molecule. In the *a* axis direction the packing involved alternating C-10-O-13′ and C-4-O-22″ interactions.

Registry No. β-Pinene, 127-91-3; *cis*-pinocarvyl *p*-nitrobenzoate, 42540-80-7

Supplementary Material Available. A listing of anisotropic temperature factors, observed and calculated structure factors, and distances of atoms in *cis*-PNB from the least-squares plane through the molecule will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $5.00 photocopy or $2.00 for microfiche, referring to code number JOC-74-86.

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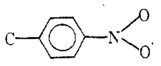

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Acidities of Nitroalkanes in Ammonia. A Warning Concerning the Use of Nuclear Magnetic Resonance as a Method of Analysis

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Received July 23, 1973

The deprotonation of nitromethane and of nitroethane by ammonia is readily studied by nmr; the carbon acids and their conjugate bases each show separate signals. At a constant temperature the per cent deprotonation of each acid increases as the concentration of the sample increases. The deprotonation of nitromethane at −33° increases linearly from 34 to 80% as the total concentration of acid plus conjugate base increases from 0.18 to 2.18 *M*. Over this concentration range the chemical shift of the nitromethide ion decreases by 13 Hz. Both carbon acids undergo more deprotonation with decreasing temperature. Significant deprotonation is achieved below −10° for nitromethane and below 5° for nitroethane, the stronger acid. Attempts to express the results at a constant temperature in terms of equilibrium constants were unsuccessful, perhaps because changes in ion aggregation and in solvent polarity accompany variations in sample concentration.

An acidity scale for acids in liquid ammonia solvent is just beginning to be developed. A few pK_a values are available for very weak acids which require amide ion to bring about deprotonation as well as for considerably stronger acids which undergo deprotonation by ammonia itself.[1] For dilute solutions results generally have been obtained by means of potentiometric titration[2] and by using ultraviolet absorption spectroscopy to analyze reaction mixtures.[3] For more concentrated mixtures, nmr has been employed.[4,5]

Nmr is an especially attractive method of analyzing liquid ammonia reaction mixtures. Experimental techniques are relatively simple. Separate signals may be observed for both an acid and its conjugate base, greatly facilitating analysis of mixtures.

We decided to study the deprotonation of nitromethane (I) and nitroethane (II) in ammonia by an nmr method.

CH_3NO_2
I

$CH_3CH_2NO_2$
II

We hoped to determine the acidities of these carbon acids in this solvent and to test the suitability of nmr as a method of analysis.

Results

Deprotonation of I and II in ammonia to give III and IV was found to be extensive below room temperature. Studies were carried out using reaction mixtures kept at a constant temperature by means of the variable-temperature nmr probe. All reaction mixtures were clear, colorless, and free of precipitates. Discrete spectra were observed for the acid and its conjugate base under all conditions; no signal averaging of the type found for nitrogen, oxygen, and some carbon acids was evident.[6]

$CH_2{=}NO_2^-$ III $\qquad$ $CH_3CH{=}NO_2^-$ IV

Because the nmr spectra of nitromethane and its conjugate base consist of a pair of singlets, it is necessary to examine signal areas in order to make assignments with structures. For this purpose, mixtures of nitromethane and benzene in ammonia were prepared by weight and the signals for benzene, nitromethane, and nitromethide ion then were integrated. The molar ratio of nitromethane (both forms) to benzene was calculated and compared with the ratio obtained from weighed materials. Consistent agreement between the two ratios was found only when the low-field signal (τ 4.6) was assigned to the anion and the high (τ 5.47) to the acid. Thus, ionization leads to a downfield shift of the signal. The shift of an 0.18 *M* solution is 46 Hz.

Coupling patterns were used to make assignments in the case of nitroethane. This acid shows a quartet (τ 5.35, CH_2, J = 7.5 Hz) and a triplet (τ 8.60, CH_3) while its conjugate base shows a quartet (τ 4.2, CH, J = 6.0 Hz) and a doublet (τ 8.42, CH_3) spectrum. Ionization in ammonia results in downfield shifts of 9 and about 65 Hz for the two types of protons, the acidic center undergoing the larger change. (Similar changes are observed when nitroethane undergoes deprotonation in aqueous solution; the protons are deshielded by 16 and 98 Hz.) Thus, carbon acids I and II both show downfield shifts when they are deprotonated.

The effect of concentration on the degree of deprotonation was examined extensively in the case of I. At −33°, the normal boiling temperature of ammonia, the degree of deprotonation ranges from 34 to 80% as the total concentration of acidic and basic forms ranges from 0.18 to 2.18 *M*, respectively (Table I). Deprotonation is markedly favored by high concentrations at a constant temperature.

A significant change in chemical shift occurs for the protons of the nitromethide ion (III) as concentrations are varied in the above experiments. As the total amount of material in solution increases, the signal of the anion shifts to lower fields. Thus, when the total concentration of I and III is 0.18 *M*, the protons of the anion show a signal 126 Hz upfield from that of benzene. However, when the total concentration is 2.18 *M*, the signal is only 113 Hz away. There is a downfield shift of 13 Hz over the indicated concentration range (Table I). The position of the signal for the methyl group of the acid remains constant (±0.5 Hz) during the variations in total concentration.

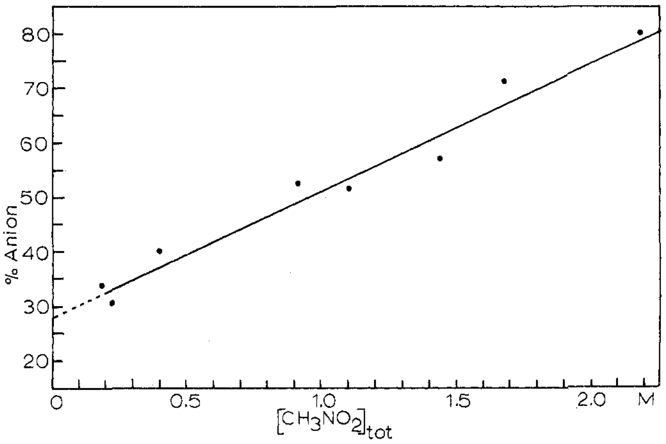

Figure 1. Plot of the percentage of nitromethane which is deprotonated in ammonia at −33° *vs.* the total concentration of the acid and its conjugate base.

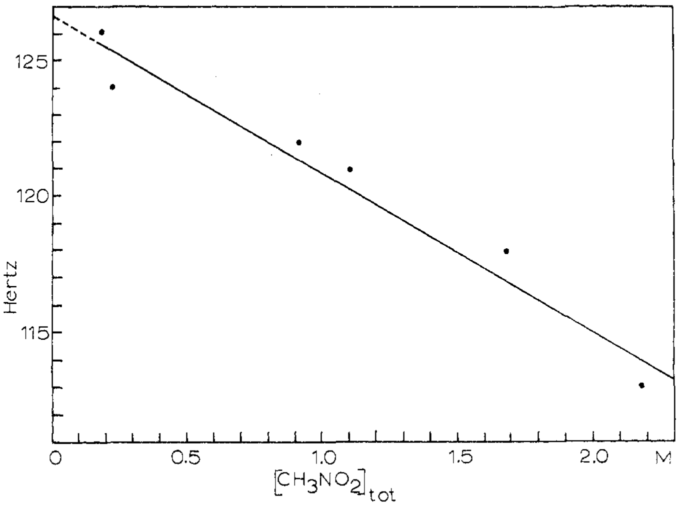

Figure 2. Dependence of the chemical shift of the nitromethide ion in ammonia at −33° on the total concentration of nitromethane and the nitromethide ion. Upfield shifts relative to benzene are indicated.

Table I
Variations in the Per Cent Deprotonation of Nitromethane and in the Chemical Shift of Its Conjugate Base in Ammonia at −33°

Total concn, *M*	% conj base	[Conj base]/[acid]	Hz[a]
0.18	34	0.51	126
0.22	31	0.45	124
0.39	40[b]	0.67	
0.91	53	1.1	122
1.10	52	1.1	121
1.44	57[b]	1.3	
1.68	71	2.5	118
2.18	80	4.0	113

[a] The separation between the signals for $CH_2NO_2^-$ and benzene (τ 2.60) is indicated. [b] Calculated from the data given in Table III.

The above two changes, per cent ionization of I and shift of the protons of III, are linearly related to the total concentration of acid plus base (Figures 1 and 2, respectively). The linear relationships are described by eq 1 and 2 calculated by the method of least squares. The correlation coefficients for eq 1 and 2 are 0.979 and 0.976, respectively. Indicated uncertainties represent one standard deviation. The shift is given relative to benzene (τ 2.60), which served as the internal standard.

$$\%\ \text{deprotonation (I)} = 23 \pm 2\,([I] + [III]) + 28 \pm 2 \quad (1)$$

$$\text{Shift, Hz (III)} = -5.7 \pm 0.6\,([I] + [III]) + 126.6 \pm 0.8 \quad (2)$$

The degree of deprotonation of nitroethane also appears to increase as the total amount of material increases. Only two concentrations (0.43 *M*, 16% deprotonation at 10°, and 0.58 *M*, 23% deprotonation at 11°, Table II) were exam-

Table II
Influence of Temperature on the Degree of Deprotonation of Nitroalkanes in Ammonia

Nitroalkane	Total concn, *M*	Temp, °C[a]	% conj base	[Conj base]/[acid]
CH_3NO_2	0.39	−39	56	1.3
		−30	33	0.50
		−20	14	0.16
		−10	2	0.02
CH_3NO_2	1.44	−45	90	8.4
		−40	80	3.9
		−35	71	2.5
		−30	46	0.87
		−22.5	21	0.26
		−12.5	10	0.11
$CH_3CH_2NO_2$	0.43	−24	87	6.7
		−18.5	78	3.6
		−13.5	66	2.0
		−6.5	53	1.1
		0	29	0.42
		10	16	0.19
$CH_3CH_2NO_2$	0.58	−22.5	92	12.0
		−16	86	6.4
		−7.5	70	2.4
		11	23	0.29

[a] ±1°.

ined. Owing to the small variation in total concentrations, it is not possible to conclude whether changes in chemical shift accompany changes in degree of ionization.

The degree of deprotonation of both nitromethane and nitroethane was determined at temperatures ranging from −45 to −10° for nitromethane and from −24 to 11° for nitroethane. Two samples of each material at two different concentrations were examined. The temperatures ranges for each sample differ slightly (Table II). In the case of both carbon acids an increase in temperature brings about a *decrease* in the degree of deprotonation. In other words, deprotonation of the carbon acid becomes increasingly disfavored as the temperature is increased.

The logarithm of the ratio of the concentrations of conjugate base to carbon acid is related to the inverse of the absolute temperature (eq 3). The slope (*A*) and intercept (*B*) values for this equation are given in Table III; these values when used with eq 3 make it possible to calculate acid–base ratios at a variety of temperatures. Lines were calculated by the method of least squares; correlation coefficients are >0.990.

$$\text{Log [conj base]/[acid]} = A/°\text{K} + B \qquad (3)$$

Although the concentration of the nitromethide ion varies with temperature at a fixed total concentration of acid plus base, no change in the chemical shift associated with this ion could be detected. This contrasts with the effect of concentration on the chemical shift at a constant temperature but at a variable total concentration (Table I).

Clearly nitroethane is a stronger acid than nitromethane. For example, at −33°, nitroethane exists 95% in its deprotonated form (0.43 *M* sample) while nitromethane is only 40% deprotonated (0.39 *M* sample). At 25°, both acids are only slightly deprotonated by ammonia. Similarly, it has been found that nitroethane is a stronger carbon acid than nitromethane in water.[7] Replacement of a proton by a methyl group results in a nitroalkane with a greater equilibrium acidity. Of course, deprotonation at ambient temperatures is more extensive in ammonia than water, owing to the greater basicity of the former solvent.

It should be emphasized that measurements were made on systems at equilibrium. That is, the rates of deprotonation of the nitroalkanes and of reprotonation of the conjugate bases are rapid under the conditions employed. This was shown to be the case for deuterated nitromethane. A sample of nitromethane-d_3 in ammonia was prepared in an acetone–Dry Ice bath. Before the sample was placed into the spectrometer probe at −40°, the tube was shaken for 1 min at room temperature to promote mixing. By the time the first nmr spectrum was taken, the sample had undergone complete D–H exchange. At −40° the material exists largely as its conjugate base. Thus, the cycle of dedeuteration, protonation of the conjugate base, and dedeuteration takes place very rapidly. It is likely that such rates are rapid for nitroethane as well.

Table III
Constants to be Used in Calculating the Temperature-Dependent Ratio of Conjugate Base to Acid for Nitroalkane Deprotonation[a,b]

Compd	Total concn, *M*	$10^{-3}A$	*B*
I	0.39	3.1 (0.2)	−13.1 (0.9)
I	1.44	3.6 (0.2)	−14.8 (0.8)
II	0.43	3.2 (0.1)	−12.0 (0.5)
II	0.58	3.4 (0.1)	−12.6 (0.6)

[a] See eq 3. [b] Sample standard deviations are indicated in parentheses.

Ammonium salts of nitroalkanes have been isolated by removing the solvent from mixtures of the nitroalkane and ammonia. These salts slowly revert to reactants.[8,9] No attempt was made to isolate the ammonium salts in the present study.

Discussion

Many investigations of ionic materials dissolved in liquid ammonia make it clear that ion association is an important phenomenon in this moderately polar solvent (ϵ 23 at −33°[10]), especially in the concentration range employed in the present studies.[1,11-14] Thus, conductance studies of the ammonium and sodium salts of nitromethane in ammonia are consistent with the formation of free ions only at very high dilutions; ion pairs form as concentrations are increased.[8,15] The dissociation constant, K_D, relating the ion pairs and the free ions of ammonium nitromethide, eq 4, is said to have the value 5.3 × 10^{-5} at −33°.[15] This low value clearly indicates that the ion pairs are considerably more stable than the free ions. Notably, aggregation in ammonia need not stop at the ion pair stage. Triple ions,[16] $(K, NH_2, K)^+$ and $(H_2N, K, NH_2)^-$, are believed to form when the concentration of potassium amide exceeds about 5 × 10^{-3} *M*.[11]

$$CH_2{=}NO_2^- \; NH_4^+ \overset{K_D}{\rightleftharpoons} CH_2{=}NO_2^- + NH_4^+ \qquad (4)$$

Our results need to be considered in terms of the ion aggregation phenomenon. The observed increases in the degree of deprotonation of nitromethane and nitroethane as the total concentration of material is increased at a constant temperature (Tables I and II) are consistent with the idea that the ionic products do not exist as free ions but as clusters of ions. Association of the ions gives rise to their mutual stabilization, resulting in a shift of the equilibria so as to favor more extensive deprotonation. Also, the observed deshielding of the nitromethide ion as more ions are added to the solvent (Table I) suggests that the environment of this ion is being changed.[13] Perhaps this indicates that the degree of aggregation of the ion is being modified.

Variations in the degree of deprotonation of I with changes in concentration at a constant temperature may also reflect the presence of another phenomenon. This is a medium or solvent polarity or salt effect. As the reaction medium is made more polar by the addition of ions, the formation of still more ions by deprotonation is facilitated. This type of effect is well known for aqueous solutions,[17] for example. It is likely that medium and ion aggregation effects both are important in the present study.

The present results are too complex to be analyzed solely in terms of equilibria involving ion aggregation. For example, schemes involving deprotonation of I at −33° to give an ion pair or involving deprotonation to give an ion pair which then dissociates into free ions do not quantitatively correlate the observations. It seems likely that activities rather than concentrations are required in order to take medium effects into consideration as well. However, the necessary information about activity coefficients is unavailable.

The observed variations in the anion to acid concentration ratios for I and II may be correlated linearly with the inverse of the absolute temperature (eq 3). The form of this correlation is the same as that for the ionization of an acid to give an ion pair. We do not mean to imply with eq 3 that the ion pair equilibrium scheme, or any other, is favored. Rather, this is the simplest way to deal with the results and to present them in a useful manner.

The temperature dependence of the degree of deprotonation of I and II in ammonia is unusual. Both acids become less acidic as the temperature increases. While both are largely in their acidic forms at 25°, they exist largely as their conjugate bases below about −40° for I and about −10° for II. Although this behavior is unusual, it is not unprecedented for carbon acids.[18]

Curiously, temperature variations bring about changes in the concentration of the nitromethide ion but these are not accompanied by variations in chemical shift. By contrast, the chemical shift of the nitromethide ion is highly dependent on concentration at a constant temperature (Table I). Perhaps the constancy of the shift reflects temperature dependent changes in ion aggregation.

Our new results for I require a comment about the older conductance studies.[8,15] The present results clearly show that the deprotonation of nitromethane is incomplete at −33° when the concentration of acid is $>0.1\ M$. The linear plot (Figure 1) relating per cent deprotonation with total concentration implies that at "infinite dilution" (intercept) only 28% of I is converted to its conjugate base. The conductance workers assumed that I was completely deprotonated in dilute solutions at −33°.[15] This assumption has been questioned recently.[1] Unfortunately, our results do not provide the answer. The present per cent deprotonation–concentration relationship is unusual because it is linear; linearity is not likely to result for very dilute solutions.

Clearly, nmr does provide a great deal of useful information about the deprotonation of carbon acids I and II in ammonia. The linear relationships given in Figures 1 and 2 and by eq 3 are useful in that they quantitatively express the acidity of the carbon acids as a function of total concentration and of temperature. However, owing to the necessity of employing high concentrations of material, analysis of the results in terms of pK values is made very difficult.

In this study we have been considering charge-forming reactions. Ionic products are produced from neutral reactants in ammonia. The use of high concentrations as required by the nmr method complicates the analysis of the results. It is not possible to describe the deprotonation in terms of equilibrium constants. Problems that we encountered with the analysis of nitroalkane acidity are not likely to be unique. Others who wish to determine pK values for similar uncharged acids in ammonia are warned to consider methods other than nmr. Clearly, some method employing more dilute solutions is preferred.

Experimental Section

Benzene (τ 2.60) and nitroalkane were weighed into an nmr tube. Ammonia was condensed into the tube by passing the vapor through a section of constricted glass tubing placed inside the nmr tube. Cooling was achieved with an acetone–Dry Ice bath. After the tube was sealed with a torch the level of ammonia in the tube was measured with a ruler at room temperature. This measurement then was converted to a volume measurement by the use of a calibration curve. The calibration curve was constructed by adding known volumes of water to an nmr tube and by measuring the level of the liquid in the tube. Volume corrections due to thermal expansion of the solvent are small and therefore were not made.

Spectra were recorded on a Varian A-60A spectrometer equipped with a V-6040 variable-temperature controller. Temperatures of probe were measured by the chemical shift method using a sample of methanol and a calibration chart provided by Varian Associates.

Acknowledgment. Computing time was kindly provided by the University of Florida Computing Center. Funds (GP 25500) for the support of this project were kindly provided by the National Science Foundation.

Registry No. Nitromethane, 75-52-5; nitroethane, 79-24-3.

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