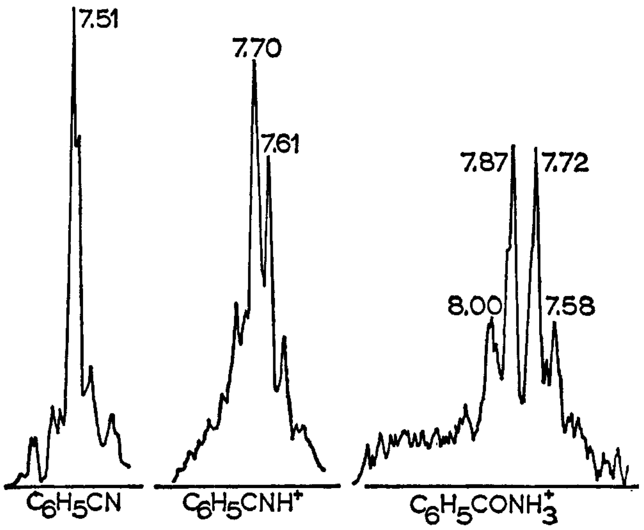

Figure 1.—Nmr spectra of C_6H_5CN in 90% H_2SO_4 (the spectrum in CCl_4 is identical), $C_6H_5CNH^+$ in 10% oleum (bands of $C_6H_5CONH_3{}^+$ are starting to appear), and $C_6H_5CONH_3{}^+$ in 100% H_2SO_4. Band positions are in parts per million downfield from tetramethylsilane using a $(CH_3)_4N^+Cl^-$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

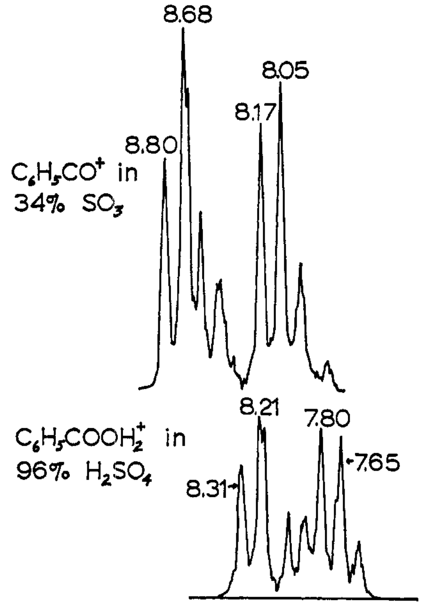

Figure 2. Nmr spectra.

$C_6H_5CO^+$ 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.

Acknowledgment.—This work was supported by a grant from the Petroleum Research Fund of the American Chemical Society. The purchase of the Varian A-60 nmr instrument was made possible by a grant from the National Science Foundation.

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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).

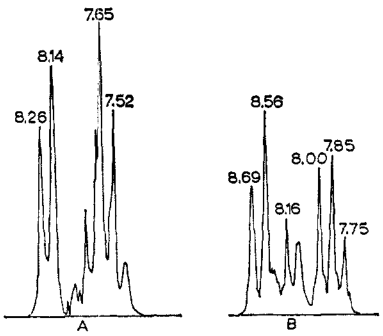

Figure 1.—Nmr spectrum of (A) nitrobenzene in 96% H_2SO_4 and (B) protonated nitrobenzene in 34% SO_3–66% H_2SO_4. The band positions are in parts per million downfield from tetramethylsilane with $(CH_3)_4N^+Cl^-$ as an internal standard.

In the course of proton magnetic resonance (pmr) studies in oleum, it was convenient to check these results. For this purpose, the pmr spectra of nitrobenzene, nitromethane, nitroethane, and 2-nitropropane were measured as a function of acid concentration. Let us say at the outset that the pmr data did not yield values of $[B^+]/[BH]$ of sufficient precision to test or establish any acidity functions. However, they did provide a reliable check on the acidity required for half-protonation.

The pmr spectra of nitrobenzene and protonated nitrobenzene are shown in Figure 1. Although complex, one was smoothly graded into the other and it was no problem to estimate that nitrobenzene was half-protonated in 99–100% H_2SO_4. This is in exact agreement with the earlier ultraviolet[1] and conductrimetric[2] studies.

Nitromethane exhibited a single pmr band of normal width. It moved from a position 4.45 ppm downfield from tetramethylsilane (tetramethylammonium ion used as a secondary standard throughout) in 0–18% SO_3 (in H_2SO_4) to 4.59 in 23% SO_3 to 4.73 in 27–31% SO_3. The position was 4.33 in CCl_4. The data indicates that nitromethane is half-protonated in 23% SO_3 and this is not in good agreement with the conductimetric work.

Nitroethane gave similar results. In CCl_4, the pmr spectrum consists of a triplet at 1.56 and a quartet at 4.42 ppm (both with $J = 7$ cps). In 0–20% SO_3, these are at 1.56 and 4.61. In 23% SO_3, they are at 1.64 and 4.86. In 27–32% SO_3, they are at 1.68 and 5.03. Again, half-protonation occurs at 23% SO_3. With both nitromethane and nitroethane, the solutions were 5% by weight and the values of % SO_3 are corrected for acidity used up in protonating CH_3NO_2. The method of making this small correction has been described.[5]

2-Nitropropane partially decomposed during the act of mixing. The isopropyl doublet was at 1.54 in CCl_4, 1.57 in 70% H_2SO_4 to 15% oleum, and 1.67 in 25–34% oleum. However, in 15–34% oleum the spectrum though stable, contained extraneous bands accounting for over 60% of the total area.

A final problem deals with the definition of protonation. Several Russian workers speak of ketones as half-protonated in 10% H_2SO_4, whereas American workers accept the value of 80% H_2SO_4. More germane to this note, the Russian workers refer to nitromethane as being "protonized" throughout 35–85% H_2SO_4.[6] The discrepancy arises because the Russian workers are concentrating on conductimetric techniques and treat nitromethane as protonated when it becomes loosely hydrogen bonded to H_3O^+ and thus migrates as a cation. In our work and this note, nitromethane is regarded as protonated when it accepts H^+ and becomes covalently bonded to such an attached proton.

Acknowledgment.—A grant from the National Science Foundation aided in the purchase of the Varian A-60 nmr instrument.

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The Basicity of Alcohols and Ethers

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Arnett and Anderson[1] established the base strengths of aliphatic alcohols in aqueous mineral acids and Arnett and Wu[2] established the base strengths of ethers. Their method was to observe the changes in distribution coefficient of the alcohol or ether between an inert organic solvent and various concentrations of aqueous sulfuric acid. The concentration of alcohol or ether in the nonaqueous phase was determined by gas chromatography. A representative selection of their estimates of base strengths appear in Table I.

In the present work, solubility studies were made in order to evaluate the basicities. Solubilities were used many years ago by Hammett[3] and the method is virtually identical in theory with the distribution method.[3,4] The novel feature was to include a phenyl group into the structure, but at a sufficient distance from the basic site to make its extinction coefficient independent of protonation. The observed extinction in the aqueous phase at 260–270 mμ was thus a measure of the sum of the concentration of B and BH^+.

In all cases, the solubility decreased from 0 to 20% H_2SO_4 due to salting out. From 20 to 35% H_2SO_4 a shallow minimum existed. From 35 to 60% H_2SO_4, the solubility increased. The data were treated on the assumption that the solubility of free alcohol or ether does not vary from 20 to 60% H_2SO_4 and that the increase in solubility observed is due solely to an increasing proportion of protonation. The uncertainties and errors in this method have been discussed.[2,4]

It was not felt that the data were of sufficient precision to test any acidity function equation so that we are content to simply list in Table I the best estimate of the per cent H_2SO_4 at which C_B equalled C_{BH^+}. Also listed are estimates of the same value for comparable compounds from previous literature work.

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[2] E. M. Arnett and C. Y. Wu, *ibid.*, **82**, 4999 (1960); **84**, 1680, 1684 (1962).

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