] Quartet, J = 7 cps for all four species. [c] This value is probably too small since the conversion to protonated nitrile is incomplete.

Benzonitrile.—Conductimetric studies at 25° indicated benzonitrile to be half-protonated in 99.8% H_2SO_4. The position of protonation equilibria are generally insensitive to temperature so that the half-protonation at 100% H_2SO_4 found from nmr studies at 35° is in good agreement. Also in accord is an estimate from cryoscopic studies at 10° that the similar *p*-tolunitrile is half-protonated in about 100% H_2SO_4.

Nmr band positions of the several species are shown in Figure 1.

Benzoyl Cation.—In an extensive study of the equilibria between $RCOOH_2^+$ and RCO^+,[9] no example of an aromatic acid was reported. This gap is now filled by a study on benzoic acid. The benzoyl cation is half-formed from protonated benzoic acid in 20% SO_3-80% H_2SO_4. This is similar to the simple aliphatic acids. Also similar was the dramatic shift in position of equilibrium with change in SO_3 concentration. The equilibrium shifted from 90% $C_6H_5COOH_2^+$ to 90%

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(1) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(2) A. Hantzsch, *Z. Physik. Chem.*, **65**, 41 (1909).

(3) M. Liler and D. Kosanovic, *J. Chem. Soc.*, 1084 (1958).

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

(5) H. Le Maire and H. J. Lucas, *J. Am. Chem. Soc.*, **73**, 5198 (1951).

(6) L. P. Hammett and A. J. Deyrup, *ibid.*, **54**, 4239 (1932).

(7) N. Deno, T. Edwards, and C. Perizzolo, *ibid.*, **79**, 2108 (1957).

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

(9) N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Am. Chem. Soc.*, **86**, 4370 (1964).

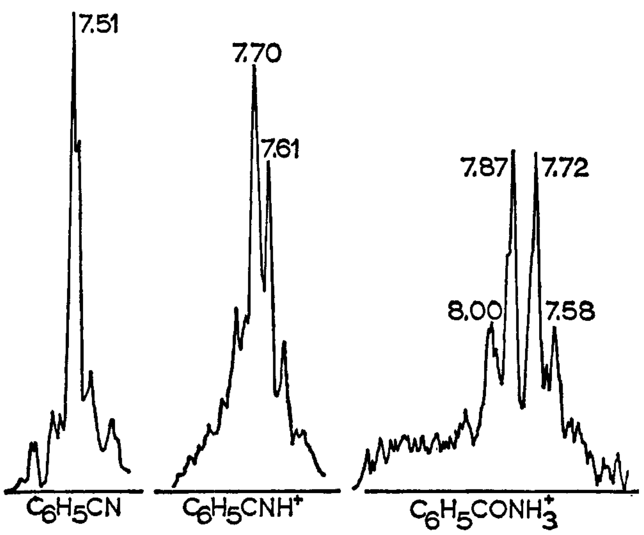

Figure 1.—Nmr spectra of C_6H_5CN in 90% H_2SO_4 (the spectrum in CCl_4 is identical), $C_6H_5CNH^+$ in 10% oleum (bands of $C_6H_5CONH_3^+$ are starting to appear), and $C_6H_5CONH_3^+$ in 100% H_2SO_4. Band positions are in parts per million downfield from tetramethylsilane using a $(CH_3)_4N^+Cl^-$ internal standard.

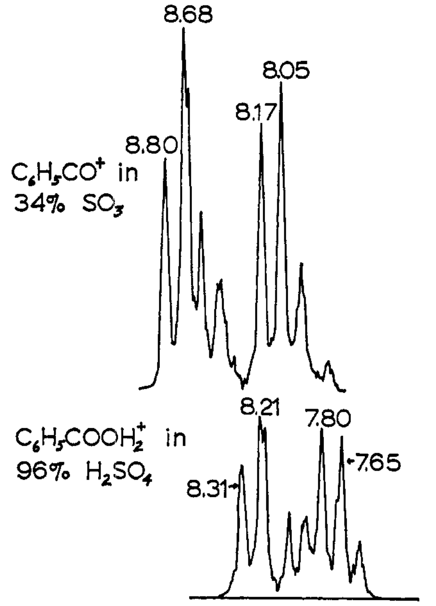

Figure 2. Nmr spectra.

$C_6H_5CO^+$ between 17 and 23% SO_3, again indicating that the activity of H_2O is changing by a factor of 10 for every 2–3% change in SO_3 concentration.[9]

Nmr band positions are shown in Figure 2.

Acidity Functions.—Values of the H_0 acidity function for the 100% H_2SO_4 region have been derived from studies on the protonation of substituted nitrobenzenes.[9,10] It would have been of interest to test these H_0 values with the data on nitrile protonation, but the latter were not of sufficient precision to justify such a test. It was necessary in the nmr studies to add 6% by weight with acetonitrile and 10% by weight with the other three nitriles. Such large concentrations of added base affect the acidity, most directly by consumption of acid in converting RCN to $RCNH^+$. A correction was made for this main effect, and the acid concentrations reported herein for half-protonation of the nitriles were corrected values.

The correction was made as follows. If it is assumed that SO_3–H_2SO_4 systems are, in fact, predominantly $H_2S_2O_7$–H_2SO_4 systems, the moles of each can be calculated. If it is further assumed that protonation of RCN primarily destroys $H_2S_2O_7$, a new ratio of $H_2S_2O_7$ to H_2SO_4 can be computed for the RCN-$RCNH^+$ solution. The corrected per cent SO_3 (in H_2SO_4) is that per cent of SO_3 which has the same ratio of $H_2S_2O_7$ to H_2SO_4 as the RCN-$RCNH^+$ solution. In effect, what is assumed is that the addition of RCN and $RCNH^+HS_2O_7^-$ has no effect on the acidity.

A similar correction was made for H_2SO_4–H_2O systems by assuming that H_2SO_4 is consumed in forming $RCNH^+$ and that the effective acidity depends only on the mole ratio of H_2SO_4 to H_2O.

The data did confirm that values of H_0 are rapidly changing at 100% H_2SO_4. For example, the ratio of concentrations of $RCNH^+$ to RCN (for acetonitrile and benzonitrile) ranged from 1 to 4 at an acidity not significantly different from 100% H_2SO_4 within the precision of our data.

Preparation of 65% SO_3–35% H_2SO_4.—Pure liquid SO_3 (commercial Sulfan) can be directly mixed with 15–34% oleum. The heat generated is small. We should like to warn that mixing of H_2O or D_2O with Sulfan in any direct way leads to cracking of Pyrex vessels. They can be combined, as for example to produce D_2SO_4, by distillation at 760 mm of SO_3 into stirred H_2O or D_2O.

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[10] J. C. D. Brand, *J. Chem. Soc.*, 997 (1950); J. C. D. Brand, W. C. Horning, and M. B. Thornley, *ibid.*, 1374 (1952).

The Basicity of Nitro Compounds

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The basicity of the nitro group has been established by three definitive studies.[1-3] Ultraviolet[1] and conductimetric[2] work showed nitrobenzene to be half-protonated in 99.5% H_2SO_4. The ultraviolet studies were extended to a series of substituted nitrobenzenes[3] and the % H_2SO_4 or % SO_3 in H_2SO_4 required for half-protonation were in accord with current theories of substituent effects.

Conductimetric studies indicated nitromethane to be half-protonated in 7% SO_3–93% H_2SO_4,[2] a result in agreement with an earlier cryoscopic study which indicated that nitromethane was unprotonated in 100% H_2SO_4.[4]

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[1] J. C. D. Brand, *J. Chem. Soc.*, 997 (1950).

[2] R. J. Gillespie and C. Solomons, *ibid.*, 1796 (1957).

[3] J. C. D. Brand, W. C. Horning, and M. B. Thornley, *ibid.*, 1374 (1952).

[4] A. Hantzsch, *Z. Physik. Chem.*, **61**, 257 (1907).