

LIQUID AMMONIA RESEARCH—1941

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I. INTRODUCTION

Attention is called to the fact that this paper represents a continuation of the review series initiated in 1933 and heretofore published in the *Journal of Chemical Education* (20, 22, 84, 85, 87, 90, 93, 94). In this and in subsequent reviews, it will be the authors' purpose to present annually a brief concise account of researches involving liquid ammonia, a solvent and reaction medium which in recent years has passed from the realm of the chemical curiosities into the category of common and useful laboratory tools. The extent to which liquid ammonia has come into general use is amply illustrated by the character and variety of the applications cited in the following pages.

II. PHYSICOCHEMICAL STUDIES

Measurement of the conductance of liquid ammonia solutions of benzamide, *o*-, *m*-, and *p*-toluamides, *o*-, *m*-, and *p*-tolusulfonamides, *o*-, *m*-, and *p*-chlorobenzamides, *o*- and *m*-bromobenzamides, and their sodium or potassium salts has been made for the purpose of determining the relationship between the position of substitution and the magnitude of the ionization constant (57). In general, methyl substitution resulted in a decrease in the ionization constant. In the case of the substituted benzamides, the relative magnitudes of the effects produced are given by the order: para > meta > ortho. With benzenesulfonamide, meta and para substitution decreased the value of the ionization constant to about one-half that of the unsubstituted compound, while ortho substitution produced only a slight decrease.

The mean activity of potassium iodate corresponding to infinite dilution has

been determined for liquid ammonia solutions at 25°C. by measuring the solubility of this salt in the presence of electrolytes at different ionic strengths and extrapolating to zero ionic strength (2). The electrolytes used were sodium chloride, potassium chloride, potassium bromide, potassium iodide, and ammonium chloride. The results failed to conform to the Debye-Hückel limiting law. The observed deviations have been attributed to the fact that the lower dielectric constant of ammonia (relative to water) causes the electrostatic forces between ions to become the predominating factor. The molar heats of solution of ammonium iodide, sodium iodide, sodium chloride, sodium nitrate, and methanol in liquid ammonia have been measured by Schmidt and coworkers (69). In contrast to ammonium chloride and ammonium bromide, which were studied earlier (23), ammonium iodide was found to have a negative heat of dilution.

Ecker (31) has described studies on the absorption spectra of saturated liquid ammonia solutions (-50°C.) of reversible polymers obtained from certain quinoline dyes. Aqueous solutions of diethyl- ψ -isocyanine exhibit an absorption band at 20,750 cm^{-1} which is attributed to the presence of a dimer. Absence of this band in the spectrum of the corresponding liquid ammonia solution suggests that the dimeric form is absent, probably because the solubility of the dye is too low to permit polymerization.

The ammonolysis of 2-chlorobenzothiazole by liquid ammonia at 20° and 30°C. has been found to be a pseudo-unimolecular reaction which is not appreciably catalyzed by relatively high concentrations of salts (55). Those salts which behave as acids in liquid ammonia failed to exhibit the catalytic activity which might be anticipated, in view of the pronounced effects which such salts are known to have upon the ammonolysis of esters. The most probable reaction mechanism has been shown to be a bimolecular interaction of molecules of the thiazole and molecules of ammonia. Reaction-velocity constants and the energy of activation for the reaction have been calculated from the experimental data.

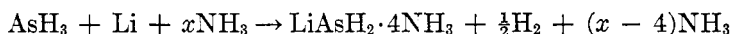
A spongy porous suspension of calcium metal in toluene has been prepared by Bergstrom and Carson (5) by adding a liquid ammonia solution of the metal to a large volume of toluene, followed by volatilization of the ammonia. As a catalyst for the hydrogenation of naphthalene, the calcium suspension so prepared exhibited essentially the same activity as calcium activated by pulverization under benzene in a ball mill.

In a study of the liquid-gas equilibrium for the system ammonia-nitrogen at pressures up to 5600 kg. per cm^2 and over a temperature range of 90-125°C., a temperature minimum between 85° and 90°C. has been observed in the critical temperature-pressure diagram (52). It was found that the composition at the critical point (53 to 57 volume per cent) varied only slightly with the temperatures to which the system was subjected. The original discussion of these results devotes considerable attention to the possible existence of a "barotropic phenomenon" in this particular two-component system. Nomographs for the solubilities of nitrogen and hydrogen in liquid ammonia have been devised (29).

III. INORGANIC REACTIONS

The reducing action of liquid ammonia solutions of sodium, potassium, and calcium toward several soluble and insoluble salts of nickel at -33.5°C . has been investigated by Burgess and Eastes (15). The finely divided elemental nickel produced in these reactions was found to be pyrophoric and to be an excellent catalyst for the conversion of the alkali and alkaline-earth metals to the corresponding amides. An appreciable quantity of the hydrogen liberated during amide formation was found to be absorbed by the finely divided nickel. However, upon being heated above 360°C . *in vacuo*, the absorbed hydrogen was liberated and the metal lost its pyrophoric properties. The elemental nickel produced by reduction with calcium was found to be more active than that formed when either sodium or potassium was employed, a behavior which has been observed previously (88) in a study of the reduction of silver iodide. The preparation of $\text{K}_4\text{Ni}(\text{CN})_4$ by Burgess (14) and of $\text{K}_4\text{Pd}(\text{CN})_4$ by Fernelius (33) has been referred to by Blanchard (7) in connection with a discussion of metal carbonyls. These unusual substances were prepared by treating solutions of potassium nickelocyanide, $\text{K}_2\text{Ni}(\text{CN})_4$, and potassium palladocyanide, $\text{K}_2\text{Pd}(\text{CN})_4$, respectively, in liquid ammonia with potassium. Further discussion of these interesting compounds will be deferred until additional details are published.

The reaction between arsine and lithium in liquid ammonia (54) at -70°C . has been shown to proceed in accordance with the equation:



The tetraammonate of lithium dihydrogen arsenide undergoes a two-stage decomposition *in vacuo* at 0°C ., as follows:

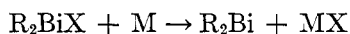


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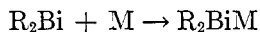


Dilithium hydrogen phosphide, Li_2PH , has been found to form a white crystalline pentaammonate, $\text{Li}_2\text{PH} \cdot 5\text{NH}_3$, which is only slightly soluble in liquid ammonia and which, *in vacuo*, loses ammonia to form successively a tri- and a di-ammonate (53).

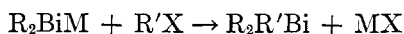
A recent study (37) of the reduction of aryl-substituted bismuth halogenides by solutions of alkali and alkaline-earth metals in liquid ammonia at its boiling point has shown that these reactions may be represented by the equations



and



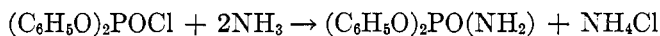
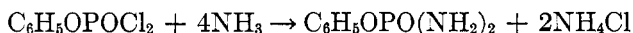
where R represents an aryl substituent, M represents an alkali metal, and X represents a halogen. The metal salts in liquid ammonia solution react with compounds of the type $\text{R}'\text{X}$ as shown by the equation



The order of relative stability of diarylbismuth halides is $R_2BiI > R_2BiBr > R_2BiCl$, while for the corresponding R_3BiX_2 types the order is $R_3BiCl_2 > R_3BiBr_2 > R_3BiI_2$.

The preparation, properties, and certain reactions of the amides of trivalent chromium and cobalt have been described by Schmitz-Dumont (70). A red polymeric amide corresponding to the formula $[Cr(NH_2)_3]_n$ was produced by the reaction between the hexamine of chromium(III) nitrate and potassium amide in liquid ammonia at room temperature. The amphoteric character of this amide was shown by the fact that it reacts with ammonium bromide in liquid ammonia to form the complex salt $[(NH_3)_3Cr(NH_2)Br]_nBr_n$, and by the fact that the ammonia-insoluble polymeric amide is dissolved by an excess of potassium amide with formation of the salt $[Cr(NH_2)_4]_nK_n$. An analogous amidimido potassium salt, $[(HN)Cr(NH_2)_2]_nK_n$, was also formed by treatment of the hexamine of chromium(III) iodide with an excess of potassium amide in liquid ammonia. Similarly, a brown amorphous polymeric amide of cobalt, $[Co(NH_2)_3]_n$, was formed by treatment of the hexamine of cobalt(III) nitrate with potassium amide. That this amide is also amphoteric was demonstrated by the formation of the nitrido salt, $Co_2N_3K_3$, by reaction with excess potassium amide and by the formation of $[(NH_2)Co(NH_3)_2]_n(NO_3)_n$ by reaction with ammonium nitrate in liquid ammonia.

Audrieth and Toy (3) have recommended the use of liquid ammonia for the preparation of phenyl diamidophosphate and diphenylamidophosphate by the ammonolysis of the corresponding phenyl-substituted phosphoryl chlorides.



This procedure is characterized by its convenience and by relatively high yields.

The extraction of water from a number of silicate minerals and hydrated oxides by liquid ammonia at $-77^\circ C$. has been described (6). The residues contained both water and ammonia in varying ratios which approached the proportions $2H_2O:4NH_3:6SiO_2$ for minerals of low base content. Minerals of high base content formed gels and the ammonia content followed typical adsorption curves. Adsorption of ammonia was also observed with certain hydrous oxides (CuO , ZnO , La_2O_3 , Fe_2O_3 , Ta_2O_5), while but little adsorption was exhibited by such hydrated oxides as Na_2O , BeO , CaO , and BaO . Of the hydrous oxides studied, the metal oxides in general formed no definite compounds with ammonia except in the cases of bauxite and hydrargillite, which gave mixed hydrate-ammonates. The more acidic oxides tended toward the formation of ammonates or mixed hydrate-ammonates, e.g., $Cb_2O_5 \cdot 2H_2O \cdot NH_3$, $Sb_2O_5 \cdot 5H_2O \cdot 3NH_3$, and $H_2WO_4 \cdot 2NH_3$. The formation of a considerable number of ammonates of complex salts of zinc(II) chloride, cadmium(II) chloride, cobalt(II) chloride, and nickel(II) chloride has been reported (75). These salts in chemical combination with benzidine, *o*-tolidine, and *o*-dianisidine were treated with liquid ammonia

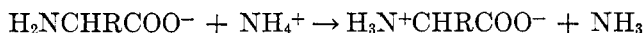
and the existence of ammonates was shown by tensimetric measurements. For example, $\text{Cd}(\text{Bzd})\text{Cl}_2$ was found to form ammonates containing 12, 10, 8, 6, 4, 2, and 1 NH_3 . The extent of ammonation, as well as the thermal stability of the ammonates, appear to increase with increase in the atomic volume of the central metal atom. The heats of formation of some seventy-six ammonates have been calculated.

Roberts (66) has called attention to the already generally known fact that no explosion hazard is involved in the use of mercury in contact with liquid or gaseous ammonia enclosed in glass containers.

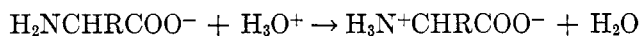
IV. ORGANIC REACTIONS

A. Ammonolysis

An investigation of the ammonolysis of the α -halogen acids,— α -bromoacetic, α -bromopropionic, α -bromobutyric, α -bromovaleric, and α -bromoisovaleric,—by liquid ammonia at 25°C . has shown that the formation of secondary and tertiary ammonolysis products is markedly inhibited by the presence of ammonium salts (27, 73). This behavior has been attributed to the fact that a relatively high concentration of ammonium ion may favor the reaction

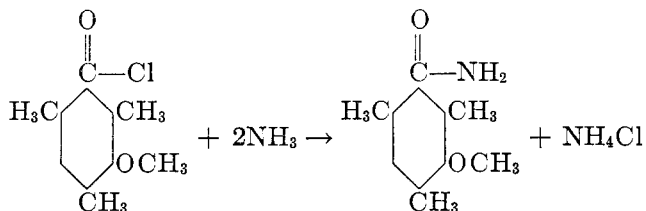


which is strictly analogous to the reaction in aqueous ammonia in which the pH influences the formation of the zwitter ion, $\text{H}_3\text{N}^+\text{CHRCOO}^-$, in a similar reaction.



In both cases, the solvated proton is believed to shield effectively the pair of electrons of the nitrogen atom. Comparative studies were made on the yield of glycine obtained using various ratios of ammonia to chloroacetic acid for both liquid and aqueous ammonia. At -33.5°C ., chloroacetic acid is not appreciably ammonolyzed by liquid ammonia over a period of 24 hr., while at 30°C . nearly complete ammonolysis was accomplished in about 5 hr. and only 1 hr. was required for complete ammonolysis at 60°C . It was further shown that the longer chain acids were ammonolyzed most readily, and it was concluded that liquid ammonia is an excellent ammonolyzing medium for the less reactive α -halogenated acids of high molecular weight.

3-Methoxymesitamide has been prepared by the interaction of the corresponding acid chloride with liquid ammonia at its boiling point (35).

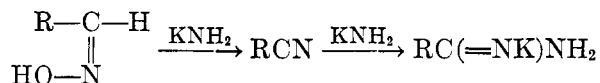


The reaction between bis(chloroacetyl)piperazine and liquid ammonia (56) has been shown to result in the formation of glycinamide and diketopiperazine.

The diamide of norcamphoric acid has been formed by the ammonolysis (by liquid ammonia) of the corresponding dimethyl ester (28). A detailed procedure for the preparation of appreciable quantities of lactamide in 70 per cent yield by the ammonolysis of ethyl lactate by liquid ammonia at room temperature has been described (50). By reaction with liquid ammonia at its boiling point, racemic α -hydroxy- β , β -dimethyl- γ -butyrolactone has been converted to racemic α , γ -dihydroxy- β , β -dimethylbutyramide (62). Starting with the corresponding (-)-lactone, (+)- α , γ -dihydroxy- β , β -dimethylbutyramide was prepared in a similar manner. At 25°C. also, the (-)-lactone is converted quantitatively to the (+)-amide (38).

B. Reactions of alkali amides

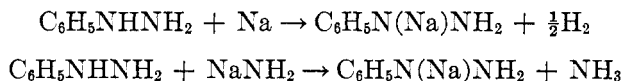
The behavior of certain *syn*- and *anti*-aldoximes and their derivatives toward potassium amide in liquid ammonia solutions has been described by Vermillion and Hauser (83). At room temperature, potassium amide and *anti*-4-methoxybenzaloxime have been found to yield both the amidine and the corresponding amide by a reaction which is believed to be represented by the equation



At -33.5°C., potassium amide reacts with *syn*- and *anti*-4-methoxybenzaloxime *O*-methyl ethers to form quantitative yields of 4-methoxybenzoxime. Under similar conditions, *syn*- and *anti*-benzaloxime acetates yield the corresponding *syn*- and *anti*-aldoximes. It has been shown that either cyclopentadiene or 1,4-pentadiene reacts with sodium amide in liquid ammonia to form a sodium salt (80). The action of sodium amide does not result in any rearrangement of the double bonds in the 1,4-diene. The reaction between sodium amide and alkyl bromides or chlorides in liquid ammonia at -50°C. has been shown to result in the formation of olefins and amines (72). Yields of amines of from 30 to 74 per cent of theory were obtained, using alkyl bromides of from four to twelve carbon atoms. Amines were formed only from halides having the halogen in the primary position, and the alkyl chlorides were found to exhibit a much slower reaction rate than the bromides and resulted in poorer yields of amines. The preparation of the monoamine of cellulose in 74 per cent yield by the interaction of cellulose nitrate and sodium amide, potassium amide, or sodium in liquid ammonia has been reported (68). Strain (77) has observed that carotenes react with potassium amide in liquid ammonia to form products having deep blue colors,

C. Reactions of solutions of metals

1. *Alkylation*: Audrieth and coworkers (4) have shown that phenylhydrazine reacts readily with alkali metals and alkali amides in liquid ammonia at its boiling point to form metal salts,



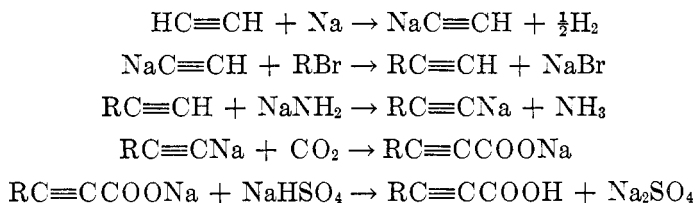
which react with alkyl halides to form unsymmetrical disubstituted α -alkyl arylhydrazines. An excess of sodium was found to cleave the N—N bond in primary and unsymmetrical disubstituted hydrazines.

An application of the methylation procedure, involving treatment with sodium in liquid ammonia at its boiling point followed by addition of methyl iodide (91), to the methylation of cornstarch and certain dextrans has been described (16). Using a similar procedure, Hassid, Joslyn, and McCready (41) have methylated an insoluble polysaccharide isolated from yeast. These workers imply an element of novelty in their use of anisole as a diluent. Actually, the use of such diluents in the alkylation procedure was first suggested by Muskat (86) and the use of anisole specifically has been described in detail by Hess and Lung (89).

2. *Reactions of alkali acetylides*: The reduction of dialkylacetylenes by sodium in liquid ammonia at its boiling point has been shown to lead, almost exclusively, to the formation of pure *trans*-olefins in good yields. By this method, the *trans* isomers of 3-hexene, 3-octene, 4-octene, 5-decene (18), 2-hexene, and 2-octene (19) have been prepared. The apparent general applicability and unidirectional character of these reactions, together with the fact that the corresponding *cis* isomers may be prepared by catalytic hydrogenation in the presence of Raney nickel, suggest that these methods will come to occupy a position of considerable importance among methods of olefin synthesis. Reduction by sodium in liquid ammonia has also been extended to the preparation of 1-alkenes from the mono-alkylacetylenes, and two acetylenic carbinols have been reduced similarly.

A study of the use of lithium acetylide in the preparation of amylicetylene (from $\text{LiC}\equiv\text{CH}$ and $n\text{-C}_5\text{H}_{11}\text{Br}$) and methylethyethynylcarbinol (from $\text{LiC}\equiv\text{CH}$ and $\text{C}_2\text{H}_5\text{COCH}_3$) in liquid ammonia at its boiling point (17) has shown that the yields obtained are comparable to those resulting from the use of sodium acetylide. Contrary to an earlier report, it is claimed that freshly prepared lithium acetylide does not contain lithium carbide but that, during isolation from liquid ammonia solutions, the acetylide decomposes to form an approximately equimolar mixture of acetylide and carbide. Lithium amylicetylide (from $n\text{-C}_5\text{H}_{11}\text{C}\equiv\text{CH}$ and LiNH_2 in liquid ammonia), on the other hand, was found to be stable both in ammonia and in the solid state. In connection with the preparation of 3-methyl-1-butyn-3-ol by the reaction between acetone and sodium acetylide in liquid ammonia, Taylor and Shenk (81) have found that the concurrent formation of 2,5-dimethyl-3-hexyn-2,5-diol is promoted by slow evaporation of the liquid ammonia and aging of the reaction mixture prior to hydrolysis. It had been shown previously (92; cf. 34) that diol formation may be suppressed by conducting the condensation of acetone and sodium acetylide at -50°C . in the presence of an excess of acetylene.

A recently developed method for the preparation of α -acetylenic acids may be summarized by the following equations (97):



The first three of the reactions indicated above were carried out consecutively in liquid ammonia solutions at temperatures below the boiling point. Carbonation and acidification were conducted in the presence of an inert diluent after removal of the solvent ammonia. By this procedure, ethyl-, propyl-, butyl-, and amyl-propionic acids were prepared.

3. *Other reduction reactions:* Further observations on the reduction of terphenyl by sodium in liquid ammonia (47) have shown that, in addition to dihydroterphenyl, there is also formed a hydrocarbon product in quantities which increase with increase in the quantity of sodium employed. The dihydroterphenyl, however, is not further hydrogenated by using an excess of sodium over and above that required for the formation of the dihydro derivative. Stoelzel (76) has reported that triphenylamine is unreactive toward solutions of sodium in liquid ammonia at -75°C . over periods up to 24 hr. Indole has been prepared in 50 per cent yield by the intramolecular condensation of *o*-formotoluide, using potassium or potassium amide in liquid ammonia as the condensation agent (82). Sodium amide was found to be unsatisfactory.

Brown and du Vigneaud (11) have prepared *S*-(β -amino- β -carboxyethyl)homocysteine by the reaction of methyl α -amino- β -chloropropionate hydrochloride with homocysteine, which was obtained by the reduction of *S*-benzylhomocysteine by sodium in liquid ammonia at its boiling point (21). Mesolanthionine (β -amino- β -carboxyethylsulfide) has been synthesized in a similar manner by the interaction of *l*-cysteine and methyl *dl*- α -amino- β -chloropropionate hydrochloride (30). The *d*-, *l*-, and *dl*-forms of lanthionine have also been prepared (12). Carter and coworkers (26) have reported the removal of the benzyl group from α -amino- β -benzylthiobutyric acid by reduction with sodium in liquid ammonia (21). The acid so obtained was treated with sodium in liquid ammonia, followed by addition of benzyl chloride to produce the original benzyl derivative. By means of a procedure described previously (24), asparthione (β -aspartylcysteinylglycine) has been prepared in 70 per cent yield by the reduction of carbobenzoxy- β -aspartyl-*S*-benzylcysteinylglycine (60). Sodium in liquid ammonia was employed as the reducing agent. The reduction product was isolated as its mercury and copper salts and finally as the tripeptide. Cystine has been prepared by the reduction (by sodium in liquid ammonia) of *S*-benzylcysteine resulting from the hydrolysis of the product obtained by treating silk with benzyl mercaptan in the presence of alkali (61). Brown and du Vigneaud (13) have reported that the physiological activity of biotin is not destroyed by exposure to the strong reducing action of sodium dissolved in liquid ammonia.

Applications of the liquid ammonia-sodium method for the determination of

total halogen in organic combination (59) to the analysis of β -dimethylaminoethyl bromide hydrobromide (1) and of products obtained by the interaction of toluene and chlorine (49) have been reported.

D. Other organic reactions

The report (36) that β -phenethylamine may be prepared in from 80 to 90 per cent yields by the catalytic hydrogenation of benzyl cyanide has been confirmed (25). The hydrogenation was carried out using liquid ammonia as the solvent and a Raney nickel catalyst. Crude glycerol, produced by the hydrogenolysis of dextrose, has been purified by crystallization from liquid ammonia (40; cf. 39). Crystallization was completed within 30 min. after seeding a 1:1 mixture of glycerol and liquid ammonia at -33.5°C .

Roberts and coworkers (67) have reported qualitative studies on the behavior of curare toward liquid ammonia at its boiling point and toward glycine in liquid ammonia. All of the products so obtained were found to be biologically active. Treatment of a number of polysaccharides with liquid ammonia has been shown to result in changes in optical rotation but only slight alterations in antigenicity (32).

V. PATENTS

With but few exceptions, the patents which have been issued during the past year are notable for absence of novelty. For the greater part, these patents are concerned with improvements or modifications of patents which have been discussed in earlier reviews in this series.

Liquid ammonia has been used as a solvent in a process for the separation of butadiene (8) from hydrocarbon mixtures resulting from cracking operations. A method for the production of crystalline reaction products of liquid ammonia and aldose sugars containing at least five carbon atoms has been described by Lorand (58). The reactions were effected under pressure at temperatures of 50° to 90°C . Aliphatic amines have been formed by the catalytic hydrogenation of nitriles in liquid ammonia solution (9). Additional patents relating to the production of melamine from dicyanodiamide (51, 79) and from guanidine or biguanidine (78) have been issued. Hill and Kropa (43) have described a process for the production of ketoximes by the interaction of ketones and hydroxylamine (or its salts) in liquid ammonia.

A process for the etherification of methylated sorbitol syrup has been described by Soltzberg (74). The material to be etherified is dissolved in liquid ammonia, treated with an alkali metal to form metal salts, followed by removal of the ammonia and addition of alkyl or aralkyl halides or alkyl sulfates in the presence of an inert hydrocarbon diluent. Similar procedures have been employed in the etherification of cellulose by reactions between alkali celluloses and benzyl chloride (63) or allyl halides (64).

Treatment of dispersions of cyanamide or of dicyanamide in liquid ammonia with, for example, ammonium acetate (45) or ammonium nitrate (46) has been used in the preparation of guanidine salts. Liquid ammonia has also been used

as a solvent in an extraction process (42) for the separation of salts such as guanidine nitrate from ammonia-insoluble salts of polybasic inorganic acids. Ammonium dithiocarbamate (44) has been produced by the interaction of carbon disulfide and liquid ammonia, and ammonium sulfamate (48) has been formed by the ammonolysis of alkali chlorosulfonates. Liquid ammonia solutions of the trihydrate of calcium nitrate have been employed in the pretreatment of gaseous ammonia used in the nitridation of steel (95). Ammonia has also been used as a solvent for ammonium nitrate in a process concerned with the incorporation of suitable sensitizers into ammonium nitrate for use as an explosive (10). Ammonium nitrite may be stored or transported with safety following treatment with liquid or gaseous ammonia at or below 0°C. under conditions such that the resulting solution has an ammonia content of approximately 30 per cent (96).

VI. GENERAL

Certain precautions to be observed in the handling of anhydrous liquid ammonia, together with information concerning suitable containers, have been discussed (65). It is of interest to note that a review of American literature relating to "the chemistry of solutions in liquid ammonia" has been published in the Russian language by Shatenshtein (71).

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