[Contribution from the Department of Chemistry, The University of Texas]

The Ammonolysis of the Sulfates of Hydrazine, Methylhydrazine, Hydroxylamine and Semicarbazide, and the Ammoniation of These Bases and Certain of their Salts[1]

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The ammonolysis of the sulfates of bases such as hydrazine and hydroxylamine with *liquid* ammonia has been shown to provide the corresponding free bases in substantially quantitative yields and high purity. The reactions that occur between these salts and *gaseous* ammonia have been followed by means of pressure–composition isotherms; the results are interpreted on the basis of the reversibility of the utilization of ammonia in these reactions and dissociation pressures. Pressure–composition isotherms for the binary systems hydrazine–ammonia, hydroxylamine–ammonia, and semicarbazide–ammonia are included.

The preparation of nitrogen bases by the ammonolysis of the corresponding sulfates with liquid ammonia, *e.g.*

$$N_2H_4 \cdot H_2SO_4 + 5NH_3 \longrightarrow N_2H_4 + (NH_4)_2SO_4 \cdot 3NH_3 \quad (1)$$

has been demonstrated for hydrazine,[2–4] hydroxylamine,[5,6] semicarbazide,[6] and methylhydrazine[6] while attempts similarly to employ guanidine and aminoguanidine sulfates were unsuccessful.[6] In all cases, the ammonia-insoluble ammonium sulfate 3-ammoniate[7] was separated by either filtration or decantation and the free base recovered by evaporation of the ammonia followed in some instances by recrystallization from alcohol. The information relative to these reactions is incomplete with respect to either yields or purity, or both, and in only one case[4] is there even indirect evidence that these bases are produced strictly in accordance with the stoichiometry indicated by equation 1.

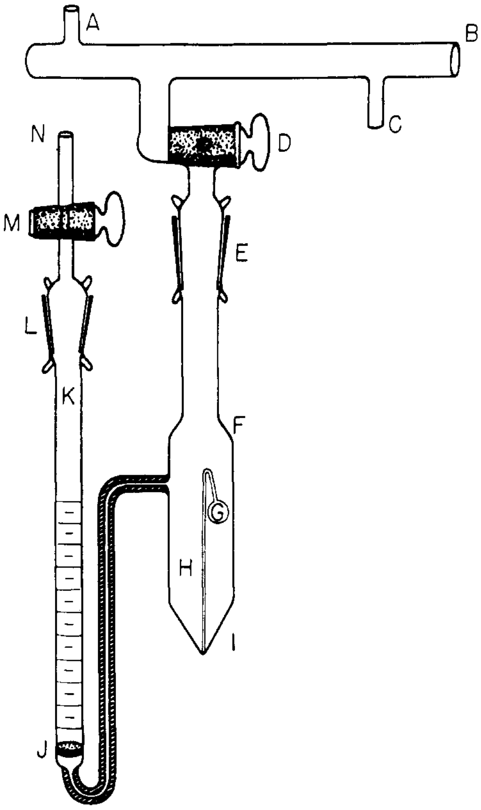

Fig. 1.—Apparatus for the ammonolysis of sulfates with liquid ammonia.

The work described below demonstrates clearly the extent of ammonolysis of the sulfates of hydrazine, hydroxylamine, semicarbazide and methylhydrazine and establishes the purity of the resultant anhydrous bases. The reactions that occur when these sulfates (excluding that of methylhydrazine) and hydroxylamine hydrochloride are treated with gaseous ammonia at low temperatures are described on the basis of pressure–composition isotherms. Similar data for binary systems comprising ammonia and the free bases are included for comparison.

Experimental

Materials.—Commercial anhydrous ammonia[8] was distilled into small tanks and dried over sodium amide. All chemicals used were either reagent grade or were purified by recrystallization and thoroughly dried prior to use. The purity of hydroxylamine sulfate was determined by an analytical method[9] based upon the oxidation of hydroxylamine with iron(III) ion followed by titration of iron(II) ion with potassium permanganate solution. The method used for analysis of the other sulfates is described elsewhere.[10] Purities found by direct analysis were: $N_2H_4 \cdot H_2SO_4$ (99.6%), $CH_3NHNH_2 \cdot H_2SO_4$ (100.7%), $H_2NC(=O)NHNH_2 \cdot H_2SO_4$ (99.5%), $(NH_2OH)_2 \cdot H_2SO_4$ (100.0%).

Equipment.—The equipment used for the ammonolysis of the sulfates is shown in Fig. 1. The buret K and the collection vessel H were attached to the permanently mounted equipment *via* joints L and E. The gas outlet A leads to a Dry Ice bath and a vacuum line; B and N are inlet lines for gaseous ammonia or helium and C leads to an open manometer. The arrangement of K with respect to H is such that ammonia can be condensed in K *via* J without condensation in H. Unless indicated to the contrary, reactions were carried out in this equipment containing an anhydrous and oxygen-free atmosphere.

The sulfate to be ammonolyzed is introduced into K and the equipment shown in Fig. 1 is attached to the permanently mounted equipment at L and E. Stopcock M is closed and the system is alternately evacuated and filled with anhydrous ammonia gas. A Dry Ice–isopropyl alcohol bath at −40 to −60° is adjusted to position I and ammonia is condensed in K *via* filter J, thereby providing agitation of the solid on J. For filtration, the bath is raised to position F, and a sufficient pressure difference across J is provided by either increasing the ammonia gas pressure

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[1] This work was supported in part by the U. S. Navy Bureau of Ordnance, Contract N123s-67363, Task Order 2.

[2] A. W. Browne and T. W. B. Welsh, This Journal, **33**, 1728 (1911).

[3] A. W. Browne and A. E. Houlehan, *ibid.*, **33**, 1734 (1911).

[4] F. Friedrichs, *ibid.*, **35**, 244 (1913).

[5] O. Baudisch and F. Jenner, *Ber.*, **49**, 1182 (1916).

[6] L. F. Audrieth, This Journal, **52**, 1250 (1930).

[7] C. M. Drew, H. W. Kruse, S. Skolnik and G. B. L. Smith, *ibid.*, **71**, 1494 (1949).

[8] This material was generously supplied by the Polychemicals Department, E. I. du Pont de Nemours and Co., Wilmington, Del.

[9] R. H. Dewey, private communication on Commercial Solvents Corporation Research Analytical Method No. 23.

[10] W. R. McBride, R. A. Henry and S. Skolnik, *Anal. Chem.*, **25**, 1042 (1953).

above the liquid in K or by lowering the pressure in H *via* A. The residual ammonium sulfate on J is washed with several portions of liquid ammonia.

Ammonia is evaporated from the combined filtrate and washings in H by maintaining a lower temperature with a Dry Ice bath in the line beyond A. Conditions for this operation are not critical except that for hydrazine the temperature in H should be maintained at about −50° so that the hydrazine crystallizes on the walls of the vessel thereby minimizing volatilization of hydrazine during distillation of the ammonia.[11] For yield determinations the pressure in the system is raised to atmospheric and the free base in H is removed in dilute acid solution; the ammonium sulfate in K is removed similarly and both solutions are made up to known volumes for analysis. For determinations of the purity of the free bases, all or nearly all of the base in H is removed in fragile glass ampoules G by a minor and obvious modification of a technique described elsewhere.[12] The ampoules were removed from H, sealed, and subsequently crushed under dilute hydrochloric acid and analyzed.

Pressure–composition isotherms were obtained using the equipment described previously.[13]

Experimental Results.—The results of experiments concerned with the preparation of free bases by the ammonolysis of the corresponding sulfates are given in Table I; the values for the purity of the bases recovered are the averages of at least three independent measurements that were in uniformly good agreement. In connection with these experiments, the following melting points (cor.) were determined: hydrazine, 0.2–1.8°; hydroxylamine, 31.5–32.5°; semicarbazide, 95–96°.

TABLE I

YIELD AND PURITY OF BASES PREPARED BY THE AMMONOLYSIS OF SULFATES

Sulfate[a]	Yield, % Recovered	Yield, % Residual[b]	Yield, % Total	Purity, %
Hydrazine	98.4	0.3	98.7	99.6
Methylhydrazine	88.9	4.2	93.1	98.9
Hydroxylamine	99.0	1.5	100.5	98.3
Semicarbazide	97.7	1.9	99.6	99.9

[a] The weights of samples ammonolyzed were within the range 175–325 mg. [b] Base accounted for by analysis of residual ammonium sulfate.

The changes that occur when hydrazine, hydroxylamine and semicarbazide sulfates and hydroxylamine hydrochloride are treated with *gaseous* ammonia have been studied by means of pressure–composition isotherms (Figs. 2–5). For comparison, isotherms for the binary systems hydroxylamine–ammonia (Fig. 6), hydrazine–ammonia and semicarbazide–ammonia (Fig. 7) were also obtained. For all of these cases, the results are plotted as moles of ammonia taken up per mole of salt or base used; the compositions of the phases present at equilibrium are listed in Table II.

TABLE II

COMPOSITION OF PHASES AT EQUILIBRIUM

Fig. no.	Curve	Phases
2	ST	$(N_2H_5)_2SO_4 \cdot NH_3(s)$, $(NH_4)_2SO_4(s)$, $NH_3(g)$
	TU	$[(N_2H_5)_2SO_4 \cdot (NH_4)_2SO_4] \cdot 6NH_3(s)$, $(N_2H_5)_2SO_4 \cdot NH_3(s)$, $(NH_4)_2SO_4(s)$, $NH_3(g)$
	UV	$[(N_2H_5)_2SO_4 \cdot (NH_4)_2SO_4] \cdot 6NH_3(s)$, $NH_3(g)$
	WX	$(N_2H_5)_2SO_4(s)$, $(NH_4)_2SO_4(s)$, $NH_3(g)$
	XY	$(N_2H_5)_2SO_4(s)$, $(N_2H_5)_2SO_4 \cdot NH_3(s)$, $(NH_4)_2SO_4(s)$, $NH_3(g)$
	YZ	$(N_2H_5)_2SO_4 \cdot NH_3(s)$, $(NH_4)_2SO_4(s)$, $NH_3(g)$
3	FG	$NH_2OH(s)$, $(NH_4)_2SO_4(s)$, $NH_3(g)$
	GH	$NH_2OH(s)$, $(NH_2OH)_2 \cdot NH_3(s)$, $(NH_4)_2SO_4(s)$, $NH_3(g)$
	H′H″	$(NH_2OH)_2 \cdot NH_3(s)$, $(NH_4)_2SO_4(s)$, $NH_3(g)$
	HI	$(NH_2OH)_2 \cdot NH_3(s)$, $(NH_4)_2SO_4(s)$, $(NH_4)_2SO_4 \cdot 3NH_3(s)$, $NH_3(g)$
	IJ	$(NH_2OH)_2 \cdot NH_3$(s, or satd. soln.), $(NH_4)_2SO_4 \cdot 3NH_3$, $NH_3(g)$
4	AB	R(s),[a] $(NH_4)_3SO_4(s)$, $NH_3(g)$
	BC	R(s), $(NH_4)_2SO_4(s)$, $(NH_4)_2SO_4 \cdot 3NH_3(s)$, $NH_3(g)$
	CD	R(s), $(NH_4)_2SO_4 \cdot 3NH_3(s)$, $NH_3(g)$
	DE	R(s), satd. soln., $(NH_4)_2SO_4 \cdot 3NH_3(s)$, $NH_3(g)$
5	KL	$NH_2OH \cdot HCl(s)$, $NH_2OH \cdot NH_3 \cdot HCl(s)$, $NH_3(g)$
	LL′	$NH_2OH \cdot NH_3 \cdot HCl(s)$, $NH_3(g)$
	LM	$NH_2OH \cdot NH_3 \cdot HCl(s)$, $(NH_2OH \cdot NH_3 \cdot HCl) \cdot 0.5NH_3(s)$, $NH_3(g)$
	MN	$(NH_2OH \cdot NH_3 \cdot HCl) \cdot 0.5NH_3(s)$, satd. soln., $NH_3(g)$
	NO	Dil. soln., $NH_3(g)$
	NN′	Supersatd. soln., $NH_3(g)$
	KP	$NH_2OH \cdot HCl(s)$, $NH_3(g)$
	PP′[b]	$NH_2OH \cdot HCl(s)$, $NH_2OH \cdot NH_3 \cdot HCl(s)$, $NH_3(g)$
	QQ′[b]	
	L′R	$NH_2OH \cdot NH_3 \cdot HCl(s)$, $NH_3(g)$
6	MN	$NH_2OH(s)$, $(NH_2OH)_2 \cdot NH_3(s)$, $NH_3(g)$
	NO	$(NH_2OH)_2 \cdot NH_3(s)$, $NH_3(g)$
	OP	$(NH_2OH)_2 \cdot NH_3(s)$, satd. soln., $NH_3(g)$
	PQ	Dil. soln., $NH_3(g)$
	PP′	Supersatd. soln., $NH_3(g)$
	P′R	[$(NH_2OH)_2 \cdot NH_3$(liq.), $NH_3(g)$][c]
	ST	[$NH_2OH(s)$, satd. soln., $NH_3(g)$][d]
	VT	[$NH_2OH(s)$, satd. soln., $NH_3(g)$][e]
	TU	Dil. soln., $NH_3(g)$
	TT′	Supersatd. soln., $NH_3(g)$
7	WX	$N_2H_4(s)$, satd. soln., $NH_3(g)$
	XY	Dil. soln., $NH_3(g)$
	ZA	R(s), $NH_3(g)$
	AB	R(s), satd. soln., $NH_3(g)$

[a] R = $H_2NC(=O)NHNH_2$. [b] Not at equilibrium. [c] Metastable. [d] Postulated. [e] Observed.

When solid hydrazine sulfate was exposed to anhydrous ammonia gas at 30°, the initial reaction of one mole of ammonia per mole of sulfate was accompanied by a slight expansion of the solid. This was followed by an uptake of one-half mole of ammonia with concurrent formation of a thick slurry. For two equilibrium points at 30°, the corresponding compositions expressed as moles of available acidic and basic components were $(H_2SO_4)_{1.00}$, $(N_2H_4)_{1.00}$, $(NH_3)_{1.58}$ at 468 mm. and $(H_2SO_4)_{1.00}$, $(N_2H_4)_{1.00}$, $(NH_3)_{1.50}$ at 250 mm. When the pressure was lowered to *ca.* 110 mm., hydrazine was liberated; the resulting composition was $(H_2SO_4)_{1.00}$, $(N_2H_4)_{0.86}$, $(NH_3)_{1.59}$.

Confirmation of the indicated partial hydrazinolysis of ammonium sulfate[14] was obtained in a separate experiment by displacing ammonia from a sample of this salt by hydrazine vapor at 30° to form a homogeneous solution. Following removal

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(11) G. W. Watt and J. D. Chrisp, forthcoming publication.

(12) G. W. Watt and D. M. Sowards, THIS JOURNAL, **76**, 4742 (1954).

(13) G. W. Watt and W. R. McBride, *ibid.*, **77**, 1317 (1955).

(14) T. W. B. Welsh and H. J. Broderson, *ibid.*, **37**, 816 (1915).

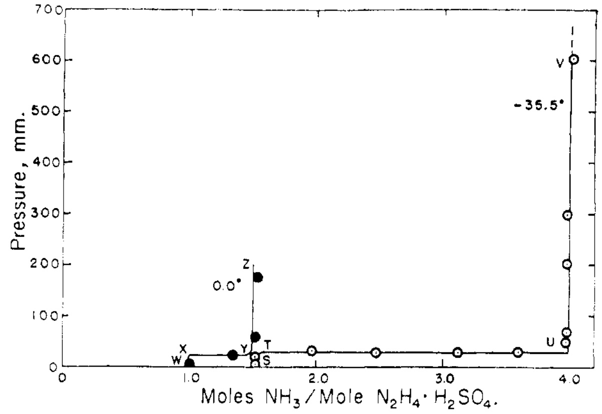

Fig. 2.—Pressure–composition isotherms at 0 and −35.5° for the reaction between solid hydrazine sulfate and gaseous ammonia at −35.5°.

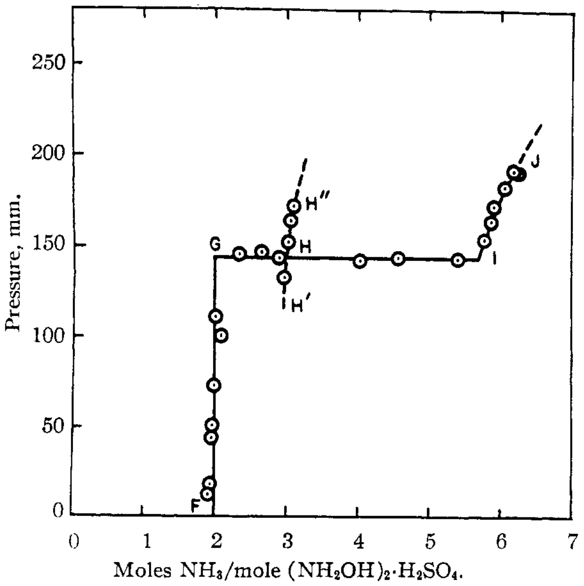

Fig. 3.—Pressure–composition isotherm at −35.5° for the reaction between solid hydroxylamine sulfate and gaseous ammonia.

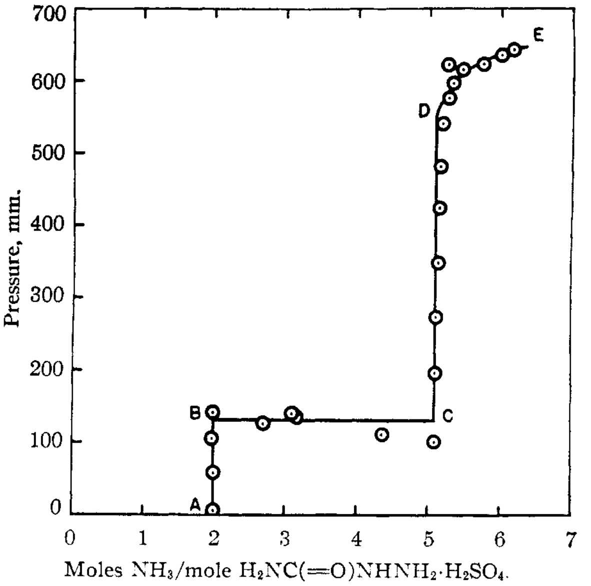

Fig. 4.—Pressure–composition isotherm at −35.5° for the ammonolysis of solid semicarbazide sulfate with gaseous ammonia.

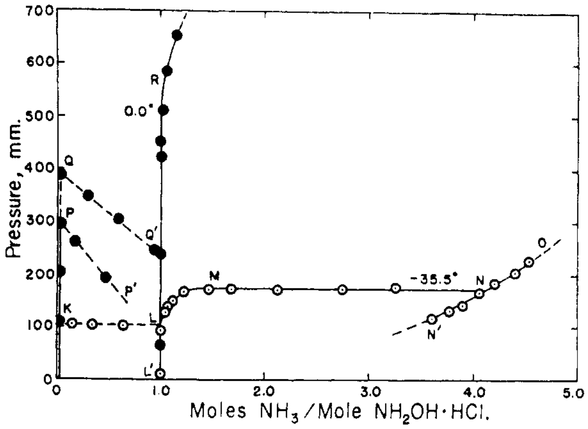

Fig. 5.—Pressure–composition isotherms at 0 and −35.5° for the reaction between solid hydroxylamine hydrochloride and gaseous ammonia.

of excess hydrazine by evacuation at a pressure of 1 mm., the final composition was $(H_2SO_4)_{1.00}$, $(N_2H_4)_{3.10}$, $(NH_3)_{0.33}$.

A brief study of the binary system hydrazine sulfate–hydrazine showed that exposure of the solid sulfate to hydrazine vapor at 30° leads to the formation of a homogeneous solution. Following removal of excess hydrazine at a pressure of 1 mm., the residual composition was found to be $(H_2SO_4)_{1.00}$, $(N_2H_4)_{2.95}$ or $(N_2H_5)_2SO_4 \cdot 0.95N_2H_4$. If, following removal of excess hydrazine, ammonia gas was added until the pressure was 750 mm., colorless needle-like crystals formed near the top of the liquid; these disappeared when the pressure was lowered to 100–150 mm. and gas evolution was observed when the pressure was lowered to 80–100 mm. Upon still further lowering of the pressure, the quartz helix balance stabilized at a new setting indicative of a net loss of hydrazine from the system. This cycle was repeated several times and the observations were the same in all cases. The composition of the final solution corresponded to $(H_2SO_4)_{1.00}$, $(N_2H_4)_{2.68}$, $(NH_3)_{0.28}$, which may be considered as $(N_2H_5)_2SO_4 \cdot 0.68N_2H_4 \cdot 0.28NH_3$.

Hydroxylamine sulfate and hydroxylamine hydrochloride reacted rapidly with two and one moles of ammonia gas, respectively, at 0°. From the resulting mixtures, hydroxylamine may be distilled *in vacuo* at 35–50° and collected in yields of 50 to 75%. In one experiment, the pressure over a dilute solution of hydroxylamine in ammonia at −28° was reduced slowly to 117 mm. Thereupon, the solution (composition, $NH_2OH \cdot 0.50NH_3$) crystallized almost instantaneously and completely to form needle-like crystals (composition, $NH_2OH \cdot 0.48NH_3$). An approximate dissociation pressure for the hemiammoniate at −28° is 20 mm.

When semicarbazide sulfate was treated with gaseous ammonia at 0° and atmospheric pressure, reaction was incomplete. Upon lowering the temperature to −35°, the solid expanded to *ca.* 8

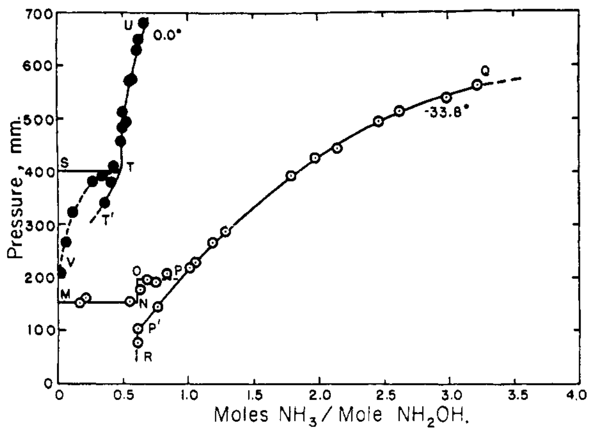

Fig. 6.—Pressure–composition isotherms at 0 and −33.8° for the system hydroxylamine–ammonia.

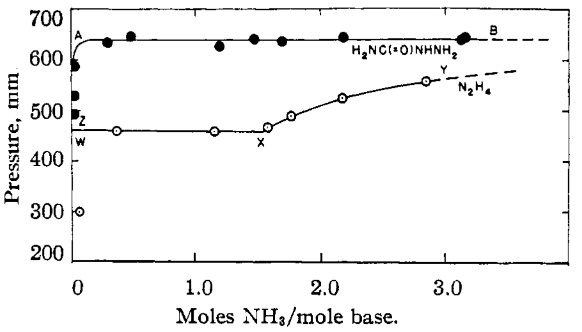

Fig. 7.—Pressure–composition isotherms at −35.5° for the systems hydrazine–ammonia and semicarbazide–ammonia.

times its original volume and reaction proceeded to completion. When the temperature was raised to 30°, the measured retention of ammonia in the system was 2.01 moles per mole of semicarbazide sulfate used. This led to the following quite convenient method for the preparation of pure semicarbazide. Semicarbazide sulfate (4.52 g.) is treated with excess liquid ammonia for 0.5 hr., the solvent is evaporated, and the residual ammonia is displaced from the solid products by a stream of dry air. The solid residue is leached with three 50-ml. portions of hot absolute ethanol and filtered to remove ammonium sulfate. Evaporation of the alcohol provides 1.90 g. (97% yield) of semicarbazide, m.p. 94–96°.

Discussion

It is evident from the data of Table I that the ammonolysis of the sulfates of bases such as hydrazine with anhydrous liquid ammonia provides the free bases in substantially quantitative yields. Both the yield and the purity of the products are quite high even when the reactions are carried out on a very small scale. Losses of hydrazine and methylhydrazine (Table I) are attributed to volatilization, and if the precautions given for the case of hydrazine are not observed, the loss may amount to as much as 25%.

The use of pressure–composition isotherms to follow the course of reactions between gaseous ammonia and solid salts potentially susceptible to ammonolysis has certain distinct advantages. Particularly over the temperature range involved in the present studies, this technique may permit one to determine whether ammonolysis is preceded by ammoniation, whether both occur simultaneously, and to determine accurately the number of moles of ammonia consumed in the solvolytic reaction on the basis of the extent to which the addition of ammonia is irreversible. On the basis of known or concurrently measured dissociation pressures of ammoniates, one may also detect and characterize reaction intermediates as well as solvates of the final reaction products.

As shown in Fig. 2, for example, curve ST apparently corresponds to the partial ammonolysis of monohydrazine sulfate by a gas–solid reaction to form ammonium sulfate, accompanied by the formation of the 1-ammoniate of dihydrazine sulfate (Table II). That ammonium sulfate is not ammoniated under these conditions of pressure follows from the fact that it forms only a 3-ammoniate[7] which has a dissociation pressure of 137 mm. at −35.5°. The other solid present would be $(N_2H_5)_2SO_4 \cdot NH_3$ by analogy with the corresponding 1-hydrate[15,16] and the 1-hydrazinate suggested by the experiments described above. Another possible formulation of the data that suggest the 1-ammoniate of dihydrazine sulfate would be $(N_2H_5)(NH_4)SO_4 \cdot N_2H_4$, but if this solvate were formed, hydrazine rather than ammonia would be expected to be liberated upon elevation of the temperature to 0°, whereas ammonia is liberated (curve XY). Alternatively, phase rule considerations do not rule out the possible existence of a double salt $(N_2H_5)_2SO_4 \cdot (NH_4)_2SO_4 \cdot NH_3$ as the solid phase corresponding to the conditions specified by curve ST. An analogous double salt is postulated (Table II) to account for continuous ammoniation (curve TU) under conditions not favorable to the ammoniation of ammonium sulfate and not known to favor more extensive ammoniation of dihydrazine sulfate. Similar double salts, *e.g.*, $N_2H_6SO_4 \cdot (NH_4)_2SO_4$ and $(N_2H_5)_2SO_4 \cdot M^{II}SO_4$ (where M is a divalent metal ion) have been reported by Sommer and Weise[15] and by Curtius and Schrader,[17] respectively. Although it is assumed that this double salt is formed reversibly by a gas–solid reaction at −35.5° (curve TU), interpretation of curve ST as involving the ammoniated double salt, $[(N_2H_5)_2SO_4 \cdot (NH_4)_2SO_4] \cdot NH_3$, is not excluded. Supporting evidence for the absence of ammonium sulfate as a separate phase is found in the fact that there is no additional uptake of ammonia when the pressure is increased well above the dissociation pressure of the 3-ammoniate of this salt (curve UV). When the temperature of the system in equilibrium at −35.5° (curve ST) is raised to 0° (curve XY), deammoniation to the extent of 0.5 mole of ammonia occurs. Following this deammoniation, an X-ray diffraction pattern showed all of the diffraction maxima characteristic of ammonium sulfate together with maxima that may be attributed to either dihydrazine sulfate or its 1-hydrate. Finally,

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[15] F. Sommer and K. Weise, *Z. anorg. Chem.*, **94**, 51 (1916).

[16] B. E. Christensen and E. C. Gilbert, THIS JOURNAL, **56**, 1897 (1934).

[17] T. Curtius and F. Schrader, *J. prakt. Chem.*, [2] **50**, 311 (1894); *cf.*, L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 173.

it should be pointed out that the complete ammonolysis of hydrazine sulfate (equation 1) with *liquid* ammonia probably proceeds through the intermediation of the double salt postulated above, *i.e.*

$$2N_2H_4\cdot H_2SO_4(s) + 8NH_3(l) \longrightarrow [(N_2H_5)_2SO_4\cdot(NH_4)_2SO_4]\cdot 6NH_3(s) \quad (2)$$

$$[(N_2H_5)_2SO_4\cdot(NH_4)_2SO_4]\cdot 6NH_3(s) + 2NH_3(l) \longrightarrow 2(NH_4)_2SO_4\cdot 3NH_3(s) + 2N_2H_4 \quad (3)$$

The initial change that occurs when solid hydroxylamine sulfate is contacted with anhydrous ammonia gas at −35.5° is the irreversible ammonolysis to form the free base and ammonium sulfate (Fig. 3, curve FG), in contrast to the preceding case in which the initial reaction involved ammonolysis accompanied by a reversible ammoniation. Curve GH is interpreted as corresponding to the formation of the hitherto unreported hemiammoniate of hydroxylamine, $(NH_2OH)_2\cdot NH_3$ (dissociation pressure, 144 mm. at −35.5°), and curve HI to the formation of the 3-ammoniate of ammonium sulfate. Since the dissociation pressures of these two systems are so nearly the same, further confirmation of the hemiammoniate is required. This is provided by the pressure–composition isotherm for the binary system hydroxylamine–ammonia (Fig. 6) which confirms the formation of the hemiammoniate with a dissociation pressure of 153 mm. at −33.8°. That this ammoniation precedes that of the ammonium sulfate is also indicated by the metastable system corresponding to curve H′H″. As shown by Fig. 5 (curve KL) the behavior of solid hydroxylamine hydrochloride toward ammonia gas is different in that irreversible ammoniation does not occur at pressures below 103 mm. at −35.5°. Irreversibility along curve LK is shown by curve LL′. If the irreversible ammoniation (curve KL) resulted in the formation of ammonium chloride and the free base, it would be expected that ammonium chloride would be ammoniated at least to the extent of its lowest known ammoniate,[13] $NH_4Cl\cdot 3NH_3$ (dissociation pressure, 94 mm. at −35.5°). Since reaction to an extent greater than that involving one mole of ammonia (curves LM and MN) does not lead to a solid phase having a dissociation pressure of 94 mm., it follows that neither ammonium chloride nor its ammoniates exist as a separate entity under these conditions. It is considered therefore that the initial irreversible ammoniation produces the mixed salt, $NH_2OH\cdot NH_3\cdot HCl$, which is analogous to the previously reported[18] $(NH_2OH)_2\cdot HCl$. Similarly, for the product of the reaction that occurs under the conditions defined by curve LM, there seems no alternative but to postulate the formation of an ammoniate of the mixed salt, $(NH_2OH\cdot NH_3\cdot HCl)\cdot 0.5NH_3$. As shown by Fig. 5 and Table II, further addition of ammonia at −35.5° leads to a homogeneous solution. At 0°, on the other hand, it might be expected that hydroxylamine hydrochloride would be irreversibly ammonolyzed to form hydroxylamine and ammonium chloride (curve L′R). The possible formation of a mixed salt, however, is not precluded since as shown by Fig. 6 (curve ST), if the free base were present under these conditions it would be expected to form a hemiammoniate and this is not observed. Therefore it must be concluded that, within the limitations inherent in this experimental method, the formation of the mixed salt is the preferred interpretation. If, following the reaction at 0°, the temperature is raised to 35–50° where hydroxylamine has an appreciable vapor pressure, the free base may be distilled and collected as a substantially pure compound. Thus if the mixed salt is formed at 0°, the limit of its thermal stability must be exceeded upon raising the temperature to 35°.

The interaction of solid semicarbazide sulfate and gaseous ammonia at −35.5° is unusual in that it leads directly to complete ammonolysis of the sulfate (Fig. 4, curve AB). As pointed out above, this serves as a basis for a convenient method for the preparation of the free base. The remainder of the pressure–composition isotherm corresponds only to the ammoniation of ammonium sulfate and the formation of a saturated solution of semicarbazide (compare, Fig. 7, curve AB). At either higher temperatures or lower pressures, ammonolysis of such salts by a solid–gas reaction is frequently incomplete. Quantitative conversion is realized under the conditions of these experiments apparently owing to the fact that the solid expands markedly during ammoniation of the ammonium sulfate, thus providing optimum contact between the solid and gaseous reactants.

Results obtained in the study of the pressure–composition isotherms for systems involving the free bases and gaseous ammonia (Figs. 6 and 7) do not require extensive comment beyond that included above. As shown by Fig. 6, the dissociation pressure of the hemiammoniate of hydroxylamine is 153 mm. at −33.8° and approximately 400 mm. at 0°. It is of interest to note that deBruyn[19] has reported that a saturated solution of hydroxylamine in ammonia contains 20% NH_3 at 15° and 26% NH_3 at 0°; the ammonia content of $(NH_2OH)_2\cdot NH_3$ is 20.5%. With decrease in pressure, a dilute solution of hydroxylamine in ammonia (Fig. 6, curve QP) first forms a supersaturated solution (curve PP′) followed by a liquid phase (curve P′R), the composition of which remains constant for an unpredictable time interval. Thereafter, the metastable system undergoes violent deammoniation to form solid hydroxylamine. When, however, a dilute solution of hydroxylamine in ammonia is treated similarly at −28°, the behavior described above is not observed and the hemiammoniate of hydroxylamine crystallizes readily. Consequently, neither the dissociation pressure nor the phases for this system is directly comparable to the invariant systems corresponding to curve GH, Fig. 3, or curve MN, Fig. 6. It is believed that a transition point for these two invariant systems must exist in the region of −30°.

From Fig. 7 and Table II it is evident that neither hydrazine nor semicarbazide forms solvates with ammonia. For the system hydrazine–ammonia, the pressure corresponding to the invariant system is 465 mm. at −35.5°. This is in good

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(18) W. Lossen, *Ann.*, **160**, 242 (1871).

(19) L. deBruyn, via A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Third Ed., Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 1040.

agreement with the values of 462 mm. at −36° and 480 mm. at −35° reported by Friedrichs.[20] For the system semicarbazide–ammonia, the corresponding pressure is 640 mm. at −35.5°.

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[20] F. Friedrichs, *Z. anorg. allgem. Chem.*, **127**, 221 (1923).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

The Anodic Oxidation of Some Active Metals in Pyridine

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The anodic oxidation of magnesium, aluminum, beryllium and cadmium in pyridine solutions containing a non-oxidizing inorganic electrolyte results in the conversion of the metals to their normal, stable oxidation states. However, when certain organic additives which are potential electron acceptors also are present in the anolyte, the metals enter solution with initial mean valence numbers significantly lower than their normal values. On the basis of valence number measurements, it has been possible to arrange the metals in an activity series, and also to construct an apparent electron affinity series for the organic additives. Indium and thallium are anodically oxidized in lithium chloride–pyridine solutions to species which are lower valent than that corresponding to removal of three valence electrons, the former element giving initial mean valence numbers in the neighborhood of 2.4, and thallium being converted essentially quantitatively to the unipositive state.

In a recent communication from this Laboratory[1] it was demonstrated that upon electrolysis of a solution of sodium iodide in pyridine between magnesium electrodes in a divided cell, magnesium is oxidized anodically to its familiar dipositive state. However, when benzophenone also is present in solution, the magnesium dissolves at the anode with an initial mean valence number (V_i) appreciably less than two. Although no lower state of this element is detectable in solution after electrolysis, hydrolysis of the anolyte yields benzopinacol, a reduction product of benzophenone, in quantity corresponding to the oxidation of the magnesium from its measured mean valence state to the common +2 state. It was noted further in the previous paper that initial mean valence numbers less than two also are obtained for magnesium when the metal is anodically oxidized in the presence of other organic compounds, *e.g.*, benzaldehyde, nitrobenzene and benzonitrile, which are susceptible to reduction.

The present report is concerned primarily with the anodic oxidation of the active metals magnesium, beryllium, cadmium and aluminum in electrolytic pyridine solutions, both in the presence and absence of organic substances potentially capable of undergoing reduction. Some observations on the behavior of indium and thallium in the absence of organic additives also are described. The initial mean valence number, V_i, of the cation formed has been employed to characterize the anodic behavior of the various metals, since it gives a measure of the extent of departure from normal current efficiency. This quantity has been calculated, as previously described,[1] by means of the equation

$$V_i = \frac{\text{wt. of Ag deposited in coulometer} \times \text{at. wt. of metal}}{107.88 \times \text{wt. of metal lost from anode}}$$

Experimental

Materials.—Magnesium and aluminum were obtained in rod form from the Aluminum Co. of America; the former metal had a purity of 99.8% and the latter of 99.99%. Beryllium, purchased from the Brush Beryllium Company was described as "of highest purity." Cadmium was J. T. Baker reagent grade. Indium, supplied by the Fairmount Chemical Company, was of 99.9% purity, and thallium was obtained from the Fisher Scientific Company in the form of purified sticks. Cylindrical electrodes approximately 5.5 cm. long and 0.5 cm. in diameter were constructed from these metals. The sodium iodide and lithium chloride employed as electrolytes were of reagent grade and were dried at 110° before use. Pyridine was Mallinckrodt analytic reagent grade, and was dried over anhydrous barium oxide for several weeks, fractionally distilled through a 45-cm. packed column at atmospheric pressure, and stored over additional anhydrous barium oxide until used. The nitrobenzene, benzaldehyde, bromobenzene, benzonitrile and 1-heptyne were all originally of high purity and were dried and fractionally distilled before use. The benzophenone, *trans*-stilbene and ethyl benzoate, obtained from Eastman Kodak Co., were of White Label quality and were used without further purification.

Apparatus and Procedure.—The source of direct current was a full-wave mercury tube rectifier capable of supplying up to 1000 v. The quantity of electricity passed through the circuit was determined by means of a silver coulometer. The electrolyses were carried out in a divided cell similar to that described by Davidson and Jirik,[2] with compartments of a capacity of about 100 ml. each. The cell was immersed in a constant temperature bath maintained at 40 ± 0.5°.

All electrodes were thoroughly cleaned, washed, dried and weighed before use; the magnesium, beryllium, cadmium, thallium and indium electrodes were cleaned by treatment with dilute nitric acid solution, the aluminum electrodes with dilute sodium hydroxide solution. The sodium iodide–pyridine solutions (0.5 *m*) and lithium chloride–pyridine solutions (2.0 *m*) were prepared with a minimum exposure to air and moisture. When an electrolysis was performed in the presence of an organic additive, the anolyte and catholyte contained equivalent quantities of this substance. In each electrolysis experiment the metal used as anode was also employed as cathode. Dry oxygen-free nitrogen was passed over the surface of both anolyte and catholyte during electrolysis and the current density was maintained between 0.004 and 0.007 amp. per sq. cm., corresponding to an applied potential of 20 to 35 v. for the sodium iodide–pyridine solutions and 130–190 v. for the lithium chloride–pyridine solutions. The time of electrolysis varied from 10 minutes to 2 hours; the variation had little effect on the initial mean valence numbers obtained.

Some remarks regarding choice of electrolyte are pertinent at this point. Sodium iodide, although not so soluble as lithium chloride, appears to be a better conductor in pyridine. With sodium iodide, however, there exists the considerably greater possibility that the oxidation of the anion may compete with the dissolution of metal as the anode reaction. On the other hand, when lithium chloride is employed as electrolyte there is the definite possibility that at current densities sufficiently high to obtain a reasonable rate of dissolution of the anode, sparking may occur, and

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[1] M. D. Rausch, W. E. McEwen and J. Kleinberg, THIS JOURNAL, **76**, 3622 (1954).

[2] A. W. Davidson and F. Jirik, *ibid.*, **72**, 1700 (1950); Fig. 1.