AMMONOLYSIS IN LIQUID AMMONIA[1]

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I. INTRODUCTION

The term "ammonolysis" (75, 88) is used to designate those reactions of ammonia which are analogous to the familiar hydrolysis reactions of water. Thus an ammonolytic reaction is one of double decomposition in which ammonia is a reactant. Since substances having acid and basic characteristics are formed in such reactions, ammonolytic reactions constitute one type of protolytic equilibria. Numerous ammonolytic reactions are known, and certain of them are widely used in preparative chemistry. To one interested in reactions in liquid ammonia the possibility of ammonolysis is always present and must be taken into consideration at all times. In many cases ammonolytic reactions may be turned to good advantage; in others, ammonolysis acts to prevent one from realizing a desired preparation. Further, the study of certain ammonolytic reactions offers considerable promise in providing a better understanding of the physical-chemical characteristics of liquid ammonia.

One is naturally interested in knowing wherein ammonolysis differs from hydrolysis. Ammonolysis, like hydrolysis, is dependent upon the degree of auto-ionization of the solvent,

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

The character of many reactions in liquid ammonia as well as the low specific conductance of this solvent indicate that the ion-product of ammonia,

$$K = [NH_4^+]\,[NH_2^-]$$

is much less than the corresponding constant for water. However, the quantitative measurement of this constant is difficult. Because of the difficulty of purifying ammonia, calculations based on the specific conductance and the independently determined conductivities of the ammonium and amide ions give a value for K that is much too large. The best value for this constant,

$$K = 1.9 \times 10^{-33}\ (-50°\text{C.})$$

is that of Pleskov and Monoszon (223), who based their calculations on the E.M.F. of acid–base cells of the type,

$$\begin{array}{r|c|c|c|l} \text{Pt, H}_2 & \text{NH}_4\text{NO}_3 & \text{KNO}_3 & \text{KNH}_2 & \text{Pt, H}_2 \\ & 0.1\ \text{normal} & \text{saturated} & c & \end{array}$$

The stability of solutions of metals in liquid ammonia and the lack of ammonolysis of aluminum cyanide solutions (9) are undoubtedly due to the low self-ionization of liquid ammonia.

Many hydrolytic reactions, especially those of esters, are known to be subject to acid–base catalysis (39, 40, 49, 50, 67, 111, 127, 146). Several years ago, Franklin and coworkers (26, 47, 86, 264) performed a number of experiments which indicated that ammonolytic reactions were acid-catalyzed. More recently the ammonolysis of a number of esters has been studied in a quantitative manner (5, 56, 240–1, 243–4, 246, 251). At this point one would expect to find considerable difference between the behavior of water and ammonia because of the inherent greater basicity of the latter (7, 109, 110, 242). Owing to the more pronounced "leveling effect" of ammonia upon acidity, it is impossible to obtain as strongly acid solutions in ammonia as in water. In other words, the acid strength and, consequently, the catalytic activity of the ammonium ion is less than that of the hydronium ion.

Although ammonolytic reactions have been extensively studied, comparatively little work has been directed toward establishing definitely the influence of conditions upon the nature and extent of a reaction. The techniques commonly used for studying reactions in liquid ammonia may be divided into two major classes: (*1*) reactions at low temperatures (up to −33°C.) and at atmospheric pressure or less and (*2*) reactions under pressure: (*a*) in sealed glass tubes (temperatures up to about 80°C.) and (*b*) in autoclaves (temperatures up to and beyond the critical temperature, 132°C., of ammonia) (*cf.* reference 58 for bibliography). Since the results of any study on ammonolysis will vary, depending upon the particular technique used, the experimental conditions are given in this review wherever they are known.

The extent to which ammonolysis will proceed in any instance will depend upon (*1*) the ion-product of liquid ammonia, (*2*) the relative strengths of the acid and base concerned, (*3*) the ratio of ammonia to substance ammonolyzed, and (*4*) the solubilities of the substance undergoing ammonolysis and of the ammonolytic products. Since the ion-product of ammonia is undoubtedly increased with rise in temperature (7), the degree of ammonolysis will also depend upon the temperature. Finally, ammonolysis may be brought to completion by removing one of the substances formed by the reaction. Thus, providing the solubility relationships are suitable, simple extraction of a soluble product with liquid ammonia will bring the reaction to completion, or ammonium ion may be destroyed by adding amide ion or a soluble metal

$$NH_4^+ + NH_2^- \rightarrow 2NH_3$$

$$NH_4^+ + e^- \rightarrow NH_3 + \tfrac{1}{2}H_2$$

and amide ion may be destroyed by adding ammonium ion.

Like water, many of the alcohols enter into solvolytic reactions. Similarly, the simple primary and secondary amines exhibit reactions of *aminolysis* (*cf.* 59). For any given substance, the extent of aminolysis is less than that of ammonolysis. Consequently, in many preparations where the use of liquid ammonia is unsuited because of extensive ammonolysis, the difficulties may be overcome (provided the solubility relationships are favorable) by using a simple amine such as ethylamine (156, 161, 165).

II. Ammonolysis of Inorganic Compounds

A. INTRODUCTION

Although there have been numerous studies on the reactions of ammonia with inorganic substances, particularly halides, much of this work has not been conducted in such a manner as to enable one to state definitely whether or not ammonolysis has taken place. This situation arises because many investigators have failed to distinguish between *ammonolysis* and *ammonation*. The literature of chemistry contains many references to "ammonates" prepared by treating a halide, either in the pure state or in solution in an inert solvent, with ammonia. The solid obtained in such cases is not of necessity an ammonate but may be a mixture of an amide, imide, nitride, or ammonobasic salt and ammonium halide. To illustrate, on treatment with ammonia germanic iodide gains in weight by an amount corresponding to 6 NH_3. On the basis of this fact *alone*, one may represent the resulting solid equally well as $GeI_4 \cdot 6NH_3$ or $Ge(NH)_2 + 4NH_4I$. In several cases, the extraction of such mixtures with liquid ammonia has demonstrated the existence of ammonolytic products (34, 137, 140, 236, 259, 270).

B. HYDRIDES

The alkali-metal hydrides react with liquid ammonia, yielding hydrogen and metal amides (229; *cf.* 3).

$$MH + NH_3 \rightarrow MNH_2 + H_2$$

With sodium hydride, the reaction proceeds slowly at −40°C. and rapidly at 20°C. The volatile hydrides of the fourth and fifth groups of the periodic table (carbon, silicon, germanium, phosphorus, arsenic) are unreactive toward ammonia, while those of the sixth and seventh groups (oxygen, sulfur, selenium, fluorine, chlorine, bromine, iodine) form ammonium salts. The alkali-metal derivatives of most of these hydrides [$NaGeH_3$, NaGe (159; *cf.* 61), $Na(K)PH_2$(133, 136; *cf.* 120), $Na(K)AsH_2$, CH_3AsHK (139), Na_4Ge_x (x = 1 or greater), M_4Sn_x, M_4Pb_x, M_3P_x, M_3As_x, M_3Sb_x, M_3Bi_x, M_2S_x, M_2Se_x, and M_2Te_x (see reference 60, for primary references)] are not ammonolyzed to any considerable extent. On the other hand, phosphonium iodide is vigorously ammonolyzed at −33°C., forming phosphine (57). (For the behavior of M_2O consult section II C and for that of MCH_3 consult section IV A.)

Anhydrous hydrazine (93) and hydroxylamine (*cf.* 4) may be readily prepared by the ammonolysis of the corresponding sulfates,

$$N_2H_4 \cdot H_2SO_4 + 2NH_3 \rightarrow N_2H_4 + (NH_4)_2SO_4$$

The ammonate of hydrazine azide, $2N_2H_5N_3 \cdot NH_3$, undergoes ammonolysis in liquid ammonia to an extent that varies directly with the temperature and with the concentration of ammonia (118).

$$2N_2H_5N_3 \cdot NH_3 + NH_3 \rightleftharpoons 2NH_4N_3 + 2N_2H_4 \quad \text{(above } -9°\text{C.)}$$

$$2N_2H_5N_3 \cdot NH_3 + 5NH_3 \rightleftharpoons 2(NH_4N_3 \cdot 2NH_3) + 2N_2H_4 \quad \text{(below } -9°\text{C.)}$$

C. OXIDES

In general, the oxides of metals are unreactive toward liquid ammonia. However, the monoxides of the alkali metals are completely ammonolyzed (for primary references *cf.* reference 21).

$$M_2O + NH_3 \rightarrow MNH_2 + MOH$$

In contrast to the monoxides, the alkali peroxides M_2O_2 and M_2O_4 are not ammonolyzed.

D. HALIDES

Observations relative to the ammonolysis of halides are assembled in table 1. Although the data are not complete, certain generalities are

TABLE 1

Ammonolysis of halides

GROUP	COMPOUNDS TREATED WITH AMMONIA	SUBSTANCES FORMED	NOTES	REFERENCES
Group IB:				
Gold	AuCl	$AuCl \cdot 12NH_3$(−28°C.)	At 20°C. $AuCl \cdot 3NH_3$ (white powder) forms	(189)
	AuBr	$AuBr \cdot 2NH_3$(+18°C.)	White powder	(189)
	AuI	$AuI \cdot 6NH_3$(−28°C.)	At 20°C. $AuI \cdot NH_3$ (white powder) forms	(189)
Group IIB:				
Beryllium	BeX_2(X = Cl, Br, I, CN)		Probably somewhat ammonolyzed; both soluble and insoluble ammonobasic salts known	(12)
Magnesium	$MgCl_2 \cdot 2H_2O$	$MgCl_2 \cdot 6NH_3$(20°C.)	$MgCl_2$ results on heating (at 290–320°C.) for 3 hr.	(192)
Mercury	$HgCl_2$	$Hg(NH_2)Cl$	White precipitate; ammonolysis arrested by NH_4Cl, promoted by $NaNH_2$	(78, 82; *cf.* 81)
	$HgBr_2$	Hg_2NBr	Yellow precipitate, soluble in NH_4Br; formation promoted by KNH_2	(68, 77)
	HgI_2	Hg_2NI	Yellow precipitate, soluble in NH_4I; formation promoted by KNH_2	(76)
Group IIIB:				
Boron	BF_3		Appreciable ammonolysis (−33°C.)	(157)
			Aminolysis in $C_2H_5NH_2$ brought to completion by Li(−33°C.)	(158)
	BCl_3	$B(NH_2)_3$(−23°, 0°C.)	Amide insoluble	(134)
	BBr_3	$B_2(NH)_3$(−10°, +20°C.)	Imide insoluble	(135)
	$B_2S_3 \cdot H_2S$	$B_2S_3 \cdot 6NH_3$	Yellow crystals; ammonolysis to $B_2(NH)_3$ on heating to 115–120°C.	(260)

Aluminum	AlI_3	$AlI_3\cdot 20NH_3$(−33°C.) $AlI_3\cdot 6NH_3$(8–13°C.)	Ammonolysis by KNH_2 to soluble and insoluble ammonobasic salts	(83; *cf.* 11, 80)
Gallium	$GaBr_3$	$GaBr_3\cdot 6NH_3$(−33°C.)	No ammonolysis	(138)
	GaI_3	$GaI_3\cdot 6NH_3$(−33°C.)	No ammonolysis	(138)
Group IIIA:				
Cerium	CeI_3	Soluble	KNH_2 gives ammonobasic salts	(13)
Samarium	$SmCl_3$	$SmCl_3\cdot 13NH_3$(−78°C.)	Between −78° and 280°C., ammonates with 11.5, 8, 5, 4, $2\frac{2}{3}$, 2, and 1 NH_3 are formed	(147)
Group IVB:				
Carbon	CCl_4		No reaction at ordinary temperatures	
		$HNC(NH_2)_2$	140°C.; high pressures	(258)
Silicon	$SiCl_4$	$Si(NH_2)_4$(−50° to 0°C.)	Changes to $Si(NH)_2$ above 0°C.	(271)
		$HNSi(NH_2)_2$ (low temperatures)	Changes to $Si(NH)_2$(0–110°C.)	(261)
		$Si(NH)_2$(20°C.)	Benzene solution; mixture with NH_4Cl not separated	(184)
	$SiBr_4$		Ammonolysis observed (20°C.)	(91)
	$SiSCl_2$	$Si(NH)_2$		(31)
	SiS_2	$Si(NH)_2$		(31)
	SiH_3Cl	$(SiH_3)_3N$	Gaseous NH_3(20°C.); some decomposition to SiH_4 and $[SiH_2(NH)]_x$ with excess NH_3	(260a)
	SiH_2Cl_2	$[SiH_2(NH)]_x$	Gaseous NH_3(20°C.)	(260a)
	$SiHCl_3$	$[SiH(NH)]_2NH$(−110°, 20°C.)	Forms HSiN on heating to 450°C.	(260b)
	Si_2Cl_6	$[Si(NH)NH_2]_2$ (low temperatures)	Forms $Si_2N_3H_3$ at −10°C.	(237)
Germanium	$GeCl_4$	$Ge(NH)_2$(−80°C.)	Same product in ether solution	(232, 236, 270)
			Aminolysis by $C_2H_5NH_2$, $(C_2H_5)_2NH$, $C_6H_5NH_2$, etc.	(270a)
	$GeHCl_3$	$GeHCl_3\cdot 2NH_3$	GeNH formed on further treatment with NH_3	(51)
	GeI_4	$Ge(NH)_2$(−33°C.)	Imide obtained by extraction with liquid NH_3; same reaction in CCl_4(20°C.)	(140)
			Aminolysis by $C_2H_5NH_2$ and $(C_2H_5)_2NH$	(140)

TABLE 1—*Concluded*

GROUP	COMPOUNDS TREATED WITH AMMONIA	SUBSTANCES FORMED	NOTES	REFERENCES
	GeI_2	$GeNH$(−33°C.)	NH_3 gas diluted with N_2 to avoid $2Ge^{++} \rightarrow Ge^{+4} + Ge$; GeNH obtained by extraction with NH_3	(137)
	GeS_2		Not ammonolyzed (−33°C.)	(141)
	GeS		Not ammonolyzed (−33°C.)	(141)
Tin	$SnCl_4$	$2Sn(NH_2)_3Cl \cdot NH_4Cl$(0°C.)	Washing with NH_3; after heating to 100°C. and again extracting $Sn(NH_2)_3Cl$ obtained	(234)
	SnI_4		Ammonobasic salt (probably) (20°C.); ammonolysis prevented by NH_4I	(70)
Lead	$PbCl_4 \cdot 4NH_3$		Apparently no ammonolysis (20°C.)	(57)
	$(NH_4)_2PbCl_6$		Complex ammonobasic salt by washing with NH_3	(234)
	PbI_2	$PbNH \cdot Pb(NH_2)I$ (probably)	Slight ammonolysis, prevented by NH_4I and promoted by KNH_2	(79)
Group IVA:				
Titanium	$TiCl_4$	$TiNCl \cdot xNH_3$	Washed with NH_3	(228; *cf.* 30, 257)
	$TiCl_3$	$TiCl_3 \cdot 6NH_3$(−78°C.)	White compound	(231)
	$TiCl_2$	$TiCl_2 \cdot 4NH_3$(−78°C.)	Pearl-gray powder	(231)
	$TiBr_4$	$TiNBr \cdot xNH_3$	Yellow solid, obtained by washing with NH_3	(90, 228)
		$2Ti(NH_2)_4 \cdot TiBr_4 \cdot 8NH_3$		(230)
Zirconium	$ZrBr_4$	$3Zr(NH)_2 \cdot 7NH_4Br \cdot xNH_3$ (0–20°C.)	Ammonolysis prevented by excess NH_4Br; further ammonolysis to $Zr(NH)_2$ in presence K or KNH_2	(34, 279; *cf.* 284)
	ZrI_4		Ammonolysis indicated by extraction of NH_4I	(259)
Group VB:				
Nitrogen	NOCl	$NO(NH_2)$ (temperature of liquid air)	Unstable red liquid	(233)

Phosphorus	PCl_5	$P(NH)_2NH_2$(−50°C.)	Forms PN_2H at 400-450°C.	(199, 200)
	$PNCl_2$	$PN(NH_2)_2$(−70°C.?)	Forms PN_2H at 220°C.	(25)
	$(PNCl_2)_3$	$(PN_3H_4)_3$		(201)
	PCl_3	$P(NH_2)_3 + P_2(NH)_3$		(135)
		$P(NH_2)_3$	Forms P_4N_6 at 550°C.	(202)
	PBr_3	$P(NH_2)_3$(−70°C.)	Forms $P_2(NH)_3$ at 0°C. and PN at 250-300°C.	(122)
	PI_3	$P(NH_2)_3$(−65°C.)		(122)
Arsenic	AsX_3(X = Cl, Br, I)	$As(NH_2)_3$(−40° to −30°C.)	Insoluble; forms $As_2(NH)_3$(0-60°C.) and AsN(250°C.)	(121)
Antimony	$SbCl_3$	SbN	Yellow to orange solid; obtained by extraction with NH_3	(235)
Bismuth	$BiCl_3$	$BiCl_3 \cdot 12.5NH_3$(−78°C.)	No ammonolysis on washing; ammonates with 1(0°C.) and 0.5 NH_3	(238)
	$BiBr_3$	$BiBr_3 \cdot 18.5NH_3$(−78°C.)	Ammonates with 14(0°C.), 3, 1.5, and 0.5 NH_3	(238)
	BiI_3	$BiI_3 \cdot 22NH_3$(−78°C.)	Ammonates with 18, 16, 12.5 (0°C.), 12, 8, 4, 3, 2 NH_3	(238)
Group VA:				
Vanadium	$VOCl_3$	$VO(NH_2)_3$(−80°C.)	Yellow solid	(213)
	VCl_3, VBr_3	$V(NH_3)_6X_3$(−33°C.)		(189a)
Tantalum	$TaCl_5$	$Ta(NH_2)_2Cl_3 \cdot 3NH_3$	Below 0°C. ammonates of $TaCl_5$ are formed	(254; *cf.* 197-8)
Group VIIB:				
Tellurium	$TeBr_4$	Te_3N_4(−80°C.)	Yellow solid	(268)
Group VIA:				
Chromium	$CrCl_3$	$[Cr(NH_3)_6]Cl_3 +$ $[Cr(NH_3)_5Cl]Cl_2$	Apparently no ammonolysis	(45a)
Molybdenum	$MoCl_5$	$Mo(NH)_2NH_2$ or $Mo(NH_2)_4Cl$		(10)
	$MoCl_3$, $MoCl_2$		Ammonolysis and oxidation	(10)
Tungsten	WCl_6		Ammonolysis	(10)
	WCl_5, WCl_2, WBr_2		Ammonolysis and oxidation	(10)
Uranium	UCl_4	$UCl_4 \cdot 12NH_3$(−78°C.)	Ammonates with 10, 6, 5, 4, and 3 NH_3	(253)
	UO_2Cl_2	$UO_2Cl_2 \cdot 10NH_3$(−78°C.)	Ammonates with 5, 4, 3, 2, and 1 NH_3	(253)

evident. Essentially, the conduct of halides (and oxyhalides) toward ammonia resembles their conduct toward water and ranges all the way from complete ammonolysis, in the case of the covalent halides, to no ammonolysis at all in the case of true salts. The principal difference is that many salts, such as those of bismuth, which are noticeably hydrolyzed, are apparently not ammonolyzed. In any particular family, ammonolysis decreases in passing from the elements of low atomic weight to those of higher atomic weight. This relationship is evident in Group III, where the boron halides are completely ammonolyzed, aluminum iodide slightly, and the gallium halides not at all; in Group IVB, where the silicon and germanium halides are completely ammonolyzed,[2] while stannic and plumbic halides form ammonobasic salts; in Group IVA, where titanium and zirconium halides form ammonobasic salts, while thorium halides appear not to be ammonolyzed; and in Group VB where phosphorus, arsenic, and antimony are completely ammonolyzed while bismuth is little if any ammonolyzed. Mercuric salts are exceptional in the ease with which they are ammonolyzed.

While samaric chloride forms ammonates, samarous chloride is oxidized by ammonia with the formation of ammonobasic samaric chloride (147).

$$2SmCl_2 + 2NH_3 \rightarrow 2Sm(NH_2)Cl_2 + H_2$$

$$Sm(NH_2)Cl_2 + 2NH_3 \rightarrow Sm(NH_2)_2Cl + NH_4Cl$$

Mono- and di-chlorogermane react with ammonia, but the reactions are not ammonolytic in character (51).

$$3xGeH_3Cl + 3xNH_3 \rightarrow 3xNH_4Cl + xGeH_4 + 2(GeH)_x \quad (-78^\circ \text{ to } -50^\circ\text{C.})$$

$$GeH_2Cl_2 + 2NH_3 \rightarrow Ge + 2NH_4Cl \quad (-27^\circ\text{C.})$$

E. SULFIDES

The behavior of sulfides toward liquid ammonia has been little investigated. Data relative to the ammonolysis of boron and silicon sulfides are included in table 1.

F. SALTS OF OXY ACIDS

Although many reactions of salts of oxygen acids have been studied in liquid ammonia, ammonolysis has been reported in only two instances, lead nitrate (79) and bismuth nitrate (89).

An ammonolytic reaction of a somewhat different type is that between various metal nitrates and the alkali amides in liquid ammonia (87).

[2] The lack of reactivity in the case of the carbon halides is unique and may be attributed to the fact that carbon is here exerting its maximum covalence, so that ammonation as a preliminary step to ammonolysis is not possible (248).

$$KNO_3 + 2KNH_2 \rightarrow KN_3 + 3KOH + NH_3$$

The above reaction takes place at 80–90°C. but better yields (up to 75 per cent), in a shorter time, result from operating at a higher temperature (130–140°C.; at 200°C. much of the azide decomposes). Other nitrates and amides likewise yield azides: sodium nitrate and sodium amide, 16 per cent; lead nitrate and excess potassium amide, 80 per cent.

G. SALTS OF AMMONO ACIDS AND AMPHOTERIC AMMONO BASES

Because the ammonolytic power of liquid ammonia is weak compared to the hydrolytic power of water, many salts of very weak acids are perfectly stable in ammonia. However, salts of extremely weak acids are ammonolyzed. Because of this tendency it is practically impossible to prepare pure specimens of potassium ammonosilicate (14, 91) and potassium ammonozirconate (34). During the washing process to remove impurities, the potassium amide formed by ammonolysis

$$Zr(NK)_2 \cdot 2NH_3 \rightarrow Zr(NH)_2 + 2KNH_2$$

is continuously removed. Ammonolysis may well be a contributing factor to the difficulty of isolating potassium ammonotitanate in pure form (90).

Evidence of the low ammonolytic power of liquid ammonia is afforded by the marked stability of salts of amphoteric bases in this solvent.

$$Zn(NH_2)_2 + 2KNH_2 \rightarrow Zn(NHK)_2 \cdot 2NH_3$$

Of the many compounds of this type (Be, Mg, Zn, Cd, Ca, Sr, Ba, La, Ce, Mo, W, Mn, Ni, Cu^{I}, Ag, Al, Ga, Tl, Sn^{II}, Sn^{IV}, and Pb^{II}; for bibliography, *cf.* references 15 and 19), only one, potassium ammonosodiate (280), has been found to be extensively ammonolyzed.

H. MISCELLANEOUS

The weak ammonolytic power of liquid ammonia is utilized to good advantage in the purification of alkali cyanides (101) and in the preparation of calcium (73) and aluminum cyanides (9).

III. AMMONOLYSIS OF ORGANIC COMPOUNDS

A. INTRODUCTION

When one surveys the field of ammonolytic reactions in organic chemistry, one is impressed by the wide variety of substances which undergo this type of reaction. Halogen (in alkyl and aryl halides, as well as acid halides), hydroxyl (in hydroxynitriles and carbohydrates), oxygen (in aldehydes, ketones, and even certain acids and their derivatives), and sulfur may be replaced by amino or imino groups through reactions of ammonolysis. Further, Schiff bases, esters, acyl and sulfonyl derivatives, lactones, and other similar compounds are all capable of ammonolysis. It is not difficult to envision a time in the near future when liquid ammonia reactions will have become standard practices in the organic laboratory. This will result (*1*) because liquid ammonia can bring about reactions that are not possible with aqueous or non-aqueous solutions of ammonia; (*2*) because there are inherent differences in the extent and type of reactions taking place in solutions of ammonia and in the anhydrous solvent; and (*3*) because the ease of varying conditions and thus varying both the extent and type of reaction give further variety when using liquid ammonia.

Despite the large number of investigations on the ammonolysis of organic substances in liquid ammonia, there is still need for considerable work. At present the available data are not sufficient to enable one to state definitely just what kinds of substances may be ammonolyzed, and what may not. Although some comparative studies between the action of solutions of ammonia and of the anhydrous material have been made, more information is needed to establish definitely the differences in the reactivity of the two systems. Likewise there is need for a more careful evaluation of the influence of reacting conditions (temperature, catalysis, etc.) upon ammonolysis. The catalytic effect of ammonium salts (acid catalysis) upon many ammonolytic reactions has been clearly established. More investigations in this fascinating area will be very valuable. In particular, it is desirable to establish whether or not the alkali amides exert a catalytic effect (basic catalysis) similar to that of acids.

In the discussion following, comparison is made in several cases between reactions involving liquid ammonia and those involving either aqueous or non-aqueous solutions of ammonia. For a detailed discussion of the behavior of the latter type of reactions, the reader is referred to other compilations, particularly those of Groggins (102–6).

B. HALOGEN COMPOUNDS (EXCLUSIVE OF ACYL HALIDES)

1. *Alkyl halides*

When the alkyl halides (chlorides, bromides, iodides) are heated to 100°C., in sealed tubes, with alcoholic ammonia, a mixture of the hydrohalides of primary, secondary, and tertiary amines, as well as the quaternary ammonium compounds results. The alkyl halides are not as reactive toward liquid ammonia as might be expected, and therefore have been used on numerous occasions for alkylations

$$\mathrm{RONa} + \mathrm{R'X} \rightarrow \mathrm{ROR'} + \mathrm{NaX} \quad (66)$$

$$\mathrm{RC{\equiv}CNa} + \mathrm{R'X} \rightarrow \mathrm{RC{\equiv}CR'} + \mathrm{NaX} \quad (64)$$

in liquid ammonia and for the production of olefins (18). While on certain occasions the methyl halides have been used successfully for alkylations (129, 185, 203; *cf.* 206), this practice is not to be recommended, since they are readily converted into the tetramethylammonium salts (44, 276).

$$4CH_3X + 4NH_3 \rightarrow 3NH_4X + (CH_3)_4NX$$

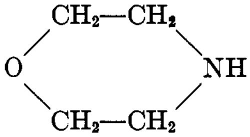
Ethyl iodide reacts very little with liquid ammonia (-33°C.), while ethyl bromide and *n*-butyl bromide do not react (276). However, at room temperature ethyl bromide and ethyl iodide react completely in 24 hr. At the end of 4 hr., there are formed 28 per cent of primary amine, some secondary amine, and a small amount of tertiary amine. Ethyl chloride under similar conditions shows no reaction in 1 hr. and very little in 24 hr. (220; *cf.* 258). Tetrakis(bromomethyl)methane, $C(CH_2Br)_4$, gives only small amounts of the corresponding amine, $C(CH_2NH_2)_4$. The same halide on heating with alcoholic ammonia (180–190°C. for 10 hr.) gives a yield of 35 per cent of the amine (100). Braun (35) has shown that *n*-amyl, *n*-octyl, and *n*-dodecyl bromides are ammonolyzed at room temperature to give a mixture of the primary and secondary amines, the yield of primary amine increasing with increasing molecular weight:

BROMIDE USED	YIELD OF PRIMARY AMINE	YIELD OF SECONDARY AMINE
	per cent	*per cent*
n-Amyl bromide	10	80
n-Octyl bromide	45	43
n-Dodecyl bromide	90	Little

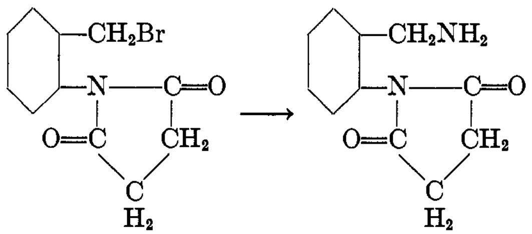
On heating equal volumes of dodecyl chloride and liquid ammonia for 72–90 hr. at 75–80°C., Wibaut and coworkers (277) obtained 28 to 33 per cent of dodecylamine and 27 to 36 per cent of didodecylamine. After 170 hr. at 45°C. about 35 per cent of the chloride had reacted and, after 75 hr. at 75°C., 75 per cent had reacted.

2. Substituted alkyl halides

Morpholine



is prepared in 80 per cent yield by treating a benzene solution of β,β′-dichlorodiethyl ether with liquid ammonia in an autoclave at 50°C. for 24 hr. (42). *N*-(α-bromo-*o*-tolyl)succinimide is ammonolyzed by liquid ammonia at room temperature over a period of 6 hr. (255).



Benzyl chloride reacts only slightly with liquid ammonia (−33°C.) (276). The ammonolysis of α-phenylethyl chloride in a sealed tube over a period of 6 weeks at room temperature results in the formation of the corresponding primary amine (119).

TABLE 2

Action of ammonia upon substituted alkyl halides

SUBSTITUTED ALKYL HALIDE	LIQUID AMMONIA			ALCOHOLIC AMMONIA		
	Primary	Secondary	Tertiary	Primary	Secondary	Tertiary
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Benzyl chloride	53	39		9	35	48
1-(Chloromethyl)naphthalene	72	20		11	38	47
9-(Chloromethyl)phenanthrene	70	26		29	25	43
β-Phenoxyethyl bromide	71			65		
N-(β-bromoethyl)-*N*-methylaniline	71	20		15	60	
N-(γ-chloropropyl)-*N*-methylaniline	65	20		18	70	
α,3,4-Trichloroquinaldine	72	22			90	
4-Anilino-α,3-dichloroquinaldine		20				
α,3-Dichloro-6-ethoxy-4-*p*-phenetidinoquinaldine	65	28		30	50	

In a general examination of the action of ammonia upon substituted alkyl halides, Braun (35) has compared the yields of primary, secondary, and tertiary amines obtained by using anhydrous liquid ammonia with those using alcoholic ammonia. Three generalizations are evident: (*1*) liquid ammonia is superior to alcoholic ammonia in the preparation of primary amines; (*2*) the greater the molecular weight of the halide, the larger the percentage of primary amine produced; and (*3*) when halogen is present on the ring as well as in a side chain, only that in the side chain is replaced. The experimental results are assembled in table 2.

The simple act of treating the *N*,*N'*-bis(chloroacetyl) derivative of 1,3-propanediamine, $ClCH_2CONH(CH_2)_3NHCOCH_2Cl$, with liquid ammonia and permitting the ammonia to evaporate yields the corresponding diamine (37). On standing for 40 hr. with liquid ammonia, the dihydrobromide of γ-bromopropylputrescine, $NH_2(CH_2)_4NH(CH_2)_3Br$, is converted to the corresponding amine, spermidine. The dihydrobromide of γ-bromopropylcadaverine on similar treatment yields *as*-homospermideine, $NH_2(CH_2)_5NH(CH_2)_3NH_2$. δ-Chlorobutylbenzamide yields small quantities of δ,δ'-dibenzamidodibutylamine, $[C_6H_5CONH(CH_2)_4]_2NH$, through a side reaction (38). Liquid ammonia rapidly acts upon ω,ω'-dibromo-*p*-ditolyl to yield the diamine (26 per cent) and a high molecular weight base, $NH_2CH_2C_6H_4C_6H_4CH_2[NHCH_2C_6H_4C_6H_4CH_2]_nNH_2$ (35).

3. Paraffin polyhalides

Whereas ethylene bromide is unreactive toward liquid ammonia (276; *cf.* 258), 1,3-propanediamine is readily prepared by simply adding 1,3-dibromopropane to liquid ammonia and allowing the latter to evaporate (37). At room temperature, 1,3-dibromopropane forms both 1,3-diaminopropane (45 to 50 per cent) and $NH_2(CH_2)_3NH(CH_2)_3NH_2$ (25 per cent). Similarly, 1,2-dichloro- or 1,2-dibromo-ethane yields ethylenediamine (65 per cent) and some diethylene triamine, while 1,11-dichloroundecane yields the diamine as the chief product. On the other hand, 1,4-dibromobutane and 1,5-dibromopentane yield bispyrrolidinium bromide and bispiperidinium bromide, respectively, as the principal products (36).

Benzotrichloride is ammonolyzed by liquid ammonia to benzonitrile in 75 per cent yield at room temperature. At 100°C., both benzonitrile and cyanphenine, $(C_6H_5CN)_3$, are formed (86).

A mixture of tri- and tetra-chloroethylenes is obtained by treating tetra- and penta-chloroethanes with an excess of anhydrous liquid or gaseous ammonia at a temperature not above 0°C. (224; *cf.* 258). 9,9-Dichlorofluorene and 1,2-dichlorodibiphenyleneëthane do not react with liquid ammonia at room temperature (221).

4. Aryl halides

While the ammonolysis (aqueous ammonia) of chlorobenzene constitutes an important industrial synthesis of aniline (107), practically no information is available on the behavior of the phenyl halides toward liquid ammonia except that iodobenzene does not react at −33°C. (276; *cf.* 258). 9-Phenyl- and 9-(α-naphthyl)-9-fluorylamines may be prepared readily by the ammonolysis of the corresponding 9-aryl-9-chlorofluorenes (at room temperature over a period of several hours). The ammonolysis of 9-methyl-9-bromofluorene is more difficult, but is accomplished by a mixture of toluene and liquid ammonia (at 75°C. for 20 hr.) (222).

5. *Heterocyclic halides*

2- and 3-aminoquinolines have been prepared in good yields by the treatment of the corresponding bromides with liquid ammonia (at 70°C. for several hours) in the presence of copper powder as a catalyst. In the absence of the copper catalyst, 2-bromoquinoline is only slowly ammonolyzed (131).

C. ALCOHOLS

Hydroxyacetonitrile is converted to aminoacetonitrile by a mixture of alcohol and liquid ammonia (1:3 by weight) (36 hr. at room temperature). Similarly, hydroxycapronitrile forms leucine nitrile with liquid ammonia (autoclave) (94; *cf.* 95). A 95 per cent yield of aminoacetonitrile is obtained by allowing a mixture of hydroxyacetonitrile and liquid ammonia to stand for 24 hr. at room temperature (188).

D. AMINES

One would expect the salt of an amine to be ammonolyzed (*1*) when the amine is less basic than ammonia or (*2*) when an insoluble compound is formed. Aniline and *p*-toluidine are liberated from their salts by simple solution in liquid ammonia (−33°C.) and evaporation of the latter. Under ideal conditions, as much as 87 per cent of the theoretical amounts of aniline may be recovered. The same treatment is partially effective with the more basic benzylamine but is ineffective with ethylamine, which is more basic than ammonia (250). Semicarbazide may be obtained in 93 per cent yield by the ammonolysis of its sulfate (4).

$$NH_2CON_2H_3 \cdot H_2SO_4 + 2NH_3 \rightarrow NH_2CON_2H_3 + (NH_4)_2SO_4$$

Liquid ammonia is not a suitable solvent for the preparation of alkali-metal salts of the aliphatic amines, since such substances are extensively ammonolyzed (225).

$$MNHR + NH_3 \rightarrow MNH_2 + H_2NR$$

Monoalkali-metal salts of aromatic amines (aniline, ethylaniline, *o*-toluidine, diphenylamine) have been prepared in liquid ammonia (142, 219, 275; *cf.* 172).

E. ALDEHYDES AND RELATED COMPOUNDS

1. *Aldehydes*

Familiar cases of ammonolysis not involving liquid ammonia are the formation of hexamethylenetetramine and hydrobenzamide from formaldehyde and benzaldehyde, respectively. The formation of aldehyde ammonia, $(CH_3CH{=}NH)_3 \cdot 3H_2O$, is essentially an ammonolysis. The behavior of several of the higher aliphatic aldehydes (propionaldehyde, butyraldehyde, isobutyraldehyde, and heptaldehyde) toward liquid ammonia has been studied (267). The results indicate partial ammonolysis and the formation of aquo-ammono aldols.

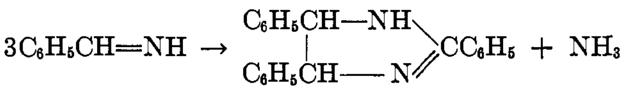
2. Acetals

The acetals are readily hydrolyzed by dilute acids but are insensitive toward bases. In contrast, the acetals are practically unaffected by liquid ammonia even over long periods of time and in the presence of ammonium salts. Dimethyl acetal yields only a trace of nitrogen-containing material after heating for 24 hr. at 130°C., either with or without ammonium chloride. Diethyl acetal gives a similar trace of nitrogenous material on standing at room temperature over a period of 3 years; it is unaffected by ammonium salts over a period of 2 years at room temperature and a period of 24 hr. at 130°C. Di-*n*-propyl and di-*n*-butyl acetals show no sign of reaction after heating for 12 hr. at 200°C. in the presence of ammonium chloride. Diethyl propional gives a trace of nitrogenous material after heating at 130°C. for 24 hr. (130).

3. Schiff bases

Anhydroformaldehyde aniline in contact with liquid ammonia (35 days) at room temperature undergoes no reaction. The addition of ammonium chloride to the solution is also without effect. On the other hand, this Schiff base is ammonolyzed to hexamethylenetetramine on heating to 150–180°C. for 12 hr. (267). Benzylideneaniline and benzylidene-*p*-toluidine are ammonolyzed (30 to 35 days) at room temperature to amarine (60 to 91 per cent) and to aniline and *p*-toluidine, respectively.

$$3C_6H_5CH{=}NC_6H_5 + 3NH_3 \rightarrow 3C_6H_5NH_2 + 3C_6H_5CH{=}NH$$

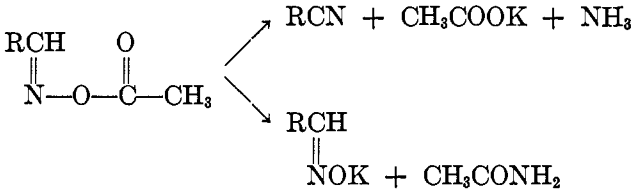


The same reactions may be accomplished in from 10 to 14 hr. by heating in the presence of ammonium chloride to 120–150°C. (264).

Benzylideneaniline, $C_6H_5CH{=}NC_6H_5$, and benzylidene-*p*-toluidine, $C_6H_5CH{=}NC_6H_4CH_3$, do not undergo simple ammonolysis with solutions of potassium amide but react in the sense of a Cannizzaro reaction (264).

$$2C_6H_5CH{=}NC_6H_5 + KNH_2 \rightarrow C_6H_5NH_2 + C_6H_5C(NCH_2C_6H_5)NKC_6H_5$$

Acetyl-α-benzaldoximes react with potassium amide in liquid ammonia (−33°C.) to form both the nitrile and the oxime:



The yields of the various products for several acetyl derivatives are assembled in table 3 (112).

Carbethoxy-α-benzaldoximes react similarly (113) (see table 4).

TABLE 3

Products obtained in the action of acetyl-α-benzaldoximes with potassium amide in liquid ammonia

ACETYL DERIVATIVE	YIELD			
	Nitrile	Acid	Oxime	Total
	per cent	*per cent*	*per cent*	*per cent*
4-Methoxy-	47	Trace	43	90
3-Nitro-	23	60 gum	8	31
2-Chloro-	80		9	89
Blank		[2 gum]	[88]	[88]
3,4-Methylenedioxy	58	2	39	99
Blank		[1]	[96]	[97]

TABLE 4

Products obtained in the action of carbethoxy-α-benzaldoximes with potassium amide in liquid ammonia

CARBETHOXY DERIVATIVE	YIELD		
	Nitrile	Oxime	Total
	per cent	*per cent*	*per cent*
3-Nitro-	60	3	63
4-Methoxy-	70	12	82

F. KETONES AND RELATED COMPOUNDS

1. *Ketones*

After heating acetophenone with twice its volume of liquid ammonia (at 180°C. for 4 hr.), a 3 per cent yield of acetophenone imine is obtained.

$$R_2CO + NH_3 \rightleftharpoons R_2C{=}NH + H_2O$$

By repeating the experiment in the presence of a large excess of ammonobasic aluminum chloride, the yield is increased to 30 per cent. Methyl *p*-tolyl ketone, fenchone, camphor, and benzophenone are ammonolyzed to the corresponding imines in the same manner (20 per cent yield in the last case). The behavior of benzil toward liquid ammonia is somewhat complex and is similar to the reaction with alcoholic ammonia. At room temperature, benzamide and imabenzil are slowly formed; on heating (at 200°C. for 2 hr.) 40 per cent of the ketone is converted into lophine, triphenylimidazole (265). The alkali and alkaline-earth amides do not promote the ammonolysis of ketones but instead form salts of the enolic forms (benzophenone forms $(C_6H_5)_2C(NH_2)ONa$ (266)). Benzophenone does not react with liquid ammonia at room temperature over a period of several weeks, whereas fluorenone gives a practically quantitative yield of fluorenone imide by the same treatment (221).

2. Ketals

Diethyl benzophenone ketal exhibits no reaction with a liquid ammonia solution of ammonium chloride over a period of 20 hr. at 120°C. (130).

3. Schiff bases

Fluorenone anil gives a 61 per cent yield of fluorenone imide when heated to 60°C. for 4 days in the presence of ammonium chloride. Heating for 20 hr. at 60°C. in the absence of the ammonium salt gives none of the imide (221).

G. CARBOHYDRATES AND THEIR DERIVATIVES

Glucose is quantitatively transformed into aminoglucose upon solution in liquid ammonia and evaporation of the solvent (204). Inulin is not ammonolyzed in liquid ammonia at −33°C. (24).

Liquid ammonia (−33°C.) dissolves the acetylated and benzoylated derivatives of any sugar compound in which the reducing group is suitably blocked (i.e., the methyl glycoside and 1,2-acetone compounds) without removing the acyl group. If, however, the acyl group is attached to the aldehyde (or ketonic) carbon atom, it is readily removed with the subsequent formation of aldehyde ammonia derivatives and amino sugars. At room temperature, liquid ammonia removes all acyl groups from the sugars (205). When cellobiose octaacetate is heated with liquid ammonia (at 55°C. for 48 hr.), 1-aminocellobiose is formed. Treatment of cellotriose with liquid ammonia likewise introduces nitrogen into the molecule (285, 286). 6-Mesyl-1,2-acetone-3,5-glucose is converted to 6-amino-1,2-acetone-3,5-glucose on standing in liquid ammonia (for 3 weeks at room temperature (116a)).

H. ACIDS AND THEIR DERIVATIVES (EXCLUSIVE OF ESTERS)

1. Acids and acid anhydrides

The preparation of acid amides by the action of liquid ammonia upon acids and acid anhydrides has been patented (209). Acetic and palmitic acids are cited as examples. The removal of water is accomplished by reacting in the presence of anhydrous salts or by evaporation with ammonia. Butyric anhydride is likewise cited as well as acetic anhydride. In the case of the latter, equimolecular quantities of ammonia and the anhydride (at 20°C. for several hours) produce acetamide and acetic acid which are separated by distillation, preferably under reduced pressure. No acetic acid is formed if two molecular proportions of ammonia are used.

When alkali bicarbonates are treated with anhydrous liquid ammonia or strong aqueous ammonia, alkali carbamates are formed (47a, 185a, 185b).

The preparation of sodium salts of amino acids by reaction of the acid with sodium in ammonia solution gives products (monosodium salts) which in the case of dicarboxylic acids, such as asparagine, are contaminated with small amounts of the monoamides (272).

2. Acid halides

Bartow and McFarland (8) first observed that acid chlorides, when dropped slowly into liquid ammonia, react vigorously with the formation of dense white fumes. Good yields of the amides of mono-, di-, and trichloroacetic and benzoic acids were obtained from the corresponding acid chlorides. Ethyl chlorocarbonate reacts vigorously, but the reaction products have not been determined. Difficulty was experienced in separating acetamide from the admixed ammonium chloride. Govaert (99) obtained acetamide in 88 per cent yield and benzamide in 98 per cent yield by adding solutions of the respective chlorides dropwise to liquid ammonia. 2-(4-Bromobenzoyl)benzoyl chloride is readily ammonolyzed (−33°C.) to 2-(4-bromobenzoyl)benzamide in 95 per cent yield (190). The ammonolysis of acid halides has been patented, and the reaction of butyryl chloride with liquid ammonia in a sealed tube has been cited as an example. Acetyl bromide and benzoyl chloride are given as further examples (209).

3. Acid amides and other mixed aquo-ammono acids

Acetamide is partially converted into acetamidine when heated with ammonium chloride in liquid ammonia (86). Urea on being heated with liquid ammonia (at 300°C. for 120 hr.) in the presence of ammonium chloride yields guanidine (19.6 per cent). Under the same conditions cyanuric acid yields both guanidine (16.6 per cent) and urea (49.3 per cent). These ammonolytic reactions do not go to completion but result in an equilibrium mixture of guanidine, urea, and probably carbonic acid. Biuret, ammeline, ammelide, guanylurea, and triuret give, when heated (at 300°C. for 65 hr.) with ammonium chloride, considerable quantities of both urea and guanidine. Upon similar treatment, thioammeline likewise yields guanidine (26).

Of recent years there has been considerable study of the synthesis of urea from carbon dioxide and ammonia. One step in this process involves the ammonolysis of carbamic acid (ammonium carbamate) to urea. It is claimed that by operating at high pressures and temperatures as much as 79 per cent conversion may be obtained or even 81 per cent if a considerable excess (280 per cent) of ammonia over the carbamate is used (32–3, 52–4, 108, 149, 150, 183).

One might well expect that the alkali amides (ammono bases) would promote the ammonolysis of such substances as acetamide and urea. The action of alkali amides at higher temperatures has never been investigated, but at room temperatures salts are formed without any evidence of ammonolysis. Alkali-metal salts of the following substances have been prepared: acetamide, phenylacetamide, benzamide, benzenesulfonamide, toluenesulfonamide, *m*- and *p*-methoxybenzenesulfonamides (92), urea (28, 92), carbamic acid, biuret, triuret (28), and cyanourea (29).

I. ESTERS

1. *Esters of carboxylic acids*

By dropping the esters into a large excess of liquid ammonia (−33°C.) and allowing the mixtures to stand until the evaporation of the ammonia, Bartow and McFarland (8) observed no action with the ethyl esters of formic, acetic, propionic, valeric, caprylic, and phenylacetic acids and partial reaction with ethyl pelargonate. By the same treatment, the ethyl esters of mono-, di-, and tri-chloroacetic acids gave quantitative yields of the corresponding amides. Similarly, the ethyl esters of cyanoacetic, dibromoacetic, and chloropropionic acids gave good yields of the amides, while the esters of mono- and tri-bromoacetic acids gave unidentified reaction products (apparently the bromine atoms are partially ammonolyzed). Ethyl oxalate formed the amide in good yield, and ethyl tartrate formed it in poor yield. The ethyl esters of carbonic, malonic (*cf.* 258), succinic, lactic, levulinic, citric, benzoylacetic, benzoic, phthalic, and salicylic acids and methyl benzoate exhibited no reaction. In order to determine the effect of temperature on the ammonolysis of esters, these investigators prepared sealed tubes containing the ester and ammonia (1:4 by volume). After standing 12 hr. at room temperature, ethyl acetate, pelargonate, carbonate, succinate, benzoylacetate, and benzoate had reacted no more than at −33°C., while ethyl malonate had formed malonamide. Similar standing at 60–70°C. produced no reaction with ethyl valerate, ethyl benzoylacetate, ethyl succinate, and ethyl benzoate, slight reaction with ethyl acetate, and somewhat more with ethyl tartrate. Ethyl acetoacetate (at both −33°C. and room temperature) yields with liquid ammonia a mass of white crystals rapidly changing to a yellow oil. Ethyl carbonate is ammonolyzed to both urea and guanidine when heated (at 300°C. for 65 hr.) with an ammonia solution of ammonium chloride (27).

More recently Glattfeld and Macmillan (98) have shown that butyl acetate, ethyl benzoate, methyl salicylate, and glycerol monoacetate are not ammonolyzed (−33°C.), while methyl, ethyl, propyl, and butyl lactates, ethyl mandelate, and ethyl phenylacetate are ammonolyzed (30 to 50 per cent in the case of the lactates). Ôeda (212) states that ethyl lactate and ethyl mandelate are ammonolyzed (−33°C.) to the extent of 2.5 per cent and 25 per cent, respectively (see page 32). Ethyl acetate gives a very small amount of acetamide after heating (for 24 hr. at 130°C.) with an excess of liquid ammonia (130). If the heating is carried out in the presence of ammonium chloride, acetamide (43 per cent yield) and acetamidine (small amounts) are obtained.

The experimental evidence of Shatenshtein and of Audrieth and coworkers clearly demonstrates that the ammonolysis of ethyl benzoate (0° and 25°C.) (56), diethyl malonate (−33° and 0°C.) (251), and diethyl tartrate (20°C.) (243, 245–6) is catalyzed by ammonium salts. The ammonolysis of ethyl benzoate is a pseudo first-order reaction. The catalytic effect of equivalent concentration of various ammonium salts is given by the series

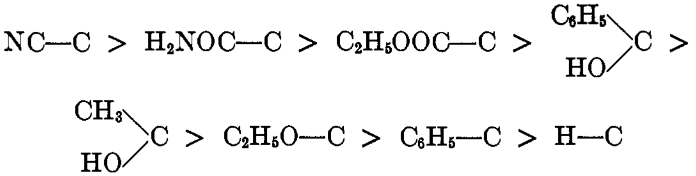
$$C_6H_5COONH_4 > NH_4Cl > NH_4Br > NH_4ClO_4$$

The ammonolysis of ethyl malonate proceeds so rapidly at 0°C. that its study is not susceptible to the degree of accuracy attained in other cases. The quantitative interpretation is further complicated by the fact that ammonolysis proceeds through the intermediate malonamate stage,

$$CH_2(COOC_2H_5)_2 \rightarrow CH_2(COOC_2H_5)(CONH_2) \rightarrow CH_2(CONH_2)_2$$

However, in the early stages of the reaction the yields of malonamide were found to be proportional to the concentration of added ammonium chloride.

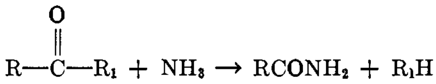
Audrieth and Kleinberg (5) have examined the influence of various α-substituents on the reactivity of esters toward ammonolysis in liquid ammonia (0°C.; 24 to 48 hr.). The effect of the α-substituent is given by the following series:



$$NC{-}C > H_2NOC{-}C > C_2H_5OOC{-}C > \begin{matrix}C_6H_5\\HO\end{matrix}\!\!>C > \begin{matrix}CH_3\\HO\end{matrix}\!\!>C > C_2H_5O{-}C > C_6H_5{-}C > H{-}C$$

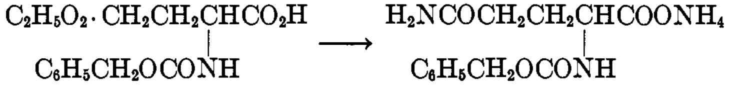
The reactivities of esters towards ammonolysis in liquid ammonia parallel, qualitatively, the reactivities of esters toward alkaline hydrolysis in aqueous solution. While the magnitude of the catalytic effect of the addition of ammonium chloride varies with different esters, there is in every case a marked increase in the yields of the corresponding acid amides. These investigators recommend liquid ammonia ammonolysis (room temperature) of esters for the preparation of α-hydroxy acids and give details for the preparation of mandelamide (81 per cent) and lactamide (71 per cent; 74 to 76 per cent with ammonium chloride).

The possibilities of utilizing ester ammonolysis commercially have not been overlooked. Many such reactions are covered by patents (208–9):

> "Acid amides are prepared by reacting carboxylic acids, or their anhydrides, halides, or esters, having acid radicals containing at least two carbon atoms, with liquid anhydrous ammonia at superatmospheric pressure and room temperature. With esters, anhydrous alcohols are also obtained. The reaction is represented
>
> 
>
> $$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R_1 + NH_3 \rightarrow RCONH_2 + R_1H$$
>
> More than one $=CO$ group may be present as in polybasic acids, e.g., malonic or succinic, or their derivatives, or polybasic alcohols partly or completely esterified with mono- and/or poly-basic acids. R is any organic radical such as methyl, propyl, butyl, amyl, phenyl, benzyl, cinnamyl, naphthyl, pyridine, and quinoline. It may contain substituents such as hydroxy, as in lactic or malic, amine groups, as in anthranilic, or halogen, in which case the amide may contain an amine group in place of halogen. R_1 may be . . . . OR, for example, in melissyl palmitate, ... Crude animal and vegetable oils, fats, waxes or resins may be used as initial materials. Catalysts for the reaction may be used. In examples: (1) coconut oil is mixed in an autoclave with excess of liquid ammonia. After standing for 12 hrs. the amides which separate are filtered off and the filtrate distilled to recover ammonia and pure glycerol. Sardine, olive, linseed, cottonseed, soya bean, or corn germ oil, or oils obtained by oxidation of paraffin wax may be similarly treated; (2) *n*-butyl acetate and excess of liquid ammonia in a sealed vessel are kept at about 20°C. by water cooling. Excess ammonia and then butyl alcohol are distilled off to give a residue of acetamide."

Oda (210, 211) has demonstrated the ammonolysis of fatty oils (olive, coconut, castor, fish, spermacetic, wood, and linseed oil) by heating them for 0.5 to 1 hr. at 100–150°C. with liquid ammonia in an autoclave.

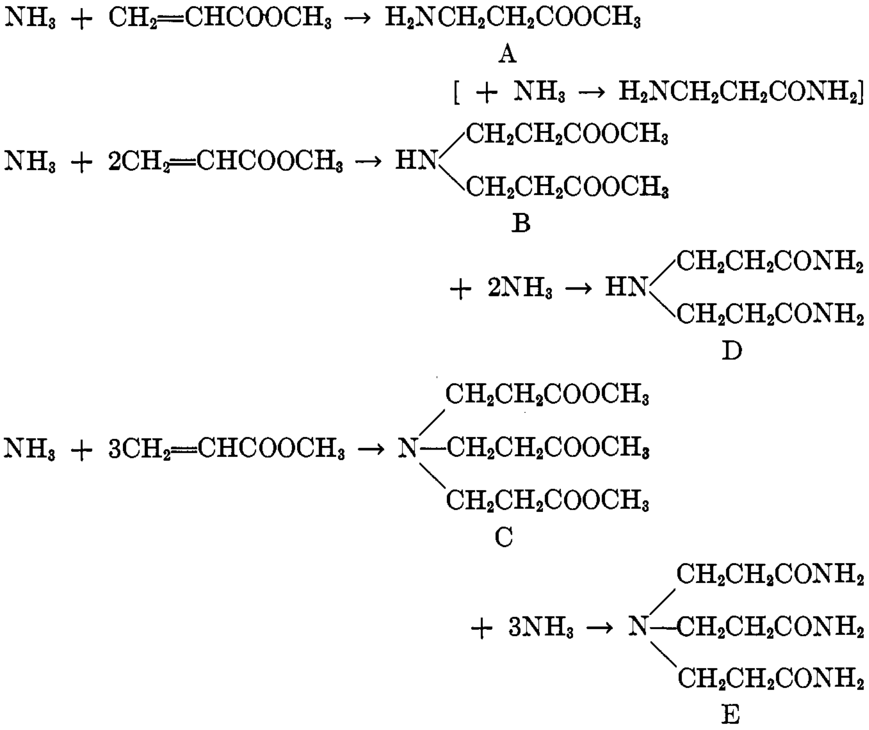
Methyl *l*-*β*-hydroxybutyrate, on standing with liquid ammonia for 60 hr. at room temperature, gives a syrup from which the crystalline amide may be obtained (144). Similarly, *γ*-ethyl-*N*-carbobenzoxy-*d*-glutaminate (20 hr. at 15–20°C.) furnishes the ammonium salt of *N*-carbobenzoxy-*d*-glutamine (126, 207).



$$\underset{C_6H_5CH_2OCONH}{C_2H_5O_2\cdot CH_2CH_2\overset{}{C}HCO_2H} \longrightarrow \underset{C_6H_5CH_2OCONH}{H_2NCOCH_2CH_2\overset{}{C}HCOONH_4}$$

2. Esters of unsaturated acids

When an ester of an unsaturated acid is treated with ammonia, addition of ammonia to the double bond as well as ammonolysis may result. Morsch (195) investigated the action of liquid ammonia at room temperature on methyl acrylate[3] and found that the following reactions take place:



$$NH_3 + CH_2{=}CHCOOCH_3 \rightarrow \underset{A}{H_2NCH_2CH_2COOCH_3}$$

$$[\ + NH_3 \rightarrow H_2NCH_2CH_2CONH_2]$$

$$NH_3 + 2CH_2{=}CHCOOCH_3 \rightarrow \underset{B}{HN\left\langle\begin{matrix}CH_2CH_2COOCH_3\\ CH_2CH_2COOCH_3\end{matrix}\right.}$$

$$+\ 2NH_3 \rightarrow \underset{D}{HN\left\langle\begin{matrix}CH_2CH_2CONH_2\\ CH_2CH_2CONH_2\end{matrix}\right.}$$

$$NH_3 + 3CH_2{=}CHCOOCH_3 \rightarrow \underset{C}{N\left\langle\begin{matrix}CH_2CH_2COOCH_3\\ CH_2CH_2COOCH_3\\ CH_2CH_2COOCH_3\end{matrix}\right.}$$

$$+\ 3NH_3 \rightarrow \underset{E}{N\left\langle\begin{matrix}CH_2CH_2CONH_2\\ CH_2CH_2CONH_2\\ CH_2CH_2CONH_2\end{matrix}\right.}$$

The dependence of the yields of the various products upon the length of

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[3] For the behavior of acrylic acid toward liquid ammonia see reference 124.

time for reaction is shown in table 5. The results may be compared to those obtained with alcoholic ammonia (194), as shown in table 6.

Ethyl α-ethylacrylate (200 hr.), ethyl elaidate (3 weeks), and ethyl oleate (300 hr.) are unreactive toward liquid ammonia at room temperature, while ethyl allylacetate (25 days) gives a small amount (0.05 g. from 7.5 g. of ester) of reaction product (probably an amide) (214). Ethyl β,β-dimethylacrylate (6 months) yields ethyl aminoisovalerianate but no amide (214); ethyl β,β-diethylacrylate (6 weeks) yields β,β-diethylacrylic amide (45 per cent) (215); ethyl crotonate (100 hr.) yields ethyl β-aminobutyrate (55 per cent) but no amide (*cf.* 196); and methyl hydrosorbate (14 days) yields some amide but no amino ester or amino amide (214). Methyl sorbate shows very little action in 8 days, but reacts almost completely after 4 to 6 weeks to form substances which are unstable and gradually lose ammonia under vacuum. For shorter reaction periods the products are largely soluble in ether (amino esters ?) but after 3 months' action, the products are almost completely insoluble in ether (amino amides, cyclic substances ?). From the latter, up to 10 per cent of sorbamide may be isolated. The action of the ester of crotylidenemalonic

TABLE 5

Effect of reaction time upon yields of products obtained by the reaction of liquid ammonia with methyl acrylate at room temperature

TIME	A	B	C	D	E
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
100 hr.	2.5	42	15.5		
14 days				*ca.* 35	*ca.* 13
5 months				*ca.* 33	*ca.* 56

TABLE 6

Effect of reaction time upon yields of products obtained by the reaction of alcoholic ammonia with methyl acrylate

	TEMPERATURE	TIME	A	B	C	D	E
			per cent	*per cent*	*per cent*	*per cent*	*per cent*
Methyl alcohol:							
10 per cent NH_3	Room temperature	1 day		23	48		
20 per cent NH_3	Room temperature	1 day		2	5	26	4
Saturated	Room temperature	14 days				39.5	36.5
Saturated	Room temperature	5 months				35	44
10 per cent NH_3	100°C.	8 hr.	3	6.5			
Ethyl alcohol:							
10 per cent NH_3	100°C.	8 hr.	8	54	5		

acid is similar to that of methyl sorbate, but the isolation of definite compounds has not been successful (214).

The behavior of ethyl cinnamate is recorded in table 7. Phenyl isocrotonate (2 months at room temperature) yields an oil as a primary product and crystals of phenyl isocrotonamide as a secondary product (214).

TABLE 7

Action of ethyl cinnamate with liquid ammonia

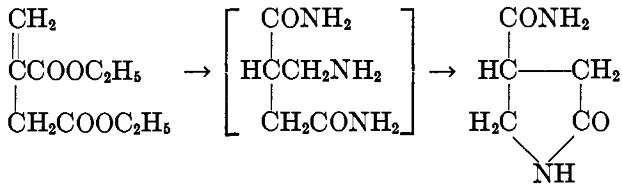
TEMPERATURE	TIME OF REACTION	UN-CHANGED ESTER	ETHYL β-AMINO-HYDRO-CINNA-MATE	CINNAMAMIDE	β-AMINOHYDRO-CINNAMAMIDE	REFER-ENCE
		per cent	*per cent*	*per cent*	*per cent*	
Room temperature	7 days	100				(218)
Room temperature	4 months			9.4	16.5	(263)
100°C.	27 hr.	55.1	22.2	14.1 per cent of amides, principally cinnamamide		(193)
100°C.	70 hr.	35	35	21.4		(193)

TABLE 8

Action of diethyl citraconate with liquid ammonia

TIME OF REACTION	UNCHANGED ESTER	DIETHYL HOMOAS-PARIGINATE	HOMOAS-PARIGIN-DIAMIDE	DIAMIDE OF CITRACONIC ACID	REFERENCES
	per cent	*per cent*	*per cent*		
1.5 days..............	73	5.2			(217)
5 days................		Small amount			(262)
6 days................		Largely		Small amount	(217)
1 month..............			Some		(262)
2 months.............		10.5	28.3		(262)
3.5 months...........		1.4	73		(262)
7 months.............		14.1			(262)
Bomb; 12 days.......			51.4	Some	(262)

Diethyl itaconate (6 days) yields a hygroscopic product from which only a small quantity of itaconamide has been isolated (216). On longer standing (2 to 3 months), diethyl itaconate yields the amide of 2-oxypyrrolidine-4-acid (7 g. from 14 g. of ester) (262).

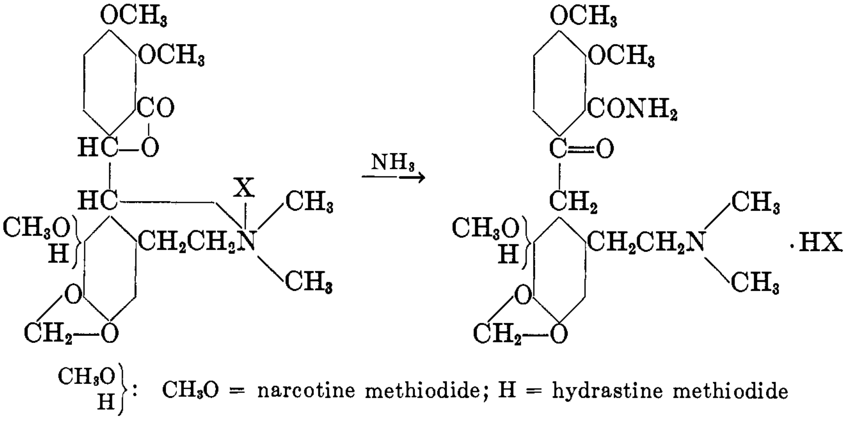


α-Mesaconic monoethyl ester (1 month) yields the corresponding amide and homoasparagine (0.56 g. from 4 g. of the acid ester). Diethyl mesaconate (3 weeks) yields mesacondiamide (0.8 g. from 9 g. of ester) (262). The results obtained with diethyl citraconate are assembled in table 8.

The ammonolysis of β-diethylaminoethyl β-chlorocrotonate, $CH_3CCl{=}CHCO_2(CH_2)_2N(C_2H_5)_2$, is interesting, since the chlorine is quantitatively removed (room temperature for 72 hr.) without ammonolysis of the ester or addition to the double bond (247).

3. *Lactones*

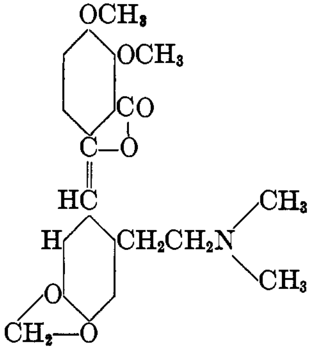
As might be expected from their relation to esters, many lactones are ammonolyzed in liquid ammonia by merely dissolving the corresponding lactones in an open vessel containing ammonia. Glattfeld and Macmillan (97; *cf.* 132) prepared the following amides in quantitative yield: *dl*-1,3-dihydroxybutyramide, *dl*-2,3-dihydroxybutyramide, *dl*-erythronamide, *d*-erythronamide, *l*-erythronamide, *d*-galactonamide, *d*-gluconamide, and *d*-mannonamide (from both the γ- and δ-lactones). Coumarin and the lactone of γ-hydroxybutyric acid are not affected by liquid ammonia at its boiling point, although the latter is ammonolyzed at room temperature in a sealed tube. Later work (98) confirmed the results on *d*-glucono-γ-lactone and coumarin and demonstrated the complete ammonolysis of 3-benzalphthalide (amide of desoxybenzoincarbonic acid). Phthalide, 3-phenylphthalide, phthalophenone, and the lactone of 2′,4′-dihydroxydiphenyl-2-carboxylic acid are not ammonolyzed (−33°C.). Phenolphthalein is temporarily ammonolyzed, but the product loses its ammonia completely on prolonged evacuation. γ-Butyrolactone and γ-valerolactone on heating for 2 to 3 hr. at 200–230°C. with liquid ammonia are converted into α-pyrrolidone (64 per cent) and 5-methyl-2-pyrrolidone (74 per cent), respectively (256). Simple solution of 2,4,6-trimethyl-



$\left.\begin{matrix}CH_3O\\H\end{matrix}\right\}$: CH_3O = narcotine methiodide; H = hydrastine methiodide δ-gluconolactone and 3,4,6-trimethyl-δ-altronolactone in liquid ammonia (−33°C.) yields the corresponding amides (182a).

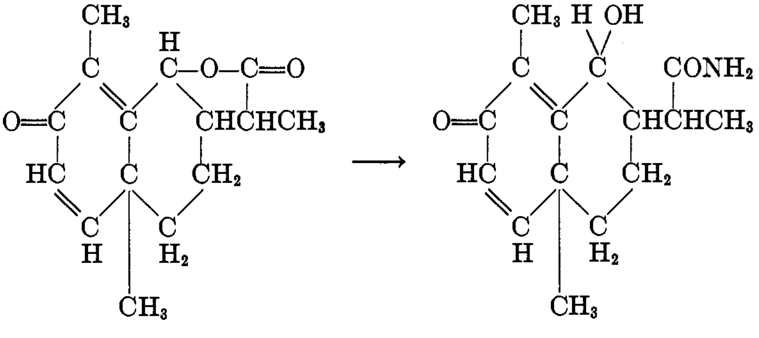
Narcotine methiodide and methochloride are converted to narceinamide hydroiodide and hydrochloride, respectively, by the action of liquid ammonia (−80° to −33°C.)

Under the same conditions hydrastine methiodide yields methylhydrastamide hydroiodide, while methylhydrastine and its hydroiodide are unaffected (2).



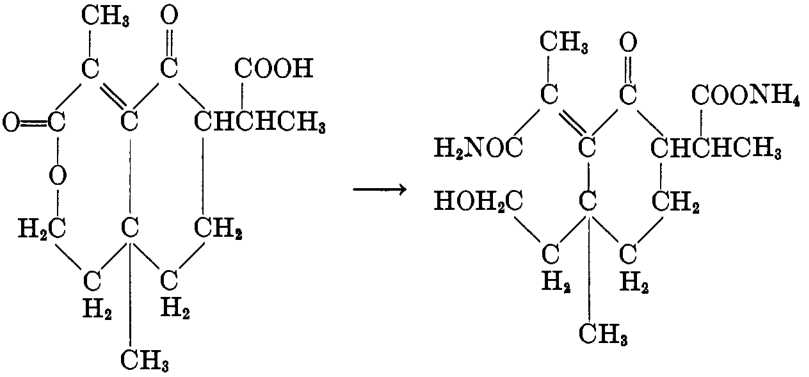
Methylhydrastine

Santonin is quantitatively ammonolyzed to the amide of santoninic acid (room temperature; 3 days) (1).

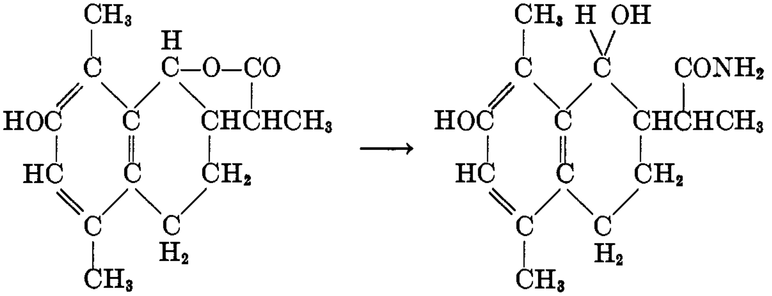


The lactone obtained by the oxidation of santonic acid is likewise ammonolyzed by liquid ammonia.

By following the course of the reaction polarimetrically, Shatenshtein has clearly demonstrated that the ammonolysis of santonin is catalyzed by ammonium salts, as well as by acid amides and other weak acids (239-42, 246). The order of catalytic activity for "strong" acids varies with the anion as follows: $ClO_4^- < I^- < NO_3^- < Br^- < Cl^-$, which is the reverse of the order of osmotic coefficients and of coefficients of electrical conduc-

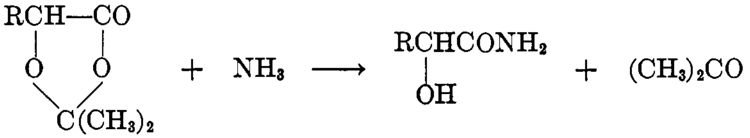


tivity of solutions of ammonium salts in liquid ammonia. The order of catalytic activity of the amides of carboxylic acids in liquid ammonia corresponds to that of the acids themselves in water ($CH_3COOH < C_6H_5COOH < HCOOH$). Such studies have also been extended to the ammonolysis of desmotroposantonin (243–4, 246).



The available evidence confirms Glattfeld's statement (98) that in contrast to simple esters lactones are never partially ammonolyzed. They are either completely ammonolyzed or not ammonolyzed at all.

Compounds closely resembling the lactones in their ease of reaction with liquid ammonia are the acetone compounds of α-hydroxy acids.



The results of Ôeda's studies are assembled in table 9 (212).

4. Esters of ortho acids

Ethyl orthocarbonate is very unreactive toward liquid ammonia. No reaction occurs on heating for 1.5 hr. at 100°C. both with and without ammonium chloride. Traces of guanidine can be identified after 3 years (at room temperature) both with and without ammonium chloride or after heating for 24 hr. at 130°C. in the presence of ammonium chloride. Ethyl orthoformate gives no indication of reaction when heated with liquid ammonia (at 100°C. for 12 hr.) or with a solution of ammonium chloride (at 200°C. for 9 hr.) (130). This lack of reactivity of ortho esters stands in sharp contrast to the preparation of guanidine by heating esters of orthocarbonic acid with aqueous ammonia.

5. *Esters of carboxazylic and mixed aquo-ammonocarbonic acids*

(*a*) *Substituted acyl amides.* A convenient way to deacetylate 1-acetyl-1,2,3-benzotriazole is that of simply dissolving the material in liquid ammonia (−33°C.), allowing the ammonia to evaporate, and working over the resulting mixture (43). 1-Benzoyl-1,2,3-benzotriazole is debenzoylated in the same manner.

TABLE 9

Action of acetone compounds of α-hydroxy acids with liquid ammonia

STARTING MATERIAL	CONDITIONS	PRODUCT			
		Lactamide	Leucic acid amide	Mandelamide	Phenylacetamide
		per cent	*per cent*	*per cent*	*per cent*
Acetone compound...	100°C.; 5 hr.	47	49	70	55
	Room temperature; 2 weeks		79	92	88
	ca. −33°C.; overnight	85	90	95	90
Ethyl ester...........	*ca.* −33°C.; overnight	<2.5		25	

Acetanilide exhibits no reaction with liquid ammonia (24 hr. at 130°C.), but in the presence of ammonium chloride gives a quantitative yield of aniline (130) and some acetamidine (86).

Ammonia solutions of potassium amide at room temperature cause no ammonolysis of substituted acyl amides, benzylacetamide and *p*-phenetolacetamide, but instead form salts (84).

(*b*) *Esters of aquo-ammonocarbonic acids.* Although ethyl allophanate is completely ammonolyzed by aqueous ammonia (at 100°C.) (117), anhydrous liquid ammonia (or ammonia containing 2 per cent of water) is without effect (48). Methyl and ethyl allophanate, urethan, carbethoxycyanamide, *s*-dicarbethoxyguanidine, methylurea (*cf.* 86), *s*-dicarbethoxyurea, and carbethoxy-*N*-phenylbiuret when heated (at 300°C. for 65 hr.) with ammonia solutions of ammonium chloride yield guanidine and urea (27). Carbanilide on similar treatment is ammonolyzed to aniline (77 per cent), urea, and some guanidine (86). With ammonia alone (at 130°C. for 24 hr.), aniline (89 per cent) and urea are formed but no guanidine (130). Diarylguanidines are prepared by treatment of the corresponding thioureas with liquid ammonia (temperatures up to 25°C.) in the presence of sulfur-binding metal compounds, such as lead oxide (249).

$$(o\text{-}CH_3C_6H_4NH)_2CS + 3NH_3 \rightarrow (o\text{-}CH_3C_6H_4NH)_2C{=}NH + (NH_4)_2S$$

Ethyl carbamate reacts with an ammonia solution of potassium amide (at −33°C. or room temperature) to form potassium cyanate and ethyl alcohol.

$$H_2NCOOC_2H_5 + KNH_2 \rightarrow KNCO + C_2H_5OH + NH_3$$

This reaction constitutes a clear case of ammonolysis being brought about by an ammono base. With potassium amide allophanic acid forms a salt which does not decompose below 215°C. (28).

$$KHNCONHCOOC_2H_5 \rightarrow KNCO + H_2NCOOC_2H_5$$

6. *Esters of carbazylic and ammonocarbonic acids*

(*a*) *Esters of carbazylic acids.* *N*,*N*′-diphenylacetamidine and *N*,*N*′-diphenylbenzamidine on heating with ammonia solutions of ammonium chloride yield aniline and acetamidine and benzamidine, respectively (86). *N*,*N*′-diphenylacetamidine with ammonia alone (at 130°C. for 24 hr.) is 13 per cent ammonolyzed (130).

(*b*) *Esters of ammonocarbonic and ammonocarbonous acids.* *N*,*N*′-diphenylguanidine is partially ammonolyzed (at 130°C. for 24 hr.) to yield aniline (18 per cent) and guanidine. With identical treatment, *N*,*N*′,*N*″-triphenylguanidine is almost completely ammonolyzed to *N*,*N*′-diphenylguanidine (130). However, heating (200°C.) triphenylguanidine with a solution of ammonium chloride yields guanidine and aniline (82 per cent) (86).

Triphenylguanidine is not ammonolyzed by ammonia solutions of potassium and sodium amides (at room temperature) but forms salts (85).

When ethyl isocyanide and an equivalent amount of potassium amide are heated (at 80°C. for a few hours) in liquid ammonia solution, ammonolysis results in accordance with the following equation (85a):

$$C_2H_5NC + KNH_2 \rightarrow C_2H_5NH_2 + KCN$$

7. *Esters of sulfur and selenium acids*

The alkyl esters of sulfuric acid and the sulfonic acids are attacked little if at all by liquid ammonia at low temperatures, since these substances have been used successfully for alkylations in ammonia: methyl, ethyl (115–6, 123, 145, 187), *n*-propyl, isopropyl, *n*-butyl, and *n*-amyl sulfates;

n-propyl and *n*-butyl *p*-toluenesulfonates (148). On standing for 24 hr. at room temperature with an excess of liquid ammonia, the tribenzenesulfonate of pyrogallol is one-third ammonolyzed to the dibenzenesulfonate (273).

The reaction of halogen sulfonic acid esters with liquid ammonia produces a mixture of amines. Thus, chlorosulfonic acid dodecyl ester dissolved in ether reacts at −30°C. to produce a mixture of the corresponding primary, secondary, and tertiary amines.

$$ROSO_2Cl + 3NH_3 \rightarrow RNH_2 + HOSO_2NH_2 + NH_4Cl$$

(R = octyl, myristyl, cetyl, octodecyl, oleyl, etc.; olefinic radical such as that of olein alcohol; polyethyleneglycol monoalkyl ethers; aliphatic radicals of low molecular weight containing aliphatic radicals of high molecular weight, etc.) (125).

N,*N*′-dimethyl-*N*,*N*′-dinitromethionamide reacts instantly with liquid ammonia to form methionamide and methylnitramine (6).

$$CH_2[SO_2N(NO_2)CH_3]_2 + 2NH_3 \rightarrow 2CH_3NHNO_2 + CH_2[SO_2NH_2]_2$$

Methyl and ethyl selenites are ammonolyzed (at room temperature) but the expected aquo-ammonoselenite is not obtained. Instead, a mixture of selenium nitride, selenium dioxide, and selenium results (269).

8. *Nitrosamines*

Di-*p*-tolyl nitrosamine exhibits no reaction with a liquid ammonia solution of ammonium chloride (at room temperature for 10 days) (274). Heated with ammonia (for 24 hr. at 130°C.), di-*p*-tolyl nitrosamine gives a 51 per cent yield of nitrogen according to the reaction

$$R_2NNO + NH_3 \rightarrow R_2NH + H_2O + N_2$$

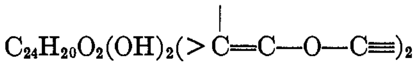
Similar treatment in the presence of ammonium chloride increases the yield of nitrogen to 61 per cent (130). Alkali amides, on the other hand, (0–20°C.) produce complete ammonolysis in the sense of the above reaction (57a).

J. MISCELLANEOUS

Two of the hydroxyl groups in gossypol are ammonolyzed (at −33°C.) to form diaminogossypol (191).

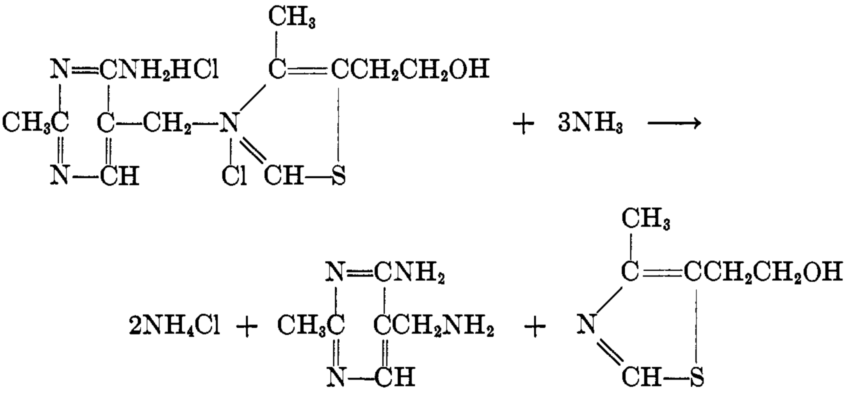
$$C_{30}H_{24}O_2(OH)_6 + 2NH_3 \rightarrow C_{26}H_{24}O_2(OH)_4(>\overset{|}{C}{=}C-NH_2)_2 + 2H_2O$$

The same compound is formed by the action of ammonia on anhydrogossypol,



$$C_{24}H_{20}O_2(OH)_2(>C{=}C{-}O{-}C{\equiv})_2$$

Thiamine or vitamin B_1 is split by liquid ammonia at room temperature into two fragments (46, 278):



Proteins are partially ammonolyzed by ammono bases (slowly by potassium amide at −33°C., not appreciably by sodium amide below 40°C.) and by ammonium salts (at 35–115°C. for 2 days) in liquid ammonia (186, 226-7).

IV. Ammonolysis of Organometallic Compounds

A. METAL ALKYLS AND ARYLS

There is no record at hand of any investigations concerning the action of liquid ammonia upon alkali alkyls, aryls, or simple aryl-substituted alkyls. However, the many reactions in ammonia solution by which these materials might well be expected to be formed, always yield an alkali amide and hydrocarbon (*cf.* 20, 62).

$$R^- + NH_3 \rightarrow RH + NH_2^-$$

Additional support to this view is given by the fact that lithium salts of the primary and secondary aliphatic and secondary aliphatic-aromatic amines are readily prepared by treating the amine with a solution of lithium phenyl or lithium *n*-butyl in absolute ether (*cf.* 22).

$$R_2NH + LiC_6H_5 \rightarrow R_2NLi + C_6H_6$$

The polyphenyl-substituted metal alkyls are less ammonolyzed than the unsubstituted ones. In general, extensive ammonolysis does not take place (at −33°C.) when an alkali metal, M, is present in the grouping $(C_6H_5)_2CM$— (17, 63, 281-2). Some indication of the influence of the metal upon the extent of ammonolysis is realized among the salts of triphenylmethane. Potassium triphenylmethide is stable in liquid ammonia and the sodium salt is slightly ammonolyzed, while the calcium salt is completely ammonolyzed (173a). On the other hand, alkali salts of acetylene and monosubstituted acetylenes are entirely stable in ammonia and serve as useful synthetic reagents (16, 63).

1,2,3,4-Tetrasodium-1,2,3,4-tetrahydronaphthalene is extensively ammonolyzed (283).

$$C_{10}H_8Na_4 + 4NH_3 \rightleftharpoons C_{10}H_{12} + 4NaNH_2$$

At −33°C. this reaction is three-fourths complete and near room temperature is entirely complete. The above equilibrium suggests the probable existence of similar alkali derivatives of other polycyclic hydrocarbons at low temperatures (*cf.* 65). 9,10-Disodium- and 9,10-dipotassium-9,10-diphenyl-9,10-dihydroanthracenes are stable in liquid ammonia (128).

Zinc ethyl reacts completely with ammonia,

$$Zn(C_2H_5)_2 + 2NH_3 \rightarrow Zn(NH_2)_2 + 2C_2H_6$$

either in the gaseous state (69, 74) or in solution in anhydrous ether (143). A similar reaction of beryllium alkyls should prove useful in preparing the at present unknown beryllium amide. Mercury dialkyls are not ammonolyzed (151, 174). Similarly, the fully alkylated and arylated compounds of the elements in the third, fourth, fifth, and sixth groups of the periodic classification appear to be unreactive toward ammonia (except for ammonation of alkyls of boron, etc., giving $R_3B \cdot NH_3$). On the other hand, triethylsilane is ammonolyzed in liquid ammonia and aminolyzed in ethylamine (176),

$$2(C_2H_5)_3SiH + NH_3 \rightarrow [(C_2H_5)_3Si]_2NH + 2H_2$$

$$(C_2H_5)_3SiH + C_2H_5NH_2 \rightarrow (C_2H_5)_3SiNHC_2H_5 + H_2$$

The first reaction takes place in the presence of potassium amide. Lithium metal serves as a catalyst for the second reaction.

A number of alkali-metal derivatives of alkyl- and aryl-substituted silanes, germanes, and stannanes have been prepared. These include $(C_2H_5)_3SiLi$ (176), $(C_6H_5)_3SiNa(Li)$ (160, 173), $(C_2H_5)_3GeK(Li)$ (162), $(C_6H_5)_3GeNa(Li)$ (166, 173), $(C_6H_5)_2GeNa_2$ (155, 166), $NaGe(C_6H_5)_2 \cdot Ge(C_6H_5)_2Na$ (155), $(CH_3)_3SnNa$ (160, 168, 175, 178), $(CH_3)_2SnNa_2$ (41, 45, 170), $NaSn(CH_3)_2 \cdot Sn(CH_3)_2Na$ (170, 175), $(C_6H_5)_3SnNa$ (45, 173), $(C_6H_5)_2SnNa_2$ (153), $NaSn(C_6H_5)_2 \cdot Sn(C_6H_5)_2Na$ (153), and $(C_6H_5)_3PbNa$ (72a).

There is no indication of ammonolysis of any of these compounds except lithium triethylgermanide, which is partially aminolyzed in ethylamine and completely ammonolyzed in liquid ammonia, and disodium diphenylstannide which is ammonolyzed at high dilutions. The stability of this type of salt makes possible their extensive use in synthetic work.

B. ORGANOMETALLIC HALIDES

Grignard reagents react with ammonia in much the same way that they react with water (47, 252).

$$(C_6H_5)_2C{=}NMgX + NH_3 \rightarrow (C_6H_5)_2C{=}NH + MgX(NH_2)$$

The destruction of the Grignard reagent by means of ammonia is particularly advantageous where, as in the above case, water would destroy the ketimine.

Kraus and coworkers have shown that the organomercuric halides, RHgX ($R = CH_3$ to C_8H_{17}, C_6H_5) (151, 169, 174), and dimethylgallium chloride, $(CH_3)_2GaCl$, are not ammonolyzed by the action of liquid ammonia (181).

In contrast, it has been found that triarylsilicyl halides, $(C_6H_5)_3SiCl$ and $(C_6H_5)_3SiBr$, are completely ammonolyzed (161, 163, 177), while the ammonolysis of triethylsilicyl bromide, $(C_2H_5)_3SiBr$, is brought to completion through the aid of metallic lithium (176). On the other hand, the trialkylsilicyl fluorides (ethyl, propyl, butyl, and amyl) are very unreactive toward liquid ammonia and even resist the action of sodium in liquid ammonia (96).

Like organosilicon halides, organogermanium halides are ammonolyzed. However, temperature seems to play an important part in the ammonolysis of triethylgermanyl bromide. At −33°C. this compound forms an ammonate, while at room temperature ammonolysis is marked and may be brought to completion by the use of sodium (164, 180). Triphenylgermanyl fluoride is also ammonolyzed (167) but not as readily as the triphenylgermanyl bromide (182), whose reaction is brought to completion by the use of potassium amide. The resulting product, triphenylgermanyl amide, very easily loses ammonia with the formation of the nitride. This property of losing ammonia is also encountered with the ethylgermanium tribromide and triiodide, in that they do not form the amide but pass directly to ethylgermanium nitride (72).

From the reaction of dialkyl- and diaryl-germanium dihalides, $(C_2H_5)_2GeBr_2$ (71) and $(C_6H_5)_2GeCl_2$ (154), one obtains the corresponding imides. It has also been shown that the organosilicon and organogermanium halides do not undergo aminolysis with ethylamine: $(C_6H_5)_3SiBr$ (161); $(C_2H_5)_3GeCl$, $(C_2H_5)_3GeBr$ (164); $(C_6H_5)_2GeCl_2$ (156).

As one passes from the organogermanic halogen compounds, which are ammonated at −33°C. but ammonolyzed at higher temperatures, one finds that the organostannic halides form ammonated products but no ammonolytic products even at room temperature: $(CH_3)_3SnCl$ (169); $(CH_3)_3SnBr$ (179); $(CH_3)_3SnI$ (169); $(CH_3)_2SnBr_2$ (171). Triphenyllead chloride and iodide are not ammonolyzed in liquid ammonia (72a, 72b).

Hein and coworkers were able to electrolyze tetraphenylchromium iodide in liquid ammonia, thereby obtaining tetraphenylchromium. It is thus evident that these compounds are relatively stable in liquid ammonia (114).

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