concentrations usually used for developers, most of the hydrochinon would unite with the alkali to form the monoquinolate if the sulfite were not present.

4. When sulfite and carbonate are both present, they appear to divide the hydrochinon between them.

5. Complete oxidation of a hydrochinon developer may be accomplished without changing its alkalinity.

6. One molecule of metol appears to be capable of combining with three molecules of sodium hydroxide, in the absence of a sulfite.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY.]

REACTIONS IN LIQUID AMMONIA. II.

1. THE ACTION OF ACID AMIDES ON THE AMIDES, IMIDES AND NITRIDES OF CERTAIN HEAVY METALS. 2. METALLIC SALTS OF ACID AMMONO ESTERS.

BY EDWARD C. FRANKLIN.

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Introduction.

Some years ago Franklin and Stafford[1] found that certain acid amides and potassium amide react with each other, when dissolved in liquid ammonia, in a manner strikingly similar to the familiar interaction of acids and bases in aqueous solutions.

Typical examples of such analogous reactions are represented by the equations,

$$C_6H_5COOH + KOH = C_6H_5COOK + H_2O$$
$$C_6H_5CONH_2 + KNH_2 = C_6H_5CONHK + NH_3$$
$$C_6H_5CONH_2 + 2KNH_2 = C_6H_5CONK_2 + 2NH_3.$$

The first equation represents the action of an aquo acid on an aquo base to form an aquo salt, the second and third, the action of an ammono acid on an ammono base to form ammono salts.

In view of the analogies thus indicated, and of others given in detail elsewhere,[2] the writer has long had in mind attempts to prepare ammono salts of some of the heavier metals by the action of liquid ammonia solutions of ammono acids on the insoluble amides, imides or nitrides of the metals. Such reactions are, of course, in principle not different from those studied by Franklin and Stafford referred to above, but at the same time it is interesting and important to show that salts of the heavy metals may be prepared in this way.

The amide of silver,[3] the imides of lead[1] and copper[4] and the nitride of

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[1] *Am. Chem. J.*, 28, 95 (1902).

[2] *Ibid.*, 47, 285 (1912).

[3] THIS JOURNAL, 27, 833 (1905).

[4] *Ibid.*, 29, 656 (1907).

thallium,[1] since they may be readily prepared in a pure state, were chosen as insoluble bases, while acetamide, benzenesulfonamide and *p*-toluenesulfonamide—the one a very weak and the other two much stronger ammono acids—were the acids conveniently at hand for use in the experiments to be described. Mercuric nitride, although easily prepared[2] in a state of purity, was not used for the reason that mercuric salts of the acid amides are readily formed in aqueous solution and as a consequence are already known in large number. That they may be as readily prepared from liquid ammonia solutions is practically certain.

Ammono Salts of Certain Heavy Metals.

The silver amide, cuprous and lead imides and thallous nitride used in the experiments described below were obtained pure by thoroughly washing the precipitates formed by the action of potassium amide upon liquid ammonia solutions of soluble salts of the respective metals. Since, however, the manipulative details whereby these substances may be prepared have already been published[3] it is unnecessary to repeat a description of them here.

Silver Ammonoacetate,[4] $CH_3CONHAg$, **and the Diammonate,** $CH_3CONHAg.2NH_3$.—When a solution of acetamide in liquid ammonia is poured upon silver amide, prepared by the interaction of approximately equivalent quantities of potassium amide and silver nitrate, the ammono base dissolves to a clear, colorless solution. After proper adjustment of the concentration of the solution thus formed, a crop of beautiful crystals separates when the solution is cooled in a bath of liquid ammonia. A product, obtained in the manner thus described, was recrystallized twice from pure ammonia distilled over from the second leg of the reaction tube. When, however, the attempt was made to dissolve the crystals a third time they disintegrated to a smeary mass which clung to the walls of the reaction tube and refused to go into solution, but which became crystalline again on evaporating off the greater portion of the solvent. In view of the fact that acetamide is a very weak acid, it may be concluded that this behavior of the salt is indicative of ammonolysis in the manner represented by the equation $CH_3CONHAg + NH_3 \rightleftarrows CH_3CONH_2 + AgNH_2$.

Preparatory to analysis the specimen of well crystallized salt was exposed over night to the action of water vapor, then dissolved in dilute sulfuric acid and removed from the reaction tube after the manner described in the papers referred to above. The silver in an aliquot part

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[1] *J. Phys. Chem.*, 16, 683 (1912).

[2] This Journal, 27, 835 (1905).

[3] *Loc. cit.*

[4] Strecker, many years ago (*Ann. Chem.*, 103, 324 (1857)), obtained acetamide silver as crystalline scales (Schuppen) from a solution formed by dissolving freshly precipitated silver oxide in aqueous acetamide.

of the solution was determined as the chloride, the nitrogen in another portion by the method of Kjeldahl.

The specimen, dried in vacuum at 20°, weighed 0.2926 g. One-half gave 0.1054 g. AgCl and two-tenths gave 0.0124 g. N.

Calc. for $CH_3CONHAg.2NH_3$: Ag, 54.0, N, 21.0; found: 54.2 and 21.2.

Silver ammonoacetate is, therefore, shown to be formed by the action of acetamide on silver amide in accordance with the equation

$$AgNH_2 + CH_3CONH_2 = CH_3CONHAg + NH_3.$$

The salt is fairly soluble in liquid ammonia and separates from cold, concentrated solutions in the form of beautiful crystals containing two molecules of ammonia.

Thallous Ammonoacetate, $CH_3CONHTl$, **and the Diammonate,** $CH_3CONHTl.2NH_3$.—Thallium nitride, which is precipitated when thallium nitrate and potassium amide are brought together in liquid ammonia solution, dissolves readily in a solution of acetamide to form a salt which separates in the form of well developed crystals when the fairly concentrated solution is cooled to a low temperature.

Preparation I.—The nitride obtained from 1.33 g. of thallous nitrate was treated with a liquid ammonia solution of one equivalent of acetamide. The solution of acetamide thallium formed was decanted from a small quantity of undissolved thallium nitride, concentrated and cooled until a crop of crystals was obtained. The specimen of salt was then recrystallized twice, hydrolyzed by water vapor and dissolved in dilute sulfuric acid preparatory to removal from the reaction tube for analysis. The thallium in a portion of the solution was determined as the iodide, the nitrogen in another portion by the method of Kjeldahl.

Dried in vacuum at 120° the specimen weighed 0.9258 g. One-half gave 0.5683 g. TlI, the other half gave 0.0248 g. N.

Preparation II.—The thallium nitride from 1.33 g. of thallous nitrate was treated with a considerable excess of acetamide, with the result that the precipitate was completely dissolved. Otherwise this experiment was a duplicate of the preceding.

Dried in vacuum at —40°, the specimen weighed 1.0406 g. Dried at 120°, it weighed 0.9212 g. One-half of the specimen after heating to the latter temperature gave 0.0246 g. N. Four-tenths gave 0.4604 g. TlI.

Calc. for $CH_3CONHTl$: Tl 77.8, N 5.4; found: (I) 75.8[1] and 5.4; (II) 77.1 and 5.4.

Calc. for $CH_3CONHTl.2NH_3$: $2NH_3$ 11.5; found: 11.5.

The action of a liquid ammonia solution of acetamide on thallous nitride is, therefore, represented by the equation

$$Tl_3N + 3CH_3CONH_2 = 3CH_3CONHTl + NH_3.$$

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[1] The low weight of the thallium iodide is probably explained by the fact that the weighing of the prepared Gooch crucible was inadvertently omitted and as a result the weight of the thallium iodide was taken as the loss on ignition.

The salt is very soluble in liquid ammonia at laboratory temperatures but is much less soluble at lower temperatures. It separates from solution in the form of beautiful, colorless crystals, containing two molecules of ammonia of crystallization, which as they approach laboratory temperature, melt and give off ammonia. At 120° the removal of ammonia is complete and at the same time a small quantity of sublimate, presumably acetamide resulting from the ammonolysis of the salt, appears in the upper, cooler portion of the specimen tube. It is interesting to note that the least trace of air gaining entrance to the tube causes a blackening of the salt in a manner similar to that observed in the case of potassium ammonothallite.[1]

Lead Ammonoacetate.—A solution of acetamide in liquid ammonia does not dissolve lead imide but converts it—slowly if the solution is only moderately concentrated, rapidly if very concentrated—into a pure white, amorphous product which settles well and is easily washed. After a few washings the precipitate begins to lose its pure white color and gradually takes on a color resembling that of lead imide, an indication, presumably, of the ammonolytic decomposition of the salt. The one specimen of this salt prepared was lost by the bursting of the container.

Silver Ammonobenzenesulfonate, $C_6H_5SO_2NHAg$, **the Monammonate,** $C_6H_5SO_2NHAg.NH_3$, **and the Diammonate,** $C_6H_5SO_2NHAg.2NH_3$.—Silver amide dissolves readily in a liquid ammonia solution of benzenesulfonamide to give a salt which separates in crystalline form when the solution, at proper concentration, is cooled in a bath of liquid ammonia. For analysis the salt was hydrolyzed by exposure to water vapor and dissolved in dilute sulfuric acid.

Preparation I.—The silver amide obtained from 0.85 g. of silver nitrate was dissolved in a solution of somewhat more than an equivalent amount of benzenesulfonamide and from the solution thus formed a crop of crystals (*a*) was obtained which was recrystallized once for analysis. From the mother liquor a second crop (*b*) was separated which was also once recrystallized.

Specimen (*a*) dried in vacuum at 130° weighed 0.5060 g. One-half gave 0.1327 g. AgCl, the other half gave 0.0193 g. N.

Specimen (*b*) dried in vacuum at —40° weighed 0.4435 g. Dried at 20° it weighed 0.4172 g. Dried at 200° it weighed 0.3914 g. One-half of the specimen dried at the highest temperature gave 0.1031 g. AgCl, the other half gave 0.0111 g. N.

Preparation II.—The silver amide formed by the action of an equivalent quantity of potassium amide on one gram of silver nitrate was dissolved in a solution of somewhat more than one equivalent of benzenesulfonamide. The crop of crystals obtained was recrystallized once for analysis.

Dried in vacuum at —40° the specimen weighed 1.0689 g. After heating to 20° it weighed 1.0054 g. and after heating to 200° it weighed 0.9433 g. Two-tenths of the

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[1] *J. Phys. Chem.*, **16**, 690 (1912).

specimen, dried at 200°, gave 0.1624 g. AgI. In addition 0.0055 g. metallic silver, resulting from some reducing action in the container, was recovered, thus making the total silver present in the specimen 0.3795 g. Three-tenths of the specimen gave 0.0150 g. N.

Preparation III.—In order to avoid some slight decomposition of the salt, brought about by the high temperature necessary for the removal of the second molecule of ammonia, the specimen was dried for analysis at 20°. When the salt was dissolved in dilute sulfuric acid, preparatory to analysis, a perfectly clear, colorless solution resulted. In all respects, other than drying at 20° instead of at 200°, the conduct of this experiment was identical with that described under Preparation II.

The specimen dried in vacuum at —40° weighed 0.9602 g. Dried at 20° it weighed 0.9057 g. One-half of the specimen dried at 20° gave 0.2290 g. AgCl, the other half gave 0.0450 g. N.

	Calc. for $C_6H_5SO_2NHAg$.	Found. Ia.	Ib.	II.	III.
Ag	40.8	39.5	39.8	40.2	....
N	5.3	7.6	5.7	5.3	....
	Calc. for $C_6H_5SO_2NHAg.NH_3$.				
Ag	38.4	....	....	....	38.1
N (total)	10.0	....	....	....	10.0
1 NH_3	6.1	....	6.2	6.2	....
	Calc. for $C_6H_5SO_2NHAg.2HN_3$.				
2 NH_3	11.4	....	11.7	11.7	....
1 NH_3	5.7	....	....	....	5.7

It is thus shown that silver amide dissolves in a liquid ammonia solution of benzenesulfonamide to form a silver salt of the acid amide in accordance with the equation,

$$AgNH_2 + C_6H_5SO_2NH_2 = C_6H_5SO_2NHAg + NH_3.$$

Benzenesulfonamide silver separates from liquid ammonia solutions in the form of beautiful crystals containing two molecules of ammonia of crystallization. Of this ammonia one molecule is lost on warming to laboratory temperature, the other is expelled at temperatures around 200°. At the higher temperature, however, the salt undergoes slow decomposition, and there is a white sublimate, presumably of benzenesulfonamide, seen to collect in the upper, cooler portion of the specimen tube. The salt is extremely soluble in liquid ammonia at laboratory temperatures, much less soluble at low temperatures. Its solution in liquid ammonia shows the phenomenon of supersaturation in a striking degree. The salt is practically unaffected by exposure to light. It is hydrolyzed in the presence of water.

Preparation of Silver Ammonobenzenesulfonate by the Action of Benzenesulfonamide in Solution in Liquid Ammonia on Silver Oxide.—Silver oxide, which is insoluble in liquid ammonia, dissolves readily in liquid ammonia solutions of benzenesulfonamide. A clear, colorless solution resulting from the treatment of 1 g. of silver oxide with slightly more than the equivalent quantity of the acid amide, after proper adjustment of the concentration, deposited a crop of beautiful needle-like crystals on cooling to the temperature of a liquid ammonia bath. After two recrystallizations the salt was treated first with water, then dissolved in dilute sulfuric acid for analysis.

Dried in vacuum at —40° the specimen weighed 1.2493 g. Dried at 20° it weighed 1.1851 g. One-half of the specimen dried at 20° gave 0.2977 g. AgCl, the other half gave 0.0471 g. N.

Calc. for $C_6H_5SO_2NHAg.NH_3$: Ag 38.4, N 10.0; found: 37.9 and 8.0.[1]
Calc. for $C_6H_5SO_2NHAg.2NH_3$: 1 NH_3 5.7; found: 5.2.

The action of benzenesulfonamide in solution in liquid ammonia on silver oxide is, therefore, represented by the equation,

$$2C_6H_5SO_2NH_2 + Ag_2O = 2C_6H_5SO_2NHAg + H_2O,$$

and the product obtained is identical with that formed by dissolving silver amide in benzenesulfonamide solution.

Thallous Ammonobenzenesulfonate, $C_6H_5SO_2NHTl$, **the Monammonate,** $C_6H_5SO_2NHTl.NH_3$, **and the Diammonate,** $C_6H_5SO_2NHTl.2NH_3$. —Thallium nitride dissolves readily in a solution of benzenesulfonamide to form a solution from which a well crystallized product may be obtained at low temperatures when the very strong tendency to form supersaturated solutions is overcome either by lucky chance or by some one of the devices known to be more or less effective to this end. After obtaining a crop of crystals the mother liquor was poured off and fresh solvent distilled back upon the crop of crystals in quantity sufficient to dissolve it when the temperature was allowed to rise. The dissolution of the crystals was carefully watched and before the last crystal remnant had disappeared, the solution was cooled to develop a new crop of crystals. The crystals grow beautifully when there are crystalline nuclei present in the solution, but in case the solid is once completely dissolved, then it becomes a difficult matter to initiate crystallization again. After three recrystallizations the preparation was submitted to the action of water vapor, then treated with liquid water, and finally dissolved in dilute sulfuric acid for analysis.

The specimen dried in vacuum at —70° weighed 1.4764 g. Dried at —40° its weight was, 1.4067 g.; at 20°, 1.3997 g.; and at 100°, 1.3422 g. One-half of the specimen dried at 100° gave 0.6090 g. TlI, the other half gave 0.0261 g. N.

Calc. for $C_6H_5SO_2HNTl$: Tl 56.6, N 3.9; found: 56.1 and 3.9.
Calc. for $C_6H_5SO_2NHTl.NH_3$: 1 NH_3 4.5; found: 4.1 and 4.6.
Calc. for $C_6H_5SO_2NHTl.2NH_3$: 2 NH_3 8.6; found: 9.1.

These results show that benzenesulfonamide thallium is formed when

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[1] Losses of ammonia were known to occur in making this determination.

thallous nitride is dissolved in a solution of benzenesulfonamide in liquid ammonia. The reaction is represented by the equation,

$$3C_6H_5SO_2NH_2 + Tl_3N = 3C_6H_5SO_2NHTl + NH_3.$$

Thallium ammonobenzenesulfonate separates from concentrated solutions at low temperatures as well-formed crystals containing two molecules of ammonia of crystallization, which are lost stepwise as the temperature is allowed to rise. No attempts have been made to determine the vapor tension of these or of any of the other ammonates made during the course of this investigation. Solutions of the salt show, in a very conspicuous manner, the phenomenon of supersaturation. In a single instance crystallization was initiated at —40°, but no one of a considerable number of other attempts to bring about crystallization was successful until, by the use of liquid air, the operator was enabled to cool the solution to temperatures in the neighborhood of —70°. The very concentrated solutions become so viscous, when cooled to low temperatures, as to become practically solid without the least indication of crystallization. Once started, however, crystallization from a supersaturated solution proceeds in a manner beautiful to behold.

Thallous Ammono-*p*-toluenesulfonate, $CH_3C_6H_4SO_2NHTl$, **and the Monammonate,** $CH_3C_6H_4SO_2NHTl.NH_3$. — Thallous nitride dissolves readily in a liquid ammonia solution of *p*-toluenesulfonamide to form a clear, colorless solution from which a thallium salt of the acid amide may be crystallized by strongly cooling the properly concentrated solution.

Preparation I.—From a solution formed by dissolving the thallium nitride from 1.33 g. of thallium nitrate in a solution of somewhat more than one equivalent of *p*-toluenesulfonamide a crop of crystals was obtained which was recrystallized once, hydrolyzed and dissolved in dilute sulfuric acid for analysis.

Two-tenths of the specimen, dried in vacuum at 140°, weighed 0.4807 g., gave 0.0854 g. TlI. One-half of the specimen gave 0.0096 g. N.

Preparation II.—From a solution formed by dissolving the thallium. nitride from 1 g. of thallium nitrate in slightly more than one equivalent quantity of the acid amide, two crops of crystals, each of which was recrystallized once, were obtained and submitted to analysis with the following results:

Specimen (*a*) dried in vacuum at 20° weighed 0.2785 g. Heated to 118°, at which temperature the salt showed signs of melting, it weighed 0.2666 g. Four-tenths of the specimen dried at 118° gave 0.0935 g. TlI and 0.0040 g. N.

Specimen (*b*) dried in vacuum at —40° weighed 0.1619 g. Dried at 140° it weighed 0.1522 g. The whole specimen, dried at the latter temperature, gave 0.1363 g. TlI and 0.0056 g. N.

	Calc. for $CH_3C_6H_4SO_2NHTl$.	Found. I.	IIa.	IIb.
Tl	54.5	54.6	54.0	55.2
N	3.7	4.0	3.8	3.7
	Calc. for $CH_3C_6H_4SO_2NHTl.NH_3$.			
1 NH_3	4.3	....	4.3	6.0

p-Toluenesulfonamide thallium is, therefore, formed when thallium nitride is dissolved in a solution of the acid amide in accordance with the reaction represented by the equation,

$$3CH_3C_6H_4SO_2NH_2 + Tl_3N = 3CH_3C_6H_4SO_2NHTl + NH_3.$$

The salt is very soluble in liquid ammonia at laboratory temperatures, much less so at lower temperatures. At low temperatures it separates from concentrated solutions with, probably,[1] two molecules of ammonia of crystallization, although this has not been proved of the specimens prepared. Dried at 20° the salt retains one molecule of ammonia. The anammonous salt melts at some temperature below 140°.

Cuprous Ammono-*p*-toluenesulfonate Diammonate, $CH_3C_6H_4SO_2NHCu.2NH_3$, **and Cupric Ammono-*p*-toluenesulfonate,** $(CH_3C_6H_4SO_2NH)_2Cu$.—Fitzgerald[2] found when a solution of cupric nitrate is treated with potassium amide that a precipitate is formed which, after being heated in vacuum to 160°, has the composition represented by the formula Cu_3N. Moreover the nitrogen set free during the reaction was determined and found to be evolved in an atomic ratio to copper always somewhat greater than one to three. It was, therefore, concluded that the reduction of the cupric to cuprous copper takes place during the reaction between the potassium amide and cupric nitrate and not during the heating of the precipitate. Proceeding on the assumption that Fitzgerald's precipitate is a cuprous compound, it was expected that it would dissolve in acid amide solutions to form a cuprous salt. However, when the supposedly pure cuprous imide was dissolved in *p*-toluenesulfonamide the resulting solution was found contaminated by the presence of more or less cupric salt.

Experiment I.—The precipitate formed by the action of potassium amide on 0.5 g. of tetrammonated cupric nitrate was treated with a liquid ammonia solution containing somewhat more than an equivalent quantity of toluenesulfonamide. On concentrating and cooling the resulting solution, a crystalline mass was formed which was made up of colorless crystals of a cuprous salt intermixed with needle-like crystals of a blue cupric compound. When crystallization took place from less concentrated solution a crop of bulky, interlacing, blue needles, containing no admixture of colorless crystals, was obtained. The mother liquor was poured from these crystals, which were then dissolved in pure solvent, distilled over from the

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[1] Cf. Thallous benzenesulfonamide, p. 2268.

[2] THIS JOURNAL, 29, 656 (1907).

second leg of the reaction tube, and recrystallized. The salt was hydrolyzed, then dissolved in dilute hydrochloric acid and from the solution thus formed the copper was precipitated as sulfide by means of hydrogen sulfide.

Preparation I, dried in vacuum at 100°, weighed 0.0341 g. and gave 0.0068 g. Cu_2S.

On adjusting the concentration of the mother liquor from the above preparation and cooling to —40° a crop of colorless crystals, contaminated with a small quantity of the cupric salt, was obtained which, after one recrystallization, was dried and removed from the reaction tube for analysis.

Preparation II, dried in vacuum at —40° weighed 0.3061 g. Dried at 130° it weighed 0.2761 g. The whole specimen dried at 130° gave 0.0876 g. Cu_2S. One-half of the filtrate from the Cu_2S gave 0.0128 g. N.

Experiment II.—In a second experiment the precipitate, formed by the action of potassium amide on a solution containing 0.75 g. of ammonated cupric nitrate, was dissolved in somewhat more than an equivalent amount of *p*-toluenesulfonamide in solution in liquid ammonia. On cooling the solution a crop of bulky, blue crystals was obtained which was simply drained of mother liquor and submitted to analysis.

Preparation III weighed 0.0889 g. after heating in vacuum to 130°. The whole specimen gave 0.0188 g. Cu_2S and 0.0051 g. N.

On adjusting the concentration of the mother liquor from the preceding preparation and cooling in a bath of liquid ammonia a crop of colorless crystals, contaminated with a small quantity of cupric salt, separated from the solution. The product was recrystallized once for analysis.

Preparation IV, dried in vacuum at 20°, weighed 0.5036 g. Dried at 135° it weighed 0.4567 g. One-half of the specimen dried at 135° gave 0.0728 g. Cu_2S. The other half gave 0.0205 g. N.

			Found.	
		Calc. for $CH_3C_6H_4SO_2NH_2Cu$.[1]	I.	III.
Cu...............		15.7	15.9	16.9
N................		6.9	....	5.7
	Calc. for $CH_3C_6H_4SO_2NHCu$,	$CH_3C_6H_4SO_2NHCu.NH_3$	II.	IV.
Cu...............	27.2	25.4	25.3	25.5
N................	6.0	11.2	9.3	9.0
		Calc. for $CH_3C_6H_4SO_2NHCu.2NH_3$.		
Cu...............		23.8	22.8	23.2
N................		15.7	16.4	15.8

It is obvious that both cupric and cuprous salts of *p*-toluenesulfonamide are formed when Fitzgerald's precipitate is dissolved in a solution

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[1] The product analyzed may have been an equimolecular mixture of $CH_3C_6H_5SO_2NHCu$ and $CH_3C_6H_4SO_2NH_2$ since it was unknown whether or not a reduction, similar to that discussed on p. 2274, had taken place at the temperature to which the preparation had been subjected.

of the acid amide, though it must be noted that the amount of cupric salt formed is relatively small. The presence of the cupric salt probably means, even in the face of the observations of Fitzgerald,[1] that the precipitate formed by the action of potassium amide on cupric nitrate contains a certain amount of cupric amide (or imide) which is completely converted into cuprous nitride only when the precipitate is heated.

From an inspection of the experimental data recorded above it is also obvious that a cuprous salt containing one molecule of ammonia cannot be obtained. Although the copper content of the preparations heated to 130–135° is in accord with that of a compound represented by the formula $CH_3C_6H_4SO_2NHCu.NH_3$, it will be noted that the amount of nitrogen present was about two per cent. too low. Elsewhere[2] in this paper it will be shown that the results obtained are best accounted for on the assumption that, under the influence of high temperature, ammonolytic decomposition accompanies the deammonation of the diammonated salt with the result that no sharply defined product is formed.

Cuprous Ammonobenzenesulfonate, $C_6H_5SO_2NHCu$, **and the Diammonate,** $C_6H_5SO_2NHCu.2NH_3$.—A consideration of the difficulties encountered in effectively separating the cupric and cuprous salts of toluenesulfonamide led to successful attempts to reduce the cupric salt, which was present in the solutions described below, by treatment with metallic copper.

Preparation I.—The blue solution formed by dissolving the precipitate of cuprous imide from 2 g. of tetrammonated cupric nitrate in a liquid ammonia solution of 1.4 g. of benzenesulfonamide was allowed to lie in contact with a few pieces of copper foil until the color was discharged. The perfectly colorless solution resulting from this treatment was decanted from the bits of metallic copper, evaporated to high concentration and finally cooled in a bath of liquid ammonia for the purpose of obtaining a crop of crystals. However, the solution showed the phenomenon of supersaturation so tenaciously that the deposition of a crop of crystals could not be brought about until the tube was cooled almost to the freezing point of the solvent by means of a bath of alcohol cooled by liquid air. After crystals were once formed, however, the recrystallization of the salt could easily be carried on at the temperature of a liquid ammonia bath, provided complete solution of the compound was avoided. The crop of crystals first obtained was recrystallized twice for analysis. On heating the salt ammonia gas escaped without any apparent tendency to stepwise evolution.

The specimen dried in vacuum at —40° weighed 0.8319 g. After heating at 200° to 210° for more than an hour, at the end of which elapsed time ammonia was

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[1] *Loc. cit.*

[2] Page 2273.

still escaping, though very slowly, the specimen weighed 0.7269 g. One-half of the specimen dried at the higher temperature gave 0.1390 g. Cu_2S, the other half gave 0.0269 g. N.

Preparation II.—The solution obtained by dissolving the cuprous imide from 1 g. of ammonated copper nitrate in 0.75 g. benzenesulfonamide in liquid ammonia solution was first decolorized, as described above, and then concentrated and cooled to a low temperature. After once overcoming the strong reluctance to crystallization the crop of crystals obtained was recrystallized once for analysis.

The specimen dried at —40° in vacuum weighed 0.6811 g. One-half gave 0.1059 g. Cu_2S, the other half gave 0.0572 g. N.

	Calc. for $C_6H_5SO_2NHCu$.	Found. I.	Calc. for $C_6H_5SO_2NHCu.2NH_3$.	Found. I.	Found. II.
Cu	29.0	28.8	25.1	25.1	24.8
N	6.4	7.4	16.6	16.9	16.8

The product of the action of benzenesulfonamide on cuprous imide is consequently a salt formed in accordance with the reaction represented by the equation,

$$2C_6H_5SO_2NH_2 + Cu_2NH = 2C_6H_5SO_2NHCu + NH_3.$$

Cuprous benzenesulfonamide separates from cold, concentrated solutions in the form of stout, colorless needles containing two molecules of ammonia of crystallization. It shows a large temperature coefficient of solubility, and is notable for its strong tendency to form supersaturated solutions. It is very susceptible to the action of atmospheric air, the least trace of which gaining entrance to the preparation tube causing the formation of a blue layer of the cupric salt on the surface of the solution. The ammonia of crystallization does not seem to come off stepwise, nor is all the ammonia removed by heating the preparation in vacuum to 200° for considerably over an hour. At elevated temperatures a quantity of colorless liquid, which solidifies on cooling, condenses in the upper portion of the container. Since it is scarcely possible that the salt itself sublimes, this liquid, which solidifies at lower temperature, must be free benzenesulfonamide resulting from the ammonolysis of the. salt.

It is easy to understand the liberation of benzenesulfonamide and the observed fact that all the ammonia of crystallization cannot be removed from the salt, if it be assumed that ammonolysis takes place after the manner indicated by the equation,

$$C_6H_5SO_2NHCu.2NH_3 = C_6H_5SO_2NH_2 + CuNH_2 + NH_3,$$

and that the resulting cuprous amide—which is incapable of existence at the temperature[1] at which the ammonolysis is assumed to take place—is deammonated in accordance with the equation, $CuNH_2 = CuN_{1/3} + {}^2/_3NH_3$.

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[1] Cf. THIS JOURNAL, 34, 1501 (1912).

Calculated in accordance with these equations the loss in weight of the specimen of diammonate, on heating, should have been 11.8%, whereas the observed loss was 12.6%, from which it may be concluded that the product analyzed was a mixture of an anammonous benzenesulfonamide copper, free benzenesulfonamide and cuprous nitride, of the approximate composition represented by the formulas ($C_6H_5SO_2NHCu$, $C_6H_5SO_2NH_2$, $CuN_{1/3}$).

It is interesting to note that the decomposition which ammonated cuprous ammonobenzenesulfonate has thus been shown to undergo is entirely similar to the familiar reactions which take place when a certain hydrated salts, for example hydrated magnesium chloride, are heated.

Cupric Ammonobenzenesulfonate Tetrammonate, $(C_6H_5SO_2NH)_2Cu.4NH_3$, **and the Heptammonate,** $(C_6H_5SO_2NH)_2Cu.7NH_3$.—After the experiments described above[1] had shown that a cupric salt is formed simultaneously with the formation of a cuprous salt by the action of a solution of an acid amide on Fitzgerald's precipitate, it was deemed desirable to attempt the preparation of a cupric salt by the action of a liquid ammonia solution of an acid amide on cupric oxide.

Preparation I.—Accordingly 0.3 g. of cupric oxide was treated with 1.4 times the equivalent quantity of benzenesulfonamide in solution in liquid ammonia. The immediate development of a blue color showed that the copper oxide was going into solution. After standing over night the solution had become intensely blue and the solution of the copper oxide was practically complete. Satisfactory recrystallization of the salt appearing impractical, because of the very bulky nature of the crop of crystals which separated when the solution was strongly cooled, such portions of the mother liquor as could be so removed were drained off and the salt submitted to the following described treatment:

Exposed in vacuum at —40° the salt dried to a blue, fibrous mass. As the temperature was raised ammonia was given off without showing the usual stepwise evolution. As the temperature approached 100° the blue color began to give way to a varicolor, while at a somewhat higher temperature the solid salt changed to a semifluid, green mass, and a white sublimate began to appear in the upper cooler portions of the tube. At 190° the preparation, which had changed in color from green to a dull yellow, was still slowly giving off ammonia which, on examination, was found to contain a permanent gas, presumably nitrogen. The temperature at which evolution of nitrogen began was not determined. When the residue was treated with liquid ammonia a pale blue solution resulted which, on cooling, failed to give a bulky mass of blue crystals, but gave instead, when very concentrated, a crop of colorless crystals intermixed with a small quantity of blue ones. Evaporation of the solvent at —40° left a light blue residue which, giving off ammonia continuously as the temperature was raised, melted at about 160°, and changed to a black, most unpromising mass as the temperature approached 270°. The salt, after this treatment, failed of complete solution when brought into contact with dilute hydrochloric acid, a mass of carbonaceous clots being left undissolved.

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[1] Cf. p. 2270.

The results of the analysis, which are in rough agreement with the formula $(C_6H_5SO_2NH)_2Cu$ or $C_6H_5SO_2NHCu.C_6H_5SO_2NH_2$, are omitted here.

A plausible explanation of this reduction of the cupric to a cuprous salt may be given as follows: On heating the ammonated cupric salt, ammonolysis is assumed to take place in accordance with the equation,

$$(C_6H_5SO_2NH)_2Cu + 2NH_3 = 2C_6H_5SO_2NH_2 + Cu(NH_2)_2.$$

Then, since Fitzgerald[1] has shown that cupric amide is incapable of existence, it follows that this product of the ammonolysis of the cupric salt must undergo reduction as represented by the equation,

$$Cu(NH_2)_2 = CuN_{1/3} + 1^1/_3NH_3 + {}^1/_3N.$$

On now treating the residual mixture with liquid ammonia, the cuprous nitride dissolves in the excess of acid amide to form the cuprous salt of benzenesulfonamide.[2]

Preparation II.—While working with the solution of another preparation, obtained in the manner described above, it was found that, by concentrating the solution at the temperature of the laboratory, the salt could be crystallized in the form of short, thick, very soluble prisms from which the mother liquor could be fairly satisfactorily drained. A crop of crystals so obtained was dissolved in dilute hydrochloric acid for analysis.

The specimen dried in vacuum at —40° weighed 0.5047 g. After heating to 20° it weighed 0.4524 g. Three-tenths of the specimen dried at 20° gave 0.0256 g. Cu_2S, another three-tenths gave 0.0266 g. N.

Calc. for $(C_6H_5SO_2NH)_2Cu.4NH_3$: Cu 14.3, N 18.9; found (II): 15.0 and 19.6.

Calc. for $(C_6H_5SO_2NH)_2Cu.7NH_3$: $3NH_3$ 10.3; found: 10.4.

It, therefore, appears that cupric oxide dissolves in liquid ammonia solutions of benzenesulfonamide to form a cupric salt in accordance with the equation

$$2C_6H_5SO_2NH_2 + CuO = (C_6H_5SO_2NH)_2Cu + H_2O,$$

and that this salt separates from solution with seven molecules of ammonia, three of which it loses in vacuum at 20°. On heating to higher temperatures the cupric salt is converted into a mixture of cuprous ammonobenzenesulfonate and the free acid amide.

Metallic Salts of the Acid Ammono Esters.

The acid amides are to be looked upon as dibasic ammono acids, and in accordance with this view Franklin and Stafford[3] found benzamide and benzenesulfonamide, for example, to react with potassium amide in liquid ammonia solutions to form acid and normal salts of the respective formulas C_6H_5CONHK, $C_6H_5SO_2NHK$, $C_6H_5CONK_2$ and $C_6H_5SO_2NK_2$.

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[1] *Loc. cit.*

[2] It may be noted that the reduction of the cupric salt may be represented as taking place in accordance with the equation, $(C_6H_5SO_2NH)_2Cu.4NH_3 = C_6H_5SO_2NHCu + C_6H_5SO_2NH_2 + 3^2/_3NH_3 + {}^1/_3N$.

[3] *Am. Chem. J.*, **27**, 83 (1902).

Now if the acid amides are in reality the acids of an ammonia system of acids, bases and salts,[1] then it follows that their alkyl and aryl derivatives must be looked upon as ammono esters, and since there are in the acid amides two replaceable hydrogen atoms, either one or both of which may be replaced by hydrocarbon radicals, then one is led to the conclusion that such derivatives of the acid amides will show the properties, respectively, of acid ammono esters and neutral ammono esters. It was to test the question as to whether such acid esters behave as acids in solution in liquid ammonia that the experiments described below were undertaken.

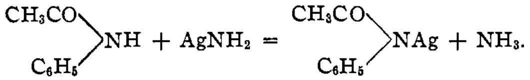
Silver Phenyl Ammonoacetate, $CH_3CONAgC_6H_5$, **and the Monammonate,** $CH_3CONAgC_6H_5.NH_3$.—A compound which is at the same time an ammono salt and an ammono ester. Pure silver amide, prepared from 1 g. of silver nitrate in a manner which has been elsewhere described, was found to dissolve readily enough in a liquid ammonia solution of 1 g. of acetanilide, especially when the solution was concentrated. The salt formed is very soluble in liquid ammonia and could be brought to crystallization only by exposing the concentrated solution to a temperature of —70° or below. The crystals separated as a very bulky mass which retained much mother liquor, so the one recrystallization to which the specimen was submitted cannot have accomplished very much toward the purification of the salt. Preparatory to analysis the compound was first hydrolyzed, then dissolved in dilute sulfuric acid.

Dried in vacuum at 20° the specimen weighed 0.3323 g. After heating to 100° it weighed 0.3100 g. The whole specimen dried at 100° gave 0.1892 g. AgCl. N was lost.

Calc. for $CH_3CONAgC_6H_5$: Ag 44.7; found: 45.9.

Calc. for $CH_3CONAgC_6H_5.NH_3$: 1 NH_3 6.6; found: 6.7.

The formation of a silver salt of acetanilide by the action of the acid ester in solution in liquid ammonia on silver amide is thus shown to take place in accordance with the equation



$$\begin{matrix}CH_3CO\diagdown \\ \qquad\quad NH \\ C_6H_5\diagup\end{matrix} + AgNH_2 = \begin{matrix}CH_3CO\diagdown \\ \qquad\quad NAg \\ C_6H_5\diagup\end{matrix} + NH_3.$$

When cooled to a low temperature the very soluble salt separates from concentrated solutions as a bulky, crystalline mass containing ammonia of crystallization. One molecule of ammonia is retained at 20° to be given off when the salt is heated to 100°.

Thallous Phenyl Ammonoacetate, $CH_3CONTlC_6H_5$.—When the precipitate of thallium nitride prepared from 1.3 g. of thallium nitrate was allowed to lie in contact with a liquid ammonia solution of somewhat more than the equivalent amount of acetanilide, the black nitride was

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[1] Cf. *Am. Chem. J.*, 47, 285 (1912).

gradually converted into a gray, granular mass which is but slightly soluble in liquid ammonia.

Preparation Ia.—By repeatedly extracting this product with liquid ammonia a good crop of colorless crystals was collected in the second arm of the reaction tube. Preparatory to analysis the specimen was first treated with water, then dissolved in dilute sulfuric acid.

Dried in vacuum at 20° the specimen weighed 0.7796 g. After heating to 100° it weighed 0.7778 g. One-half of the specimen gave 0.3773 g. TlI, the other half gave 0.0151 g. N.

Preparation Ib.—The gray residue, from which the above specimen was extracted, was washed to remove the excess of acetanilide present and submitted to analysis with the following results:

Dried in vacuum at 20° the specimen weighed 0.5541 g. Dried at 100° it weighed 0.5533 g. One-half of the specimen gave 0.2685 g. TlI, the other half gave 0.0108 g. N.

Calc. for $CH_3CONTlC_6H_5$: Tl 60.4, N 4.1; found: (I*a*) 59.8 and 3.9; (I*b*) 59.8 and 3.9.

From the results of the above described experiments it follows that thallium nitride is converted into a thallium salt of acid phenyl ammonoacetate, when the nitride is allowed to lie in contact with a solution of acetanilide, in accordance with the equation

$$3CH_3CONHC_6H_5 + Tl_3N = 3CH_3CONTlC_6H_5 + NH_3.$$

The salt is only slightly soluble in liquid ammonia but may be obtained in the form of well developed, colorless crystals by shaking the gray reaction product, mentioned above, in contact with liquid ammonia until a saturated solution is obtained, pouring the solution from the residue, and evaporating away the greater portion of the solvent. It separates from solution without ammonia of crystallization.

Potassium Benzyl Ammonoacetate Monammonate, $CH_3CONKCH_2C_6H_5.NH_3$.—(Prepared by Mr. W. R. Weaver.[1]) Liquid ammonia solutions of benzylacetamide[2] and potassium amide were brought together with the resultant formation of a bright red solution from which, after bringing to a sufficiently high concentration and cooling to a low temperature, an abundant crop of pink crystals was obtained. After draining off the mother liquor and washing a few times with small quantities of liquid ammonia, the preparation was treated with water and then dissolved in dilute sulfuric acid for analysis.

Dried in vacuum at 20° the specimen weighed 0.1338 g. One-half gave 0.0282 g. K_2SO_4, the other half gave 0.0084 g. N.

Calc. for $CH_3CONKCH_2C_6H_5.NH_3$: K 19.1, N 13.7; found: 19.1 and 12.6.

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[1] From a thesis submitted to the Department of Chemistry of the Leland Stanford Junior University in partial fulfillment of the requirements for the degree of Master of Arts.

[2] This compound was made by heating together benzylamine and glacial acetic acid and purifying the reaction product by fractional distillation. Benzylacetamide is very easily soluble in liquid ammonia.

Benzylacetamide, therefore, reacts with potassium amide in liquid ammonia solution in accordance with the equation,

$$CH_3CONHCH_2C_6H_5 + KNH_2 = CH_3CONKCH_2C_6H_5 + NH_3,$$

to form a salt which retains one molecule of ammonia of crystallization when dried in vacuum at 20°. The salt is very soluble in liquid ammonia and separates from concentrated, cold solutions beautifully crystallized.

Potassium *p*-Phenetol Ammonoacetate, $CH_3CONKC_6H_4OC_2H_5$.—(Prepared by W. R. Weaver.) Phenetolacetamide is very soluble in liquid ammonia. Solutions of approximately equivalent quantities of the acid ammono ester and potassium amide, when brought together, gave a solution from which a crop of crystals could be obtained only at very high concentration and low temperature. The mother liquor, very limited in quantity, was drained from the crystals and they were washed to some extent by first properly inclining the reaction tube so that the liquid would drain off, and then condensing small quantities of ammonia upon the crystals by the application of a swab of cotton, saturated with liquid ammonia, to the exterior of the tube. The purification of the preparation was not considered very satisfactory. For analysis the salt was dissolved in dilute sulfuric acid.

One-half of the specimen, which dried in vacuum at 20° weighed 0.2024 g., gave 0.0422 g. K_2SO_4. The remaining half gave 0.0060 g. N.

Calc. for $CH_3CONKC_6H_4OC_2H_5$: K 17.9, N 6.4; found: 18.1 and 5.9.

These analytical results show in a fairly satisfactory manner that potassium phenetol ammonoacetate is formed by the action of potassium amide on phenetolacetamide in accordance with the equation

$$CH_3CONHC_6H_4OC_2H_5 + KNH_2 = CH_3CONKC_6H_4OC_2H_5 + NH_3.$$

The salt, which is extremely soluble in liquid ammonia, separates well crystallized from very concentrated, cold solutions, and retains no ammonia when dried in vacuum at 20°.

Summary.

In this investigation it has been shown, in the first place, that the amides, imides and nitrides of certain heavy metals dissolve in liquid ammonia solutions of acid amides to form well crystallized metallic derivatives of the acid amides. The compounds obtained are to be looked upon as salts of an ammonia system of acids, bases and salts which are formed by the action of ammono acids on ammono bases in liquid ammonia solutions.

In the second place it has been shown that such compounds as acetanilide and benzylacetamide are to be looked upon as acid ammono esters which, in liquid ammonia solutions, react with ammono bases, just as the acid amides do, to form ammono salts.

The following salts, for the most part beautifully crystallized, have been prepared:

1. Diammonated silver ammonoacetate, $CH_3CONHAg.2NH_3$.
2. Thallous ammonoacetate, $CH_3CONHTl$ and the diammonate, $CH_3CONHTl.2NH_3$.
3. Lead ammonoacetate.
4. Silver ammonobenzenesulfonate, $C_6H_5SO_2NHAg$, the monammonate, $C_6H_5SO_2NHAg.NH_3$ and the diammonate, $C_6H_5SO_2NHAg.2NH_3$.
5. Thallous ammonobenzenesulfonate, $C_6H_5SO_2NHTl$, the monammonate, $C_6H_5SO_2NHTl.NH_3$ and the diammonate, $C_6H_5SO_2NHTl.2NH_3$.
6. Thallous ammono-*p*-toluenesulfonate, $CH_3C_6H_4SO_2NHTl$ and the monammonate, $CH_3C_6H_4SO_2NHTl.NH_3$.
7. Diammonated cuprous ammono-*p*-toluenesulfonate, $CH_3C_6H_4SO_2NHCu.2NH_3$.
8. Cupric ammono-*p*-toluenesulfonate, $(CH_3C_6H_4SO_2NH)_2Cu$.
9. Cuprous ammonobenzenesulfonate, $C_6H_5SO_2NHCu$ and the diammonate, $C_6H_5SO_2NHCu.2NH_3$.
10. Cupric ammonobenzenesulfonate tetrammonate, $(C_6H_5SO_2NH)_2Cu.4NH_3$ and the heptammonate, $(C_6H_5SO_2NH)_2Cu.7NH_3$.
11. Silver phenylammonoacetate, $CH_3CONAgC_6H_5$ and the monammonate, $CH_3CONAgC_6H_5.NH_3$.
12. Thallous phenylammonoacetate, $CH_3CONTlC_6H_5$.
13. Potassium benzyl ammonoacetate monammonate, $CH_3CONKCH_2C_6H_5.NH_3$.
14. Potassium *p*-phenetol ammonoacetate, $CH_3CONKC_6H_4OC_2H_5$.

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POTASSIUM AMMONOBARATE, AMMONOSTRONTIATE AND AMMONOCALCIATE.

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Introduction.

Investigations[1] conducted in this laboratory have shown that a reaction similar to that which accompanies the solution of the hydroxide of zinc in aqueous potassium hydroxide takes place when the amide of zinc is treated with a liquid ammonia solution of potassium amide. These strikingly similar reactions proceed in accordance with the equations,

$$Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O^{2}$$

$$Zn(NH_2)_2 + 2KNH_2 = Zn(NHK)_2 + 2NH_3,$$

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[1] Fitzgerald, THIS JOURNAL, **29,** 660 (1907), and Franklin, *Ibid.*, **29,** 1275 (1907).

[2] As a matter of fact this equation, which is frequently written to represent the action of potassium hydroxide on zinc hydroxide, seems never to have been experimentally demonstrated (cf. Comey and Jackson, *Am. Chem. J.*, **11,** 145 (1894)).