DAVID NICHOLLS

INORGANIC CHEMISTRY IN LIQUID AMMONIA

MONOGRAPH 17

TOPICS IN
INORGANIC
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R. J. H. CLARK

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INORGANIC CHEMISTRY IN LIQUID AMMONIA

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PREFACE

Franklin's classic work "The Nitrogen System of Compounds was published in 1935. Since that time inorganic chemistry in liquid ammonia has flourished. Whilst there have been many reviews which have periodically up-dated various aspects of ammonia chemistry and several books on the physical chemistry of alkali-metal solutions, no book on inorganic chemistry in liquid ammonia has appeared in the English language since Franklin's. This book is intended to fill that gap. The emphasis is on chemistry and it is thus a book of chemical reactions in ammonia. Detailed structures and physical properties of reaction products are not usually dealt with except in those cases of compounds which may be regarded as prototypes or which have particular relevance to ammonia chemistry.

Whilst the literature is covered up to the end of 1977 some of the references cited in this work are pre-1940. These older references are included to indicate to the reader those reactions which have not been re-studied since the original work was carried out and which were performed at a time when the handling of air- and moisture-sensitive materials was difficult and modern analytical aids were not available. For a large number of the compounds cited here no spectroscopic or other evidence is available concerning their structure. Those cases in which the original formulations must be regarded with caution, are indicated in the text.

The author would like to take this opportunity of thanking Professor G.W.A. Fowles of the University of Reading for introducing him to the field of liquid ammonia research and for the continued encouragement he has given me to write this book.

Liverpool
December 1977

D.N.

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CHAPTER 1

INTRODUCTION TO LIQUID AMMONIA CHEMISTRY

INTRODUCTION

The first investigations into the chemistry of liquid ammonia were carried out over a century ago by Weyl[1], Seely[2] and Gore[3]. In 1889 Joannis[4] began his series of publications on qualitative studies of reactions in liquid ammonia. This work appears however to have gone largely unnoticed at the time and liquid ammonia was 'rediscovered' in the classical researches of Cady, Franklin and Kraus. It was these workers who first emphasised the great similarities between ammonia and water. The early work is summarised in Franklin's historic book "The Nitrogen System of Compounds" published in 1935. Indeed the whole field of non-aqueous solvents was stimulated by these researches so that today the inorganic chemist has a wide range of well studied solvents from which to pick a medium for any particular reaction. This does not mean to say that liquid ammonia no longer merits study in its own right. On the contrary, physical studies of solutions in liquid ammonia attract widespread interest today from physicists and chemists. Many inorganic reactions are still to be discovered in liquid ammonia and for many compounds, ammonia remains the only solvent in which they may be suitably prepared.

Despite its similarities with water, it is the subtle differences in properties of liquid ammonia that enable much exciting chemistry to be carried out. One such difference is the fact that ammonia dissolves the alkali metals without reaction. These alkali metal solutions have found extensive use as reducing agents in organic chemistry as well as in inorganic chemistry where they enable the preparation of compounds containing metals in low oxidation states. Often it is merely the temperature range of liquid ammonia (-78 to -33 °C) that enables a preparation to be carried out which cannot be effected in water. Thus compounds that are thermally unstable above 0 °C cannot be isolated from water. The reaction between ammonium chloride and potassium nitrite for example, yields nitrogen when performed in water, but gives a solution from which ammonium nitrite can be crystallised in liquid ammonia. Solubility differences also lead to many useful preparations in liquid ammonia. In ionic reactions, the driving force which shifts an equilibrium is often the insolubility of one of the products. A simple example of this is the reaction:

$$Ba(NO_3)_2 + 2AgBr \rightarrow BaBr_2 + 2AgNO_3$$

which proceeds from left to right in liquid ammonia ($BaBr_2$ being the least soluble combination of ions in ammonia) but from right to left in water (AgBr then being the least soluble ionic combination). Perhaps one of the most important differences between ammonia and water is the greater stability of the N-H bonds in ammonia relative to the O-H bonds in water. That is, ammonia has a lesser tendency to react with solute species than has water so that ammonolysis occurs less extensively than hydrolysis. Thus compounds such as peroxides e.g., $Zn(O_2)_2$ and phosphohydrides e.g., $Co(PH_2)_3$ can be prepared in ammonia by metathetical reactions involving the ammonia - soluble salts Na_2O_2 and KPH_2. Similarly, germane GeH_4 prepared by the action of acids on Mg_2Ge is obtained in 20% yield in water but in 80% yield when a solution of ammonium bromide in ammonia is used.

THE NITROGEN SYSTEM OF COMPOUNDS

Having briefly mentioned some of the differences between water and ammonia, let us now consider their similarities. Both are highly associated liquids with extensive hydrogen bonding. In this respect they resemble each other much more than does ammonia and phosphine or water and hydrogen sulphide, i.e. ammonia and water are anomalous when compared to the other hydrides of their periodic groups. They thus have anomalously high melting and boiling points and high heats of vapourisation. Both are ionising solvents and excellent electrolytic solvents. Ammonia has a somewhat lower relative permittivity (dielectric constant) than water and is not therefore as good a solvent for ionic substances; it is better than water in its ability to dissolve more covalent compounds.

Ammonia, like water, is a protonic solvent. The ammonia molecule, like water reacts with a proton to give a positive ion which behaves as an acid in the parent solvent:

$NH_3 + H^+ \rightarrow [NH_4]^+$

$OH_2 + H^+ \rightarrow [OH_3]^+$

If we write down the auto-ionisations of both solvents, we see the aquo and ammono analogues:

$2NH_3 \rightleftharpoons [NH_4]^+ + [NH_2]^-$

$2OH_2 \rightleftharpoons [OH_3]^+ + OH^-$

acid base

The solvent system concept of acids and bases developed from the realisation that nitrogen compounds in ammonia behave in an analogous fashion to oxygen compounds in water. An acid is defined as a compound which, when added to the solvent, produces the cation characteristic of the solvent. A base produces the anion characteristic of the solvent. Clearly the cation and anion characteristic of liquid ammonia are the ammonium ion and amide ion respectively. Acid - base reactions in ammonia are thus analogous to those in water, e.g.

$NH_4Cl + KNH_2 \rightarrow KCl + 2NH_3$

$OH_3Cl + KOH \rightarrow KCl + 2OH_2$

acid + base → salt + solvent

On the assumption that this resemblance between ammonia and water can be extended to their other derivatives, Franklin classified aquo and ammono compounds as shown in Table 1. Such classifications have helped considerably in understanding reactions in ammonia and enabling predictions to be made about preparative methods.

REACTION TYPES IN LIQUID AMMONIA

It will be found convenient to classify inorganic reactions in liquid ammonia into a number of reaction types. These types will be the subject of future chapters and only an

TABLE 1

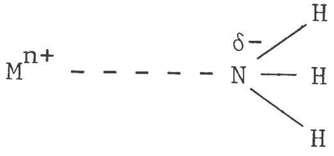
Aquo and ammono analogues

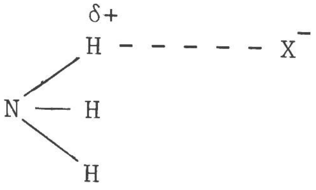
Aquo	Ammono
$LiOH$	$LiNH_2$
Li_2O	Li_3N
$(HO)_2CO$	$(H_2N)_2C(NH)$
$HONO_2$	$HN{:}N\vdots N$
$HONO$	$H_2N{\cdot}N{:}NH$
$HOCl$	H_2NCl
Cl_2O	Cl_3N
CH_3COOH	$CH_3C(NH)NH_2$
$(HO)_3PO$	$(H_2N)_2PN$
K_2CO_3	K_2CN_2
C_2H_5OH	$C_2H_5NH_2$
$(C_2H_5)_3N$	$(C_2H_5)_2O$
H_2NNH_2	$HOOH$

introduction will be given here.

Solvation (ammonation)

The process of solution of an ionic solid in liquid ammonia to some extent resembles that in water. The ammonia molecule is a dipole with a lone pair of electrons on the nitrogen atom. When an ionic solid is placed in liquid ammonia, solution will occur if the forces of interaction between ammonia and the separate ions are greater than the forces holding the ions together in the crystal lattice; i.e. if the solvation energy exceeds the lattice energy. The electrostatic forces of solvation of cations and anions can be represented thus:





The solvation of cations is usually the major contribution to the overall solvation energy. As with water, six co-ordination in the first co-ordination sphere around the cation is the most common. Recovery of ionic solids from ammonia solutions however frequently yields a range of ammoniates, cf. salt hydrates. For the ionic salts of groups IA and IIA cations, the forces holding the ammonia molecules to the salts are the electrostatic or ion-dipole forces illustrated above. The ammoniates thus exert dissociation vapour pressures of ammonia and all the ammonia can be removed by heating the ammoniates in a vacuum with re-liberation of the original salt. This behaviour is thus analogous to that of the salt hydrates of the alkali- and alkaline-earth metals. For cations having a formal charge greater than +2 however, the force of attraction between the cation and the ammonia molecule is much stronger and considerable distortion of the ligand charge cloud occurs, i.e. covalency.

Solvolysis (ammonolysis)

Solutions of such cations are able to undergo the acidity reaction shown by aquo-cations, i.e. they are able to protonate an ammonia molecule, *viz.*:

$$[M(NH_3)_6]^{3+} + NH_3 \rightleftharpoons [M(NH_3)_5(NH_2)]^{2+} + [NH_4]^+$$

$$\text{cf.} \quad [M(H_2O)_6]^{3+} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{2+} + [H_3O]^+$$

This reaction is called ammonolysis by analogy with hydrolysis. As in water the extent of such solvolysis depends to a large extent upon the charge-to-size ratio of the cation. In the presence of added base (NH_2^-) the ammonolysis proceeds in a stepwise fashion:

$$[M(NH_3)_5(NH_2)]^{2+} + NH_3 \rightleftharpoons [M(NH_3)_4(NH_2)_2]^+ + [NH_4]^+$$

$$[M(NH_3)_4(NH_2)_2]^+ + NH_3 \rightleftharpoons [M(NH_3)_3(NH_2)_3] + [NH_4]^+$$

Metal amides are ultimately precipitated because of their polymeric nature (processes akin to olation and oxolation occurring). Amphoterism is shown in ammonia just as in water so that these amides dissolve in an excess of potassium amide solution to give soluble amido metallates:

$$[M(NH_3)_3(NH_2)_3] + [NH_2]^- \rightleftharpoons [M(NH_3)_2(NH_2)_4]^- + NH_3$$

With some of the covalent halides complete ammonolysis occurs in liquid ammonia in the absence of added base, e.g.

$$SiCl_4 + 4NH_3 \rightarrow Si(NH_2)_4 + 4NH_4Cl$$

cf. $SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$

It is obviously very important to know how the chemical elements and their compounds react with the solvent ammonia if we are to be able to use the solvent predictably in preparative chemistry. We shall spend considerable time on this topic therefore in Chapter 4.

Acid-base reactions

Ammonia is a basic solvent and has a levelling effect upon the strengths of acids. Strong acids are reduced in strength to that of the ammonium ion. Acids which are weak in water however have their acidity increased in ammonia because of their ability to protonate the ammonia molecule which is a stronger base than the water molecule. Thus hydrogen cyanide becomes ammonium cyanide, and hydrogen sulphide, ammonium hydrogen sulphide in ammonia. Even some mildly basic substances in water become acidic in ammonia because of their ability to protonate the solvent. In this category are substances such as urea and guanidine, $H_2NC(NH)NH_2$.

Solubilities are very important in deciding acidity in ammonia. Sulphuric acid for example shows little or no acidity in ammonia because of the insolubility of ammonium sulphate. Some ammonium salts however are extremely soluble in ammonia. Ammonium nitrate for example is so soluble that the vapour pressure of the ammonia over saturated solutions of the salt is reduced sufficiently for the ammonia to remain liquid at temperatures approaching room temperature.

Apart from ammonium salts there are many other types of compound which produce the ammonium ion in ammonia. We mentioned metal ions and covalent metal and non - metal halides as acids under ammonolysis. Many organic compounds also behave as acids in ammonia. Acetamidine $CH_3C(NH)NH_2$ for example, the nitrogen analogue of acetic acid, does not protonate water but in ammonia protonation occurs thus:

$$CH_3C(NH)NH_2 + NH_3 \rightarrow CH_3C(NH)NH^- + [NH_4]^+$$

In contrast, there are very few bases in ammonia. Only the alkali metal amides have any great basicity and of these only potassium amide shows any marked solubility in ammonia. Alkali metal hydroxides are insoluble and exert practically no basic effects. Very strong bases can produce the amide ion in ammonia; thus potassium hydride liberates hydrogen:

$$KH + NH_3 \rightarrow KNH_2 + H_2$$

and sodium oxide forms a mixture of the amide and hydroxide:

$$Na_2O + NH_3 \rightarrow NaNH_2 + NaOH$$

Many metal amides show amphoteric properties by dissolving in both ammonium salt solutions and potassium amide solutions.

Oxidation-reduction reactions

Franklin[5] was able to show some remarkable analogies involving redox reactions in ammonia and water. The nitridation caused by hydrazoic acid in ammonia is very similar to the action of nitric acid in water. Similarly the oxidation of hydrazobenzene to azobenzene is accomplished by mercury(II) oxide in water or by mercury(II) nitride in ammonia:

$$PhNHNHPh + HgO \rightarrow PhNNPh + Hg + H_2O$$

$$PhNHNHPh + Hg_3N_2 \rightarrow PhNNPh + 3Hg + 2NH_3$$