In spite of the greater stability of the p- than of the o-nitrophenolate ion in AN, the homoconjugation constant of p-nitrophenol is 20 times as large as that of o-nitrophenol (Table V). This is due to the intramolecular hydrogen bonding in o-nitrophenol. In line with the greater stability of the p-nitrophenolate ion it is found that the heteroconjugation constant with p-bromophenol of o-nitrophenolate is three times as large as that of the para ion (Table V). The heteroconjugation constant in AN of the stable picrate ion is more than $^1/_{1000}$th as large as that of o-nitrophenolate (Table III).

The homoconjugation constant of 2,6-di-t-butyl-4-nitrophenol is too small to be measured. This is caused by the blocking effect of the 2,6-di-t-butyl groups

which hinder the homoconjugation. This acid has the same dissociation constant in water as o-nitrophenol, but in AN the constant of the blocked phenol is 1000 times as large as that of o-nitrophenol. The steric hindrance effect on homoconjugation of two methyl groups adjacent to the OH group has been observed in the conductometric titration of 2,4,6-trimethylphenol with sodium ethoxide in pyridine.[23]

Of the nitrophenols investigated, 2,6-dinitro- and 2,6-di-t-butyl-4-nitrophenol and picric acid have negligibly small homoconjugation constants and their anions negligibly small heteroconjugation constants. These three nitrophenols are suitable for the spectrophotometric determination of pa_H in AN.

(23) D. Bruss and G. Harlow, *Anal. Chem.*, **30**, 1836 (1958).

A Nuclear Magnetic Resonance Method for the Determination of Relative Acidities of Weak Acids in Liquid Ammonia

Thomas Birchall and William L. Jolly

Contribution from the Department of Chemistry, University of California, and the Inorganic Materials Research Division, Lawrence Radiation Laboratory, Berkeley, California 94720. Received July 8, 1966

Abstract: An nmr method for the establishment of a scale of acidities of weak acids in liquid ammonia is described. A pK range of 6.6 units has been covered using substituted anilines. The relative values fit a Hammett σ_ρ plot with $\rho = -5.3$. A new σ value for 4-fluorine of -0.05 is proposed for these systems.

In recent years there has been an increasing interest in strongly basic systems and in the determination of the acidities of very weak acids.[1-5] The acidities studied cover an enormous range of about 30 pK units, and no one solvent system has been used in their determination. In general, as an acid becomes weaker, the solvent system must become more basic in order to achieve a measurable ionization. The solvent systems used include aqueous hydroxide, pyridine,[1] dimethyl sulfoxide–alcohol mixtures,[2] cyclohexylamine,[3] and liquid ammonia,[5,6] to mention just a few. The principal disadvantage of most of these solvent systems is that they only cover a limited range of 5 or 6 pH units.[1] However, the high basicity and low ionization constant of liquid ammonia (10^{-27} at 25°)[7] indicate that this would be a suitable solvent in which to study acid dissociation. Recently a study of acid dissociation in liquid ammonia has been reported by Lagowski and co-workers,[6] who used a spectrophotometric technique.

The high volatility of ammonia makes it necessary either to work at low temperatures, as did Lagowski,[6] or to study the solutions under pressure, as we have chosen to do. Nmr is ideally suited for determining the concentrations of protonic species in sealed tubes, and we have used this technique to determine the relative acidities of some anilines covering a range of 6.6 pK units. Evidence will be presented to show that this method can be used to extend this range by at least 5 pK units at the weaker end of the scale. However, extension to the more acidic region where some direct measurements have been made[6] seems unlikely because of the tendency of the stronger acids to form complexes.[8]

The principal disadvantages of the spectrophotometric method are the complicated apparatus needed for the determinations and the fact that amide ion absorbs strongly at 350 mμ and so obscures bands in this region.[6] Solvent absorption has also been found to be troublesome in the determination of the acidities of anilines in dimethyl sulfoxide solutions.[9]

Experimental Section

Chemicals. All of the substituted anilines except 4-cyanoaniline were obtained commercially; 4-cyanoaniline was kindly donated by Dr. R. Stewart of the University of British Columbia. The anilines were purified by recrystallization from suitable solvents, or by drying followed by distillation, until the literature melting or boiling points were obtained.

(1) R. Stewart and J. P. O'Donnell, *J. Am. Chem. Soc.*, **84**, 493 (1962); *Can. J. Chem.*, **42**, 1681, 1694 (1964).
(2) K. Bowden and R. Stewart, *Tetrahedron*, **21**, 261 (1965), and references therein.
(3) A. Streitwieser, Jr., and H. F. Koch, *J. Am. Chem. Soc.*, **86**, 404 (1964).
(4) A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *ibid.*, **87**, 384 (1965).
(5) A. Shatenshtein, *ibid.*, **59**, 432 (1937).
(6) E. C. Fohn, R. E. Cuthrell, and J. J. Lagowski, *Inorg. Chem.*, **4**, 1002 (1965); **5**, 1002 (1966).
(7) W. L. Jolly and C. J. Hallada in "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press Ltd., London, 1965, Chapter 1.

(8) K. L. Servis, *J. Am. Chem. Soc.*, **87**, 5495 (1965), and references therein.
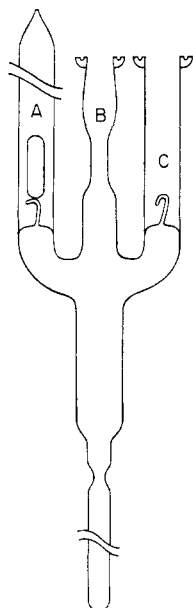(9) R. Stewart and D. Dolman, private communication.

Figure 1. Vessel used for the preparation of samples.

Commercial synthetic ammonia was dried and stored over sodium in a glass vessel attached to the vacuum line until required.

Preparation of Samples. All samples were prepared using standard vacuum line techniques in the following manner. The two acids to be compared were placed in a glass tube (A, Figure 1) fitted with a breakoff seal and glass-enclosed magnet. This tube was evacuated, sealed, and attached by glassblowing to the vessel shown in Figure 1. The apparatus was thoroughly dried by flaming under high vacuum, transferred to a dry bag where a small piece of freshly cut sodium was introduced via B under an atmosphere of dry argon, then transferred back to the vacuum line and evacuated thoroughly. Pure dry ammonia from the reservoir was then distilled into the vessel, and the apparatus was then sealed at B. The reaction between sodium and ammonia was allowed to proceed to completion at room temperature to give $NaNH_2$ and hydrogen. It was found necessary to catalyze this reaction with minute amounts of platinum introduced into the nmr tube by previously washing this tube with a 10^{-4} M solution of chloroplatinic acid, drying, and subsequent decomposition by heating. The reaction of sodium with ammonia was generally complete in 12–24 hr, as evidenced by the complete discharge of the deep blue color of the solvated electron; if the tubes were not "platinized" reaction times up to 3 months were observed.

Once reaction was complete, the hydrogen produced in the reaction was removed via C, collected, and measured by means of a Toepler pump. The hydrogen determination gave a direct measure of the sodium amide in the vessel, and although it was not needed in the calculation, it served as a check on the results since the total amount of acid ionized should equal the amount of amide ion. After the hydrogen had been removed, breakoff seal A was broken, and the acids were distilled down into the nmr tube. The tube was sealed off at the constriction, the mixture warmed to room temperature when equilibrium was rapidly achieved, and the nmr spectrum recorded on a Varian A-60 spectrometer at 31°.

The final solutions were approximately 0.5 M in each acid and in sodium amide; however, deliberate variations from these values for a given pair of acids gave the same relative acidity within experimental error.

Analysis of Nmr Spectra. The method adopted to set up the relative acidity scale was simply that of adding two acids, HA and HB, to a suspension of sodium amide in liquid ammonia, allowing the mixture to come to equilibrium, and then measuring the ratios $(HA)/(A^-)$ and $(HB)/(B^-)$. Using the relation $\Delta pK = \log [(HB)/(B^-)] - \log [(HA)/(A^-)]$, the value of ΔpK for the two acids was calculated. This was then repeated for another pair of acids, HB and HC, and so on until the required range was covered.

The ratios acid/anion were obtained from an examination of the nmr spectrum of the solution at equilibrium. Fortunately, the spectra were simple because of rapid proton exchange between the acids studied and their anions. Thus only two, rather than four, groups of peaks were observed, each group being a time-averaged

combination of an acid and its anion. Having previously obtained nmr spectra of both the acid alone and the anion alone, it was an easy matter to calculate the ratio acid/anion from the spectrum of a mixture of the two, because the nmr spectrum resulting from two species undergoing rapid chemical exchange depends only upon the nmr parameters of the species and upon their relative amounts.[10]

A typical spectrum is shown in Figure 2. This is the spectrum which results when 4-methylaniline and 3,5-dimethylaniline are added to a suspension of sodium amide in liquid ammonia. The "quartet" of peaks centered at −6.29 ppm is a typical AB spectrum which arises from an average of the ring protons of 4-methylaniline and its anion, while the two peaks at −5.77 and −5.49 ppm arise from the ring protons of 3,5-dimethylaniline and its anion. Removal of a proton from an aniline results in a shift to higher field of all the peaks in the spectrum due to the increased shielding from the negative charge on the molecule. The ring protons are the most sensitive to the negative charge, and shifts to higher field of ~1 ppm are observed. Since the negative charge on the nitrogen will effect the shielding at the ring positions via both inductive and conjugative effects, the shielding will be different at the various ring positions, and it is found that the shift to higher field is in the order para > ortho > meta. The effect is illustrated in Figure 2 for 4-methylaniline by the two sets of quartets (A and B) below the actual spectrum; the set (A) to lower field represents the ring protons of the unionized acid, while the set (B) to higher field represents the spectrum of the completely ionized acid. It is seen that the ortho and meta proton resonances have moved apart. This behavior is more obvious in the case of 3,5-dimethylaniline (the lines above the actual spectrum) where the ortho and para protons (C) have almost the same chemical shift in the parent acid but are quite different in the anion (D and E). In our measurements we have used this shifting apart of the aromatic part of the spectrum to determine the extent of ionization because this eliminates the need for a reference point from which to measure chemical shifts. However, the acids aniline and 3-trifluoromethylaniline have complicated nmr spectra which change drastically as δ/J changes, thus making the spectra rather more difficult to analyze. We found it more convenient, in these two cases, to use chemical shifts relative to an external reference of tetramethylsilane to estimate the extent of ionization. In the cases where the acidities were sufficiently close, cross checks were carried out, and agreement better than 0.1 pK unit in all cases, and to 0.05 pK unit in most cases, was obtained.

Discussion

Introduction of substituents into the ring of an aromatic acid changes the electron density at the acidic center, and thus the acidity is changed. In this way large changes in the strength of a parent acid can be produced. We have used a series of substituted anilines to cover a range of 6.6 pK units. The data are shown in Table I. The acidities are all relative to that of 2,5-dichloroaniline, the strongest acid for which we have quantitative data. The effect of substituents upon the acidity is illustrated in a conventional Hammett $\sigma\rho$ plot (Figure 3) for the meta- and para-substituted compounds. We have used σ values compiled by Barlin and Perrin[11] for all substituents except 4-cyano (for which we have used the σ^- value of 1.00 which has been used to fit experimental results for the dissociation of anilinium ions[12]). Some disubstituted compounds are also included in this plot by assuming additivity of the σ constants. A good straight-line correlation is obtained with a ρ value of −5.3. The high ρ value indicates that the acidity of the aniline is extremely sensitive to the substituent.

One noticeable feature of this Hammett plot is a lower acidity for 4-fluoroaniline than would have been predicted from the σ value of a p-fluorine. Obviously

(10) J. A. Pople, W. G. Schneider, and H J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 218.

(11) G. B. Barlin and D. D. Perrin, *Quart. Rev.* (London), **20**, 75 (1966).

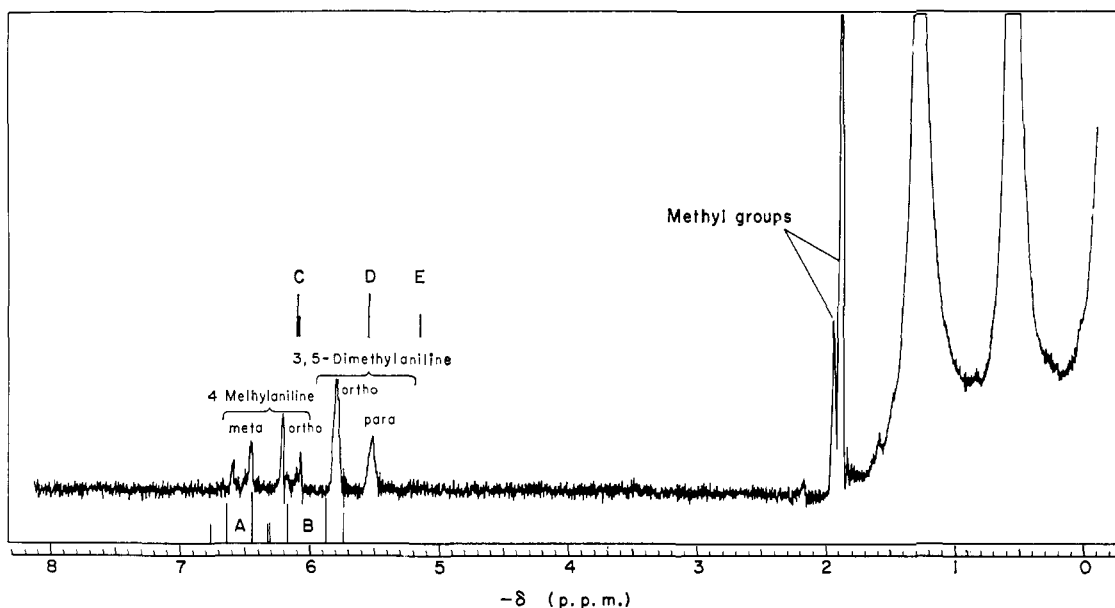(12) J. Clark and D. D. Perrin, *ibid.*, **18**, 295 (1964).

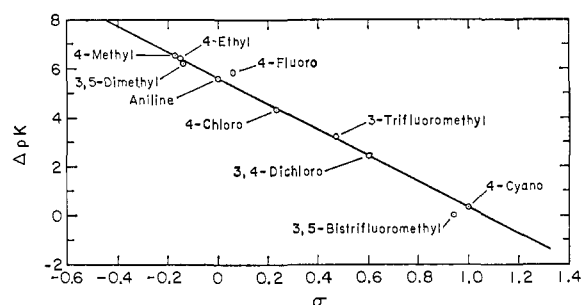Figure 2. Nmr spectrum of a solution of 4-methylaniline, 3,5-dimethylaniline, and their anions in liquid ammonia.

Figure 3. Hammett $\sigma\rho$ plot for relative acidities of substituted anilines.

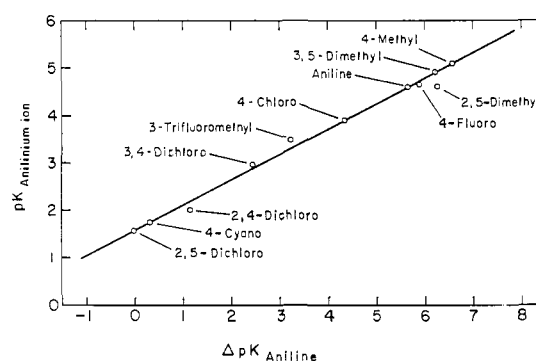Figure 4. Acidities of substituted anilinium ions (ordinate) plotted against the relative acidities of the parent aniline (abscissa).

the electron-withdrawing ability of fluorine is counteracted by a much stronger effect because of conjugation with the ring with the result that the electron density on the nitrogen is increased rather than reduced. This effect of a p-fluorine has also been observed in the pK values of phenol and anilinium ions.[13] Streit-

Table I. Relative Acidities of Some Substituted Anilines

Substituent	pK for anilines	Lit. values for pK's of anilinium ions
2,5-Dichloro	0	1.52[b]
3,5-Bistrifluoromethyl	0.06	
4-Cyano	0.34	1.74[d]
2,4-Dichloro	1.16	2.01[b]
3,4-Dichloro	2.45	2.96[b]
3-Trifluoromethyl	3.22	3.49[c]
4-Chloro	4.34	3.89[a]
No Substituent	5.65	4.60[a]
4-Fluoro	5.88	4.65[a]
3,5-Dimethyl	6.22	4.91[e]
2,5-Dimethyl	6.26	4.61[f]
4-Ethyl	6.43	
4-Methyl	6.58	5.08[a]

[a] Reference 13. [b] R. A. Robinson, J. Res. Natl. Bur. Std., A68, 159 (1964). [c] A. Bryson, J. Am. Chem. Soc., 82, 4858 (1960). [d] M. M. Fickling, A. Fischer, B. R. Mann, J. Parker, and J. Vaughan, ibid., 81, 4226 (1959). [e] B. M. Wepster, Rec. Trav. Chim., 76, 335 (1957). [f] R. N. Beale, J. Chem. Soc., 4494 (1954).

wieser[3] has suggested that a σ^- component should be added to the normal σ for 4-fluorine, and we propose that a σ value of -0.05 should be used for this substituent when considering acidities of anilines, anilinium ions, phenols, and other related systems.

Since a nitro group in the para position can conjugate with the acidic center, a σ^- should be used to obtain correlation on a Hammett-type plot; a value of 1.26 for use with anilines has been suggested.[12] Using this value we would predict that 4-nitroaniline would be 1.05 pK units more acidic than 2,5-dichloroaniline. However, we were unable to obtain any overlap between 2,5-dichloroaniline and 4-nitroaniline in anhydrous ammonia, and our data indicated that, for these two acids, $\Delta pK > 3$. Stewart and Dolman[9] have found a difference of 3.8 pK units for this pair of acids. The ability of a nitro group to transmit its effect to the reactive center appears to be greater in anhydrous liquid ammonia than it is in the aqueous systems used to establish the σ^- constants.

The dissociation of these anilines may be regarded as the second ionization of the corresponding anilinium ion, and it is of interest to compare the effect of substituents upon the two dissociations. Figure 4 shows a

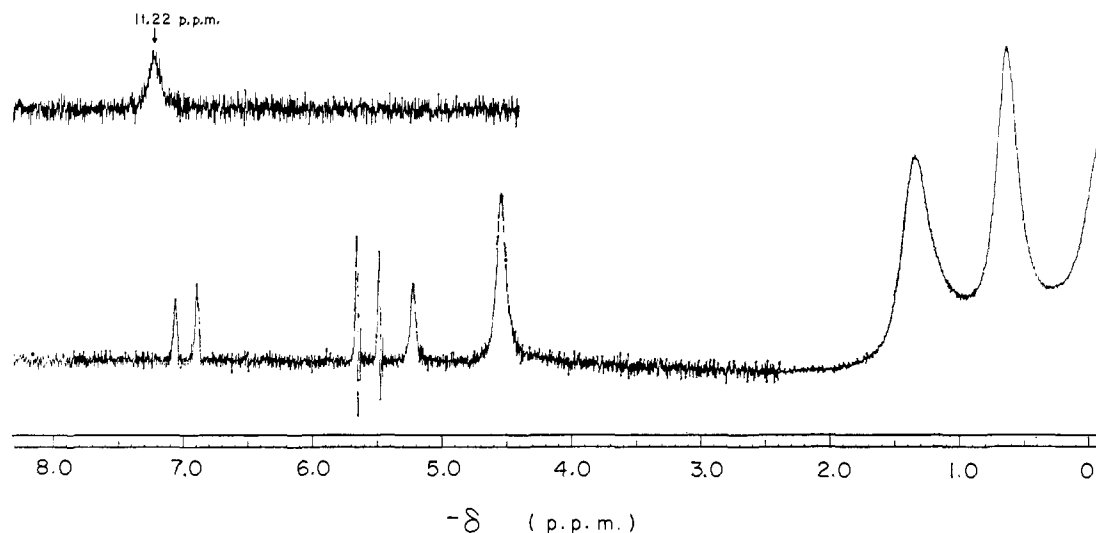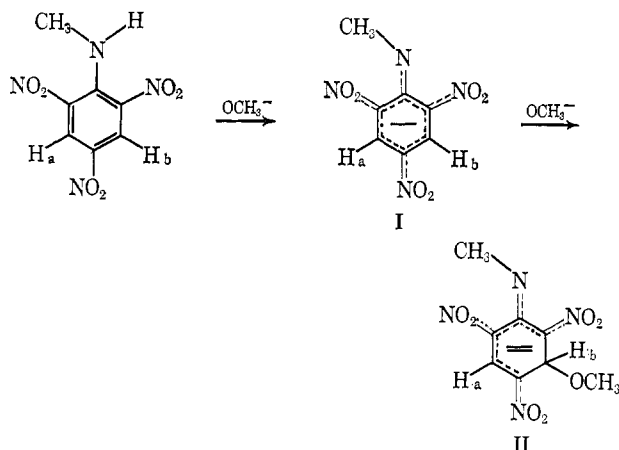(13) A. I. Biggs and R. A. Robinson, J. Chem. Soc., 388 (1961).

Figure 5. Nmr spectrum of a solution of 2,4-dinitroaniline in liquid ammonia containing more than 2 equiv of sodium hydroxide.

plot of the anilinium ion acidity *vs.* the aniline acidity and a remarkably good correlation is obtained. The slope of the line (0.53) shows the greater sensitivity to the substituent of the aniline acidity over that of the anilinium ion acidity.

Complex Formation. Attempts were made to study stronger acids in the hope that we would be able to extend our scale of relative acidities to include nitroanilines and acids such as *o*- and *p*-nitroacetanilide (whose p*K* values were recently determined directly in liquid ammonia[6]). We would then be able to put our scale on an absolute basis. Unfortunately, the susceptibility of nitroanilines to complex formation has prevented us from extending the measurements to acids stronger than 2,5-dichloroaniline. For example, a solution of 4-nitroaniline, 2,4-dimethyl-6-nitroaniline, and sodium amide in liquid ammonia gave an nmr spectrum which had only two very broad structureless peaks in the aromatic region of the spectrum. Presumably partial ionization of each acid had occurred, but complex formation occurs between anions, with rapid exchange resulting in a broadening of the spectrum.

The nature of the complexes formed between nitroanilines and base has been clarified as a result of some nmr studies of Crampton and Gold[14] and Servis.[8] This former group examined the changes which oc-


curred in the nmr spectra of some polynitroanilines in dimethyl sulfoxide upon the addition of base. They concluded that anion I was first formed, and that this was converted into II upon the addition of more than 1 equiv of base. However, they were unable to observe a signal due to H_b and concluded that rapid exchange of OCH_3^- at that site was occurring. Servis[8] in a later communication reported on the reactions of some 1-substituted trinitrobenzenes with methoxide and was able to observe signals due to both H_a and H_b.

During the course of our measurements we have found that even 4-nitroaniline is subject to complex formation of the above type and that 2,4-dinitroaniline forms dinegative anion complexes in which exchange is slow.

Table II gives the nmr parameters for solutions of 2,4-dinitroaniline (III) in liquid ammonia containing various amounts of base. A solution of this acid in plain ammonia gives an nmr spectrum which consists
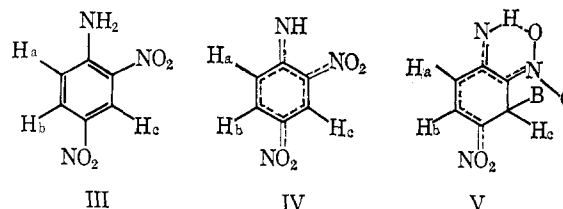
of an AB quartet for H_a and H_b and a doublet for H_c, with each component of B being further split by spin-spin coupling with H_c. The NH_2 proton signal is not visible because of rapid exchange with anion present. Lagowski[6] has shown that this acid is ionized in plain liquid ammonia. Addition of 1 equiv of base (*e.g.*, NaOH) results in complete removal of one proton to give the anion IV, and the nmr signals arising from the ring protons show a shift to higher magnetic field. It should be noted that the basic nmr pattern of the acid is retained in the spectrum of the anion and at all intermediate stages of ionization, as was found for the other anilines. Profound changes in the spectrum occur as the base concentration is further increased. A new set of peaks grows in at the expense of those due to the anion, and when 2 equiv of base has been added only the new set remains. The spectrum of the resulting

(14) M. R. Crampton and V. Gold, *Proc. Chem. Soc.*, 298 (1964); *Chem. Commun.*, 256 (1965).

Table II. Nmr Spectra of Solutions of 2,4-Dinitroaniline in Liquid Ammonia Containing Various Bases

| Base (B⁻) | $-\delta$, ppm from external TMS | | | | | J_{AB}, cps | J_{BC}, cps |
	NH	H$_o$	H$_b$	H$_a$	HB/B⁻ [a]		
None[b]	...	8.83	8.08	7.09	...	9.64	2.87
OH⁻, 1 equiv	...	8.63	7.25	6.56	...	9.7	2.9
OH⁻, >2 equiv	11.22	5.24	6.95	5.59	4.55	10.22	0.75
OMe⁻, >2 equiv	11.25	5.23[c]	7.02	5.59	3.10	10.29	...
NH₂⁻, >2 equiv	~11.0	5.19	6.94	5.52	...	10.22	0.69

[a] Time-averaged signal of rapidly exchanging proton. [b] These are the nmr, parameters for a solution of this acid in plain liquid ammonia and not of the un-ionized acid. [c] Slow OMe⁻ exchange results in broadened H$_o$ peak.

solution is shown in Figure 5 and is assigned to a complex having structure V. The AB quartet of H$_a$ and H$_b$ is retained, but shifted to higher magnetic field as a result of the extra negative charge, and H$_c$ is now found to resonate at a higher magnetic field than H$_a$. This shift is ten times the shift undergone by H$_b$ and is best explained by a rehybridization at the 3 carbon from sp^2 to sp^3. This change is accompanied by a reduction in the spin–spin coupling between H$_b$ and H$_c$. The new broad peak observed at lowest field is assigned to the NH proton internally hydrogen bonded to the 2-nitro group; this peak is present when OCH₃⁻ or NH₂⁻ are used instead of OH⁻. The areas of the peaks due to NH, H$_b$, H$_a$, and H$_c$ are in the expected 1:1:1:1 ratio. Water produced in the ionization of the aniline gives rise to the peak at −4.55 ppm, and this peak presumably also includes the signal from the proton of the OH group at the 3 position, proton exchange causing a merging of these two types of hydrogen.

Proton removal occurs when 4-nitroaniline is treated with base in liquid ammonia; but, whereas sodium hydroxide produces no further interaction, excess amide does. A collapse in the spectrum of the ring protons occurs, implying attack of one or more ring positions by amide ion.

These phenomena illustrate the stronger basicity of liquid ammonia compared to the solvents used by other investigators[9,13] who observed addition of base

to aromatic systems only with trinitro compounds. It is clear that addition occurs to dinitro and probably even mononitro compounds in liquid ammonia.

Other Acids. Recent interest in the acidities of carbon compounds[2,4] has led us to examine a few of these, in a preliminary manner, in the hope that we will be able to obtain good data for both nitrogen and carbon acids in the same solvent. We have examined solutions of the following acids in liquid ammonia in the presence of sodium amide: indene, fluorene, triphenylmethane, diphenylmethane, and toluene. With the exception of toluene all of these acids can be completely ionized with excess amide ion. Literature data[4] indicate that diphenylmethane is ~11 pK units weaker than fluorene, and it appears that fluorene is at the more acidic end of our aniline scale.[1,2] It follows that we should be able to extend our scale by at least another 5 pK units, since diphenylmethane can be completely ionized in liquid ammonia. Toluene cannot be detectably ionized, even with high concentrations of potassium amide, so it appears that the limit to our scale lies somewhere between toluene and diphenylmethane.

Mechanism of Base Hydrolysis of Some Acidopentaamminecobalt(III) Complexes

D. A. Buckingham, I. I. Olsen, and A. M. Sargeson

Contribution from the School of Chemistry, Australian National University, Canberra, Australia. Received July 5, 1966

Abstract: Base hydrolysis of [Co(NH₃)₅X](ClO₄)₂ (X = Cl⁻, Br⁻, I⁻, NO₃⁻) in aqueous solution in the presence of added anions Y (Y = N₃⁻, SCN⁻, NO₂⁻, OAc⁻, SO₄²⁻, PO₄³⁻) leads to formation of some [Co(NH₃)₅Y]ⁿ⁺. The competition ratio for monovalent ions, [Co(NH₃)₅Y]²⁺/[Co(NH₃)₅OH]²⁺, determined by ion-exchange chromatography, shows little dependence on the leaving group, is independent of [OH⁻], but depends on the concentration of Y, and varies slightly from one Y ion to the next. These results suggest the formation of a common intermediate formed by an Sn1CB mechanism and appear to exclude an Sn2 mechanism.

The controversy over the mechanism of aqueous base hydrolysis for complexes of the type [Co-(NH₃)₅X]²⁺ is expounded elsewhere and will not be

dealt with in detail. Briefly, three proposals have been discussed, all of which appear to be kinetically indistinguishable. One mechanism, supported by Ingold