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Liquid Ammonia Solutions. II. The Ionization and Dissociation Constants of *o*- and *p*-Nitroacetanilide at −55.6°

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A spectrophotometric method is described for evaluating both the ionization and dissociation constants for substances that undergo partial ionization in liquid ammonia and is applied to solutions of *o*- and *p*-nitroacetanilide. Defining the equilibrium constants for the processes $HX + NH_3 \rightleftharpoons NH_4^+,X^-$ and $NH_4^+,X^- \rightleftharpoons NH_4^+ + X^-$ as $K_i = [NH_4^+,X^-]/[HX]$ and $K_d = [NH_4^+][X^-]/[NH_4^+,X^-]$, respectively, the following constants have been evaluated: *o*-nitroacetanilide, $K_i = (2.2 \pm 1.4) \times 10^{-2}$, $K_d = (2.2 \pm 1.4) \times 10^{-4}$; *p*-nitroacetanilide, $K_i = (9.3 \pm 0.6) \times 10^{-2}$, $K_d = (0.89 \pm 0.06) \times 10^{-4}$.

Introduction

Many substances that are weak acids, or even weak bases, in aqueous solution can behave as acids in liquid ammonia, but because the dielectric constant of liquid ammonia is relatively low, ion association is important even in dilute solutions. Thus, the species present in dilute liquid ammonia solutions of incompletely ionized acids are best described by eq. 1 and 2. It is apparent that conductivity methods, which have been widely used to study incompletely ionized electrolytes, cannot distinguish between the molecular species and ion pairs because neither species has a net charge. However, in conjunction with studies directed toward the elucidation of the chemistry of liquid ammonia solutions,[1] a method was developed to estimate the values of the equilibrium constants for eq. 1 and 2 from spectrophotometric data.

$$HX + NH_3 \overset{K_i}{\rightleftharpoons} NH_4^+,X^- \qquad (1)$$

$$NH_4^+,X^- \overset{K_d}{\rightleftharpoons} NH_4^+ + X^- \qquad (2)$$

Experimental Section

Quantitative absorption measurements were made using the cell, dilution equipment, and techniques described previously.[1] Weighed quantities of the indicator acid and inert salt were introduced into the dried cell *in vacuo*, the dewar vessel was cooled to the working temperature (−55.6°), liquid ammonia was condensed into the buret, and the entire system was allowed to attain temperature equilibrium. A known volume of liquid ammonia was then introduced, the solution was thoroughly mixed, and the optical measurements were made. The solution was progressively diluted and optical measurements were made after each dilution. A series of dilution curves was obtained for various mole ratios of indicator acid to inert salt and used for the calculations outlined below.

o- and *p*-nitroacetanilide were reagent grade chemicals and were resublimed to a constant melting point. Reagent grade potassium iodide was dried in a vacuum oven and stored in a drybox, the atmosphere of which was equilibrated with sodium–potassium alloy.

Results and Discussion

The spectra of *o*- and *p*-nitroacetanilide in pure ammonia and in acidic and basic solutions suggest that these compounds behave as monobasic acids which undergo partial ionization in the pure solvent according to eq. 1 and 2.[1] The low wave length bands centered at 325 and 335 mμ for *o*- and *p*-nitroacetanilide, respectively, have been assigned to the molecular forms of these substances, while the higher wave length bands centered at 436 and 451 mμ are associated with the anions and/or ion pairs containing the anions of *o*- and *p*-nitroacetanilide, respectively. The shapes and positions of these bands are constant for solutions containing varying amounts of KI or KBr indicating that ion aggregates containing the nitroacetanilide anion and the anion itself could not be distinguished spectrophotometrically; similar results have been observed in other systems.[2] However, a marked change was observed in the relative intensities of the bands associated with the molecular and ionic forms of *o*- and *p*-nitroacetanilide as inert electrolyte was added. These results suggest that the position of equilibrium in this system is altered by a change in the activity of the species in solution brought about by the presence of an inert electrolyte.

Extinction Coefficient.—Only one form, *i.e.*, either the molecular species or the ionized species, of *o*- and *p*-nitroacetanilide[1] absorbs at the wave lengths used for determining the concentration of the species in question from spectral measurements. For each analytical concentration of indicator acid, the absorbance was determined at the two wave lengths at which the ionized and molecular forms absorb. The molal extinction coefficients for the molecular forms and for the sum of all the ionic forms of *o*- and *p*-nitroacetanilide were calculated from data of the type shown in Tables I–IV using simultaneous equations of the form

$$\frac{A_i}{\epsilon_1 b} + \frac{B_i}{\epsilon_2 b} = C_i \qquad (3)$$

where A_i and B_i are the absorbances for the molecular and ionic forms of the acid, respectively, at two wave lengths where only the species in question absorbs, b is the cell path length, and C_i is the formal molal concentration of the acid, all at dilution i. One equation using absorbances at the two characteristic wave lengths

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[1] R. E. Cuthrell, E. C. Fohn, and J. J. Lagowski, *Inorg. Chem.*, **4**, 1002 (1965).

[2] (a) A. I. Popov and R. E. Humphrey, *J. Am. Chem. Soc.*, **81**, 2043 (1959); (b) I. M. Kolthoff and S. Bruckenstein, *ibid.*, **78**, 10 (1956); (c) O. Popovych, *J. Phys. Chem.*, **66**, 915 (1962).

TABLE I

ABSORBANCE OF *p*-NITROACETANILIDE AT 355 AND 451 mμ IN LIQUID AMMONIA AT −55.6°

Molality (×10⁵)	Absorbance 355 mμ	Absorbance 451 mμ	Molality (×10⁵)	Absorbance 355 mμ	Absorbance 451 mμ
17.72	1.096	0.939	17.33	1.031	0.919
12.52	0.742	0.763	12.24	0.717	0.754
8.86	0.500	0.621	8.66	0.483	0.614
6.10	0.317	0.492	5.97	0.308	0.485
4.26	0.203	0.389	4.16	0.198	0.386
3.05	0.133	0.312	3.05	0.130	0.311

TABLE II

ABSORBANCE OF *p*-NITROACETANILIDE AT 355 AND 451 mμ IN LIQUID AMMONIA CONTAINING KI AT −55 6°

p-$NO_2C_6H_4$-$NHCOCH_3$ (×10⁵)	Absorbance 325 mμ	Absorbance 436 mμ	$\frac{[X^-] + [NH_4^+,X^-]}{[HX]}$	$f_\pm$	$\frac{1}{f_\pm[HX]^{1/2}}$ (×10⁻¹)
$[KI] = 23.70[p\text{-}NO_2C_6H_4NHCOCH_3]$					
18.40	1.020	1.410	0.504	0.607	1.473
13.00	0.688	1.080	0.573	0.646	1.684
9.20	0.466	0.828	0.648	0.681	1.941
6.34	0.297	0.618	0.759	0.716	2.314
4.42	0.191	0.466	0.890	0.745	2.772
3.18	0.118	0.359	1.110	0.722	3.404
$[KI] = 49.12[p\text{-}NO_2C_6H_4NHCOCH_3]$					
18.12	0.908	1.560	0.626	0.524	1.807
12.49	0.615	1.140	0.676	0.568	2.026
8.83	0.414	0.862	0.760	0.608	2.308
6.08	0.268	0.639	0.870	0.649	2.687
4.25	0.172	0.476	1.009	0.686	3.172
3.05	0.113	0.361	1.168	0.716	3.750
$[KI] = 99.83[p\text{-}NO_2C_6H_4NHCOCH_3]$					
17.39	0.826	1.680	0.742	0.426	2.332
12.29	0.570	1.250	0.800	0.479	2.496
8.69	0.386	0.937	0.886	0.524	2.773
5.98	0.249	0.680	0.996	0.571	3.168
4.18	0.162	0.502	1.131	0.612	3.665
2.99	0.107	0.380	1.296	0.649	4.253

TABLE III

ABSORBANCE OF *o*-NITROACETANILIDE AT 325 AND 436 mμ IN LIQUID AMMONIA AT −55.6°

Molality (×10⁵)	Absorbance 325 mμ	Absorbance 436 mμ	Molality (×10⁵)	Absorbance 325 mμ	Absorbance 436 mμ
59.14	0.762	0.061	17.17	0.208	0.058
41.79	0.539	0.041	12.14	0.145	0.045
29.56	0.373	0.033	8.58	0.100	0.037
20.35	0.251	0.021	5.91	0.063	0.026
14.21	0.172	0.013	4.12	0.040	0.021
10.19	0.119	0.012	2.96	0.027	0.018

TABLE IV

ABSORBANCE OF *o*-NITROACETANILIDE AT 325 AND 436 mμ IN LIQUID AMMONIA CONTAINING KI AT −55.6°

o-$NO_2C_6H_4$-$NHCOCH_3$ molality (×10⁵)	Absorbance 325 mμ	Absorbance 436 mμ	$\frac{[X^-] + [NH_4^+,X^-]}{[HX]}$	$f_\pm$	$\frac{1}{f_\pm[HX]^{1/2}}$ (×10⁻¹)
$[KI] = 13.07[o\text{-}NO_2C_6H_4NHCOCH_3]$					
63.96	0.768	0.233	0.194	0.529	8.168
40.36	0.476	0.172	0.216	0.585	9.386
25.68	0.293	0.111	0.258	0.637	10.99
17.08	0.189	0.078	0.296	0.680	12.81
11.87	0.128	0.058	0.330	0.713	14.85
14.85					
$[KI] = 21.23[o\text{-}NO_2C_6H_4NHCOCH_3]$					
61.27	0.705	0.272	0.247	0.471	9.577
43.30	0.496	0.196	0.252	0.517	10.40
30.64	0.346	0.143	0.270	0.562	11.46
21.10	0.230	0.106	0.316	0.604	13.07
14.73	0.156	0.077	0.354	0.645	14.86
10.56	0.110	0.059	0.377	0.677	16.98
$[KI] = 27.36[o\text{-}NO_2C_6H_4NHCOCH_3]$					
64.15	0.795	0.299	0.268	0.423	10.51
45.33	0.500	0.212	0.300	0.478	11.20
11.05	0.110	0.060	0.441	0.648	17.62

was written for each of the six dilution points, and the best values of the molal extinction coefficients (Table V) were obtained by averaging the solutions to all possible combinations of these equations. Although the relative intensities of the bands attributed to the ionic and molecular forms of *o*- and *p*-nitroacetanilide changed upon the addition of either KI or KBr, the extinction coefficients, as calculated by the method described above using data obtained on solutions containing the inert salt (0.7–30 × 10^{-3} *M*) were, within experimental error, the same as those reported in Table I.

Method of Evaluating Equilibrium Constants.—Although a third equilibrium, *i.e.*, that between the molecular form of the incompletely ionized acid and the free ions, can be written, it is derived from eq. 1 and 2; thus, these equations suffice to define the relationship between the species present in dilute solutions of *o*- and *p*-nitroacetanilide. Defining eq. 1 as the ionization process and eq. 2 as the dissociation process, the equilibrium constants can be expressed in the usual manner as

$$K_i = \frac{[NH_4^+,X^-]}{[HX]} \tag{4}$$

and

$$K_d = \frac{[NH_4^+]f_+[X^-]f_-}{[NH_4^+,X^-]} \tag{5}$$

where f represents the activity coefficient of the respective ions, the brackets represent the molal concentration of the species enclosed, and NH_4^+,X^- represents an ion pair. The activity of the molecular form of the acid and of the ion pair is assumed to be unity.

The concentration of the free anion can be calculated from eq. 6, which was derived from eq. 5 by invoking the principle of electroneutrality and introducing the average activity coefficient for a uni-univalent electrolyte, defined as $f_\pm^2 = f_+f_-$.

The concentration of the molecular form of the acid and the concentration of the anion in all its forms can be

$$[X^-] = \frac{(K_d[NH_4^+,X^-])^{1/2}}{f_\pm} \tag{6}$$

determined from the absorbance at wave lengths which are characteristic of these species. The experimental variables for the systems studied are defined as

$$a = [HX] \tag{7}$$

and

$$b = [X^-] + [NH_4^+,X^-] \tag{8}$$

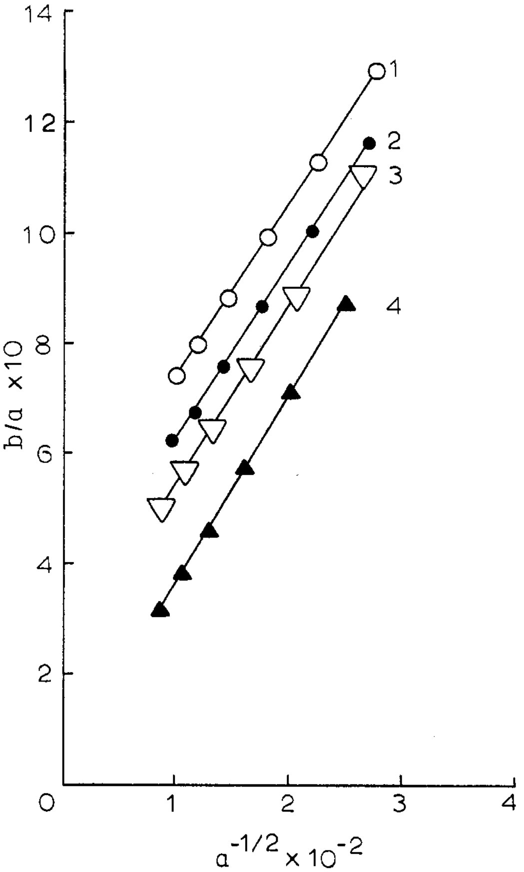

Figure 1.—Data for *p*-nitroacetanilide uncorrected for activity, plotted according to eq. 9. The molality of KI is 99.83[HX] (curve 1), 48.12[HX] (curve 2), 23.70[HX] (curve 3), and 0.0[HX] (curve 4).

Eliminating $[X^-]$ and $[NH_4^+,X^-]$ from eq. 4, 6, and 8 and combining the result with eq. 7 gives

$$\frac{b}{a} = (K_iK_d)^{1/2}[f_{\pm}^{-1}(a)^{-1/2}] + K_i \qquad (9)$$

Equation 9 represents a linear function of b/a *vs.* $a^{-1/2}$, the intercept and slope of which are K_i and $(K_iK_d)^{1/2}$, respectively. Assuming no activity effects ($f_{\pm}^{-1} = 1$), data of the type shown in Tables II and IV yield straight lines when plotted according to eq. 9 (*cf.* Figure 1). This assumption is most nearly valid for solutions of *o*- and *p*-nitroacetanilide containing no inert electrolytes.

Activity Coefficients.—The variation in the relative concentrations of the molecular and ionized forms of *o*- and *p*-nitroacetanilide in the presence of inert electrolyte is illustrated by the data in Tables II and IV. The mean activity coefficients needed to apply eq. 9 to data of the type shown in Figure 1 were estimated from the extended form of the Debye–Hückel equation

$$-\log f_{\pm} = \frac{A'Z^2(\mu)^{1/2}}{1 + Ba'(\mu)^{1/2}} \qquad (10)$$

where

$$A' = \frac{[8\pi e^2/(1000DkT)]^{1/2}e^2}{2DkT} \qquad (11)$$

and

$$B = [8\pi e^2/(1000DkT)]^{1/2} \qquad (12)$$

In these expressions D is the dielectric constant of the solvent, T the absolute temperature, μ the ionic strength, Z the charge on the ion, e the electronic charge, k the Boltzmann constant, and a' a parameter associated with the size of the ion. The dielectric constant of ammonia at −55.6° was obtained by extrapolation from data in the literature.[3] The ion-size parameter a' has been interpreted as the distance between centers of uniformly charged spheres in contact.[4a] Since the activity coefficients for KCl in liquid ammonia could be fit to the Debye–Hückel equation with a value of a' that was within 5% of the sum of the crystallographic radii of K^+ and Cl^-,[5] the ion-size parameter was taken as the sum of the crystallographic radii, 3.50 Å., for potassium iodide. Since the concentration of free ions from the acid was much smaller than the concentration of inert electrolyte, the activity effects of the latter were assumed to predominate. The ionic strength was calculated using the concentrations of free potassium and iodide ions, taking into account the association of these ions into ion pairs, which were assumed to have a unit activity coefficient. The dissociation constant, K_d, which was required to calculate the concentration of free ions, was estimated to be 1.06×10^{-3} from the Bjerrum equation[4b] and 3.90×10^{-3} from conductivity data[6] as corrected to the experimental conditions of this investigation using the Bjerrum equation. The results were relatively insensitive to the value of the dissociation constant chosen for potassium iodide; the best fit for the data was obtained with a value of 0.6×10^{-3}. The data shown in Tables III and V, corrected for activity effects as described above and plotted according to the form expressed in eq. 9, yield straight lines (*cf.* Figure 2) from which the equilibrium constants can be obtained (Table VI). When KBr was used as inert electrolyte, essentially the same results were obtained.

It is difficult to make a direct comparison between

TABLE V

MOLAL EXTINCTION COEFFICIENTS FOR *o*- AND *p*-NITROACETANILIDE AT −55.6°

	HX		$NH_4^+,X^- + X^-$	
Acid	λ, mμ	$\epsilon \times 10^{-3}$	λ, mμ	$\epsilon \times 10^{-3}$
o-Nitroacetanilide	325	1.83 ± 0.02	436	2.66 ± 0.144
p-Nitroacetanilide	355	10.36 ± 0.06	451	28.4 ± 0.3

TABLE VI

EQUILIBRIUM CONSTANTS FOR *o*- AND *p*-NITROACETANILIDE AT −55.6°

Acid	$K_i \times 10^2$	$K_iK_d \times 10^6$	$K_d \times 10^4$
o-Nitroacetanilide	2.2 ± 1.4	4.8 ± 0.5	2.2 ± 1.4
p-Nitroacetanilide	9.3 ± 0.6	8.3 ± 0.1	0.89 ± 0.06

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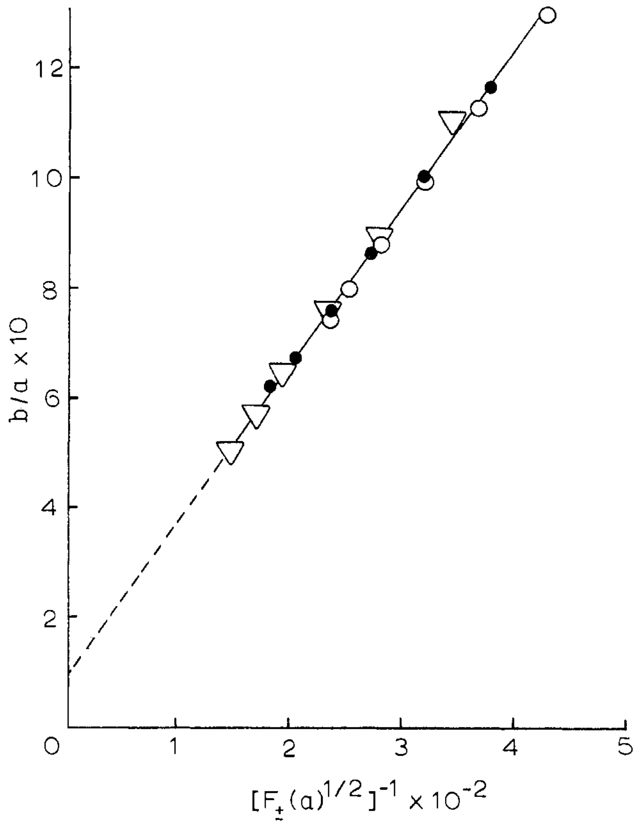

Figure 2.—Data for *p*-nitroacetanilide, corrected for activity, plotted according to eq. 9.

the ionization constants as defined in this investigation for liquid ammonia solutions and those for equilibria established in solvents of high dielectric constant such as water. Perhaps a more meaningful comparison involves the degree of ionization, at the same formal concentration, observed in these two systems. The degree of ionization in ammonia, *i.e.*, $\alpha = ([X^-] + [NH_4^+,X^-])/[HX]$, can be calculated directly from these spectrophotometric data. Expression of α in this form suggests that the properties of the species under consideration are essentially unaltered when it is involved in ion-pair formation. The value of α for both *o*- and *p*-nitroacetanilide in liquid ammonia at $-55.6°$ is about 25% at 10^{-4} *m*, which corresponds to an acid with an ionization constant of *ca.* 9×10^{-6} in aqueous solution.

The dissociation constants for the ammonium salts of *o*- and *p*-nitroacetanilide in liquid ammonia have not been reported previously; however, the constants obtained from this investigation are in reasonable agreement with the data available for similar structural types. The equilibrium constant for *o*-nitrophenol in liquid ammonia at $-33°$ is 3.90×10^{-4} as determined by a conductivity method.[7] Preliminary observations[8] on the spectra of liquid ammonia solutions of *o*-nitrophenol suggest that it is completely ionized, thus the reported equilibrium constant corresponds to K_d. Assuming the ion-size parameter for ammonium *o*-nitrophenolate and the ammonium salts of *o*- and *p*-nitroacetanilide are similar, and taking into account the temperature difference between the two measurements, the agreement between the dissociation constants is satisfactory.

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Photochemical Synthesis of Volatile Hydride Derivatives

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Mercury-sensitized photolysis techniques have been applied to the synthesis of volatile hydride derivatives of carbon, silicon, and germanium. Methylsilane, germylsilane, and germyl methyl ether have been prepared by the mercury photosensitized decomposition of methyl iodide–silane, germane–silane, and methanol–germane mixtures, respectively. Some physical properties of the new compound germyl methyl ether are described.

Introduction

Although extensive kinetic and synthetic photochemical studies have been carried out on the carbon hydrides and their derivatives,[2] only a few studies have been reported that deal with the lower members of the group IV hydrides. Recently, several articles dealing exclusively with kinetic aspects of the mercury-sensitized photolysis of silicon[3,4] and germanium[5] hydride systems have appeared in the literature. From the results reported therein this technique was deemed a promising approach to the synthesis of various mixed

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