THE REACTION OF SULFUR DIOXIDE
WITH LIQUID AMMONIA SOLUTIONS OF SODIUM

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TABLE OF CONTENTS

Page

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Introduction

Reactions of liquid ammonia solutions of metals with oxides of the non-metals have been studied but very little (1). A variety of products is obtained depending on the oxide used, as is shown by the reactions of carbon monoxide, carbon dioxide, nitrous oxide, nitric oxide and nitrogen dioxide.

Carbon monoxide (2) forms a series of metal carbonyls upon reduction. These are of two types, MCO and $M(CO)_2$, where M is either an alkali or an alkaline-earth metal. The structure of these compounds has not been completely determined.

Carbon dioxide (3) and sodium in liquid ammonia have been shown to form sodium carbamate, $NaCO_2NH_2$, at -50° to -60° C. and sodium formate, HCO_2Na, at -25° to -30° C.

Nitrous oxide (4) is reduced by sodium or potassium with the evolution of nitrogen and the formation of sodium hydroxide and sodamide. Further reaction of the nitrous oxide with the amide gives sodium azide, NaN_3, and more sodium hydroxide.

Nitric oxide (5) forms gelatinous precipitates with the alkali and alkaline-earth metals in liquid ammonia. These have been assigned such formulas as $Na(NO)$, $(NaNO)_n$, and BaN_2O_2. Although $(NaNO)_n$ forms the same silver salt as hyponitrous acid, Debye-Sherrer diffraction patterns show it to be different from sodium hyponitrite.

Nitrogen dioxide (6), while not fully investigated, seems to be reduced by a solution of barium with the formation of the same compound with barium that nitric oxide forms.

The reduction of metallic oxides by alkali metals in liquid ammonia solution, like the corresponding reaction with non-metal oxides, has not been studied to any great extent. In general (7), oxides of bismuth, tin (II) and (IV), lead (II) and (IV), zinc, and cadmium give intermetallic compounds with the reducing metal while silver, cobalt (III) (8) and to some extent iron (II) are reduced to the free metal. Copper (II) oxide is quantitatively reduced to copper (I) oxide which undergoes but little further reduction to metallic copper.

The reduction of gaseous sulfur dioxide by metals (9) has received considerable study; however, none of these investigations were carried out in liquid ammonia. Most metals when heated in sulfur dioxide gas become incandescent and form both metallic oxides and sulfides. Others, such as potassium, also give small amounts of thiosulfate while copper, silver and cadmium form sulfates together with small amounts of sulfur trioxide. In general there seems to be no way of predicting the products of the reduction as can be seen from the examples mentioned. Sulfur, sulfur trioxide, and salts of many oxy-sulfur acids are formed.

Scholder and Denk (10) reported that the reduction of sulfur dioxide by finely divided zinc in absolute alcohol resulted in the formation of zinc sulfoxylate, $ZnSO_2$; however, there seems to be some question as to whether this might not have been zinc dithionite, ZnS_2O_4. After consideration of all of these researches it seemed likely that in the reaction between sodium dissolved in liquid ammonia and sulfur dioxide, the principal product would be either sodium sulfide, sodium sulfoxylate, or possibly sodium hyposulfite. The equations corresponding to these hypothetical reactions are as follows:

(1) $\underline{6Na + 6e + SO_2 \longrightarrow Na_2S + 2Na_2O}$

$Na_2O + NH_3 \rightarrow NaOH + NaNH_2$

(2) $\underline{2Na + 2e + SO_2 \longrightarrow Na_2SO_2}$

(3) $\underline{2Na + 2e + 2SO_2 \longrightarrow Na_2S_2O_4}$

The reaction between gaseous ammonia and sulfur dioxide was studied around the turn of the century by Divers and Ogawa (11) and Schumann (12). The results of these investigations are in close agreement. According to these investigators the product obtained depends on the relative concentrations of the initial reactants. If sulfur dioxide is in excess, the product is amidosulfurous acid, NH_2SO_2H. When excess ammonia is present, the ammonium salt of this acid is obtained. The acid is an orange-yellow gum which is apparently amorphous. The salt is a deliquescent, white crystalline powder. It decomposes at 35°C. into its constituent gases and appears to be slightly volatile in a current of ammonia gas. In water it is very soluble, but it is almost insoluble in liquid ammonia.

In 1911, Ephraim and Piotrowski (13), reinvestigated the problem and confirmed the previous work. They also found that by changing the temperature and keeping excess ammonia present, a red compound was formed having the same empirical formula as the ammonium salt but double the molecular weight.

In these early investigations only the anhydrous gases were used. Reactions were carried out by mixing them directly in a suitable container or dissolving them in dry ether. In order to prevent decomposition of the ammonium salt, the reaction mixture was cooled to 0°C., or slightly below, with iced water or brine.

There seems to be no reference to these workers attempting to use liquid ammonia in their investigations nor to their having used liquid ammonia solutions of metals in any way.

STATEMENT OF THE PROBLEM

Information concerning the reactions of non-metal oxides with solutions of metals in liquid ammonia is still rather incomplete, and our understanding of such reactions is not very satisfactory. It seemed desirable, therefore, to investigate the reduction of sulfur dioxide with sodium in liquid ammonia since sulfur dioxide is one of the important and common non-metallic oxides which has not been studied.

With this in mind the following problems were outlined for investigation:

FIRST: To study the reaction of sulfur dioxide and ammonia at -33°C., the boiling point of ammonia.

SECOND: To study the reduction of sulfur dioxide by solutions of sodium in ammonia at -33°C.

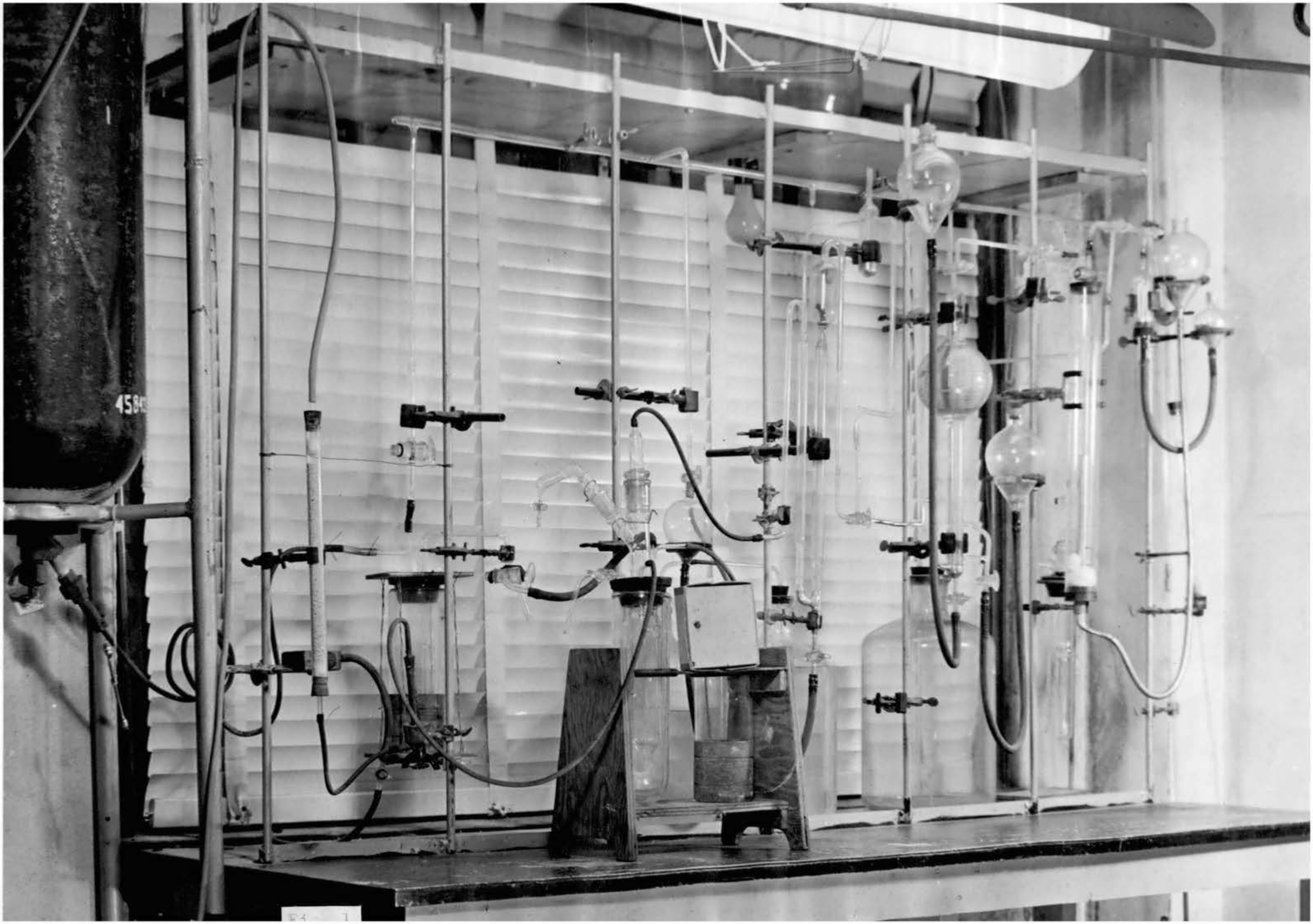
EXPERIMENTAL

APPARATUS

LIQUID AMMONIA SYSTEM: The experiments using liquid ammonia were carried out at approximately -33°C. and at atmospheric pressure. These conditions were obtained by enclosing the reactor tubes in a Dewar flask filled with boiling liquid ammonia. The type of apparatus used has been adequately described by Johnson and Fernelius (14). (See also Figure 1.)

REACTOR TUBES: The reactor tubes used in this work were of two types. One of these was a double reactor tube similar to that described by Watt and Moore (15) and is shown in Figure 3. Both tubes, however, were contained in a single Dewar flask. The two reactors were connected through a sintered glass filter sealed through the side of one and joined by means of ball and socket joints to a piece of glass tubing sealed through the side of the other. A stopcock was provided to isolate one reactor from the other. By increasing the pressure of the ammonia the contents of one tube could be filtered into the other. All connections to the apparatus were made of standard-taper ground glass.

The other reactor tube is shown in Figure 2. Improvements over the first reactor consisted of a larger reaction chamber and a means of introducing ammonia through a sintered glass disc sealed in the bottom. In this way one of the gas entry tubes, which normally extended through the top and decreased the effective volume of the cell, was eliminated.



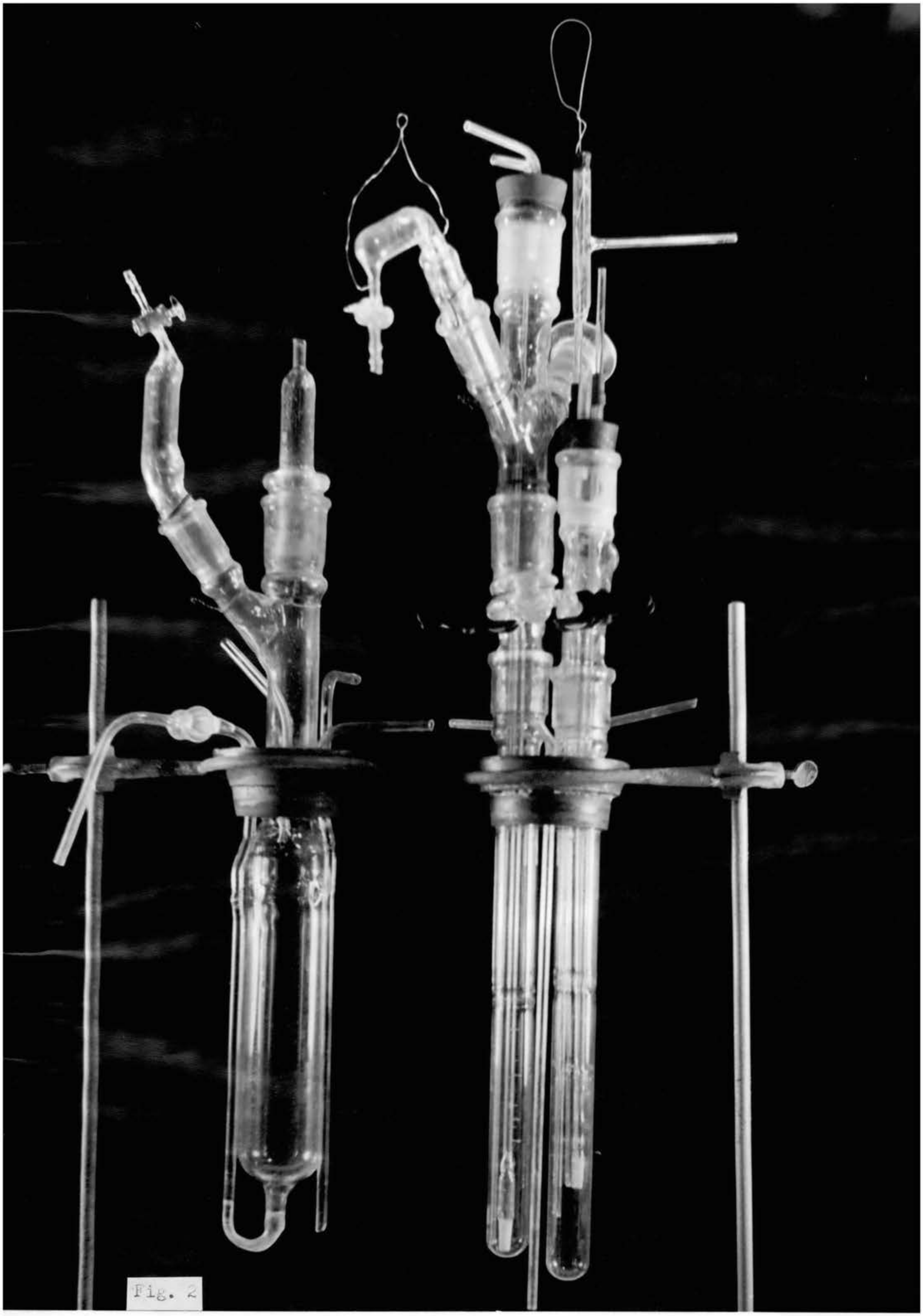


Fig. 2

MATERIALS

AMMONIA: Commercial anhydrous ammonia was distilled into small tanks containing sodium amide which served as a drying agent to remove any traces of water remaining in the ammonia. These small tanks were used to supply solvent ammonia.

SODIUM: The sodium employed was "reagent grade" metal produced by J. T. Baker Chemical Co. and stored under xylene. In preparation for use a small piece of the metal was trimmed of its oxide coating, melted under xylene, and broken up into small globules by stirring. After decanting the xylene the metal was transferred quickly to dry petroleum ether and the mixture then poured into a filtering funnel having a sintered glass bottom. A rubber stopper, through which the end of the introduction tube was inserted, was fitted to the top of this funnel. The ether was drained off and the sodium dried in a stream of dry nitrogen. The sodium was then shaken into the introduction tube, and this was then joined to the reactor tube.

SULFUR DIOXIDE: Commercial anhydrous sulfur dioxide was used either directly from the tank or first bubbled through concentrated sulfuric acid.

AMMONIUM AMIDOSULFITE: Ammonium amidosulfite was prepared by passing gaseous sulfur dioxide into a dry ether solution of ammonia following the procedures of Schumann (15) and Piotrowski (16). The white insoluble product was dried under vacuum. Analysis showed 32.5 percent sulfur. Calculated for $NH_2(SO_2NH_2)$: 32.7 percent sulfur.

SILVER NITRATE: Merck "C.P." crystals were used in the experiments. The crystals were dried for one hour in an over at 100°C. and weighed directly into the introduction tube.

ANALYTICAL METHODS

The analytical methods were for the most part similar to the procedures described in Furman's "Scott's Standard Methods of Analysis." (16)

SULFUR: Sulfur was first determined volumetrically by iodine titration, but it was found more satisfactory to determine it gravimetrically by weighing as barium sulfate after oxidation with bromine.

NITROGEN: Nitrogen was determined as ammonia by a Kjeldahl-type procedure. The weighed sample was dissolved in dilute sulfuric acid, boiled to remove sulfur dioxide, and then distilled with 30 percent sodium hydroxide into standard hydrochloric acid. The excess acid was backtitrated with standard sodium hydroxide.. A micro Kjeldahl apparatus was used for the distillation.

SODIUM: Sodium was determined gravimetrically as sodium sulfate. A few drops of dilute sulfuric acid were added to the weighed sample in a small platinum boat. This boat was ignited and the dry residue weighed.

SILVER: Silver was determined gravimetrically by the addition of a few drops of dilute hydrochloric acid to a solution of the sample in nitric acid. The precipitate was filtered through a weighed Gooch crucible and dried at 110°C. It was weighed as silver chloride.

PROCEDURES

Reaction between sulfur dioxide and liquid ammonia: The first part of the experimental work consisted of the study of the reaction between sulfur dioxide and liquid ammonia. Although the reaction of gaseous sulfur dioxide with gaseous ammonia has been rather thoroughly studied, it was believed that a preliminary investigation of the reaction between gaseous sulfur dioxide and liquid ammonia should be undertaken, even through it seemed unlikely that any previously unreported products would be obtained. This study was made under three sets of experimental conditions.

Addition of gaseous sulfur dioxide to liquid ammonia: This procedure was the most satisfactory of the three tried. The apparatus shown in Figure 2 was assembled, and the reaction cell flushed out with anhydrous gaseous ammonia to remove all noncondensable gases. Refrigeration ammonia was then admitted to the Dewar flask surrounding the cell. This ammonia was kept stirred by a stream of dried natural gas bubbled through it. In this manner the temperature was maintained in the neighborhood of the boiling temperature of the ammonia. The pressure was now increased on the gas in the cell by increasing the height of the mercury column on the outlet side. Ammonia could easily be condensed thus with a head of mercury of only a few centimeters.

Sulfur dioxide was transferred from the storage tank to the gas burette of the apparatus, and by increasing the gas pressure by means of a mercury leveling bulb, it was forced through a sintered-glass gas-dispersion tube into approximately 25 ml. of liquid ammonia which had been previously condensed in one of the reacter tubes. A slight white precipitate was observed to form immediately.

Within a few minutes the dispersion tube became plugged with an orange-yellow gum which prevented further addition of sulfur dioxide. This type of gas entry tube was replaced in a later experiment with one prepared by producing a number of small holes in a thin glass bubble blown on the end of a section of 4 mm. glass tubing. This proved only slightly better since it soon became plugged also. The most satisfactory method of introducing the sulfur dioxide was found to be by means of an open-ended tube. This tube shown attached to the right hand cell of Figure 3, was prepared by sealing a length of glass tubing to the bottom of a side delivery test tube. A nichrome wire was run through a small hole in a rubber stopper inserted in the mouth of this test tube. The wire extended the full length of the tube and could be moved easily. Sulfur dioxide gas was admitted through the side arm. By pushing the nichrome wire up and down constantly, the tube could be kept cleared of any solid deposit.

Using the technique described above, the addition of sulfur dioxide to liquid ammonia was accomplished. A sample of what was believed to be the principal product of the reaction was obtained by evaporation of the excess ammonia through a mercury trap designed to prevent air and moisture from entering the reaction cell. The solid product appeared as a white, very deliquescent powder and was kept in a vacuum desiccator. Only a small amount was obtained, however.

<u>Addition of liquid ammonia to liquid sulfur dioxide</u>: For this reaction the double reaction cell was employed. In the right half sulfur dioxide was liquefied after all of the air in this half had been displaced with gaseous sulfur dioxide. Ammonia was then condensed in the left half in the usual manner under about five centimeters of mercury pressure.

After about 25 ml. of each gas had been condensed, the stopcock between the tubes was opened and the ammonia siphoned over into the sulfur dioxide. This was accomplished by simultaneously releasing the pressure on the sulfur dioxide and increasing it on the ammonia. A vigorous exothermic reaction was observed to take place, and white smoke could be seen rising from the surface and depositing on the sides of all the tubes. Sufficient heat was produced to evaporate a considerable portion of the liquids, and the gases subsequently recombined in the tubes of the apparatus.

Since the tubes in the reaction chamber had become plugged and an obvious mixture of products was produced, the experiment was abandoned. No further work was done on this method.

<u>Addition of liquid sulfur dioxide to liquid ammonia</u>: Again the double reaction cell was used, and the reverse of the procedure just described was carried out. The characteristics of the reaction were similar, and apparently the same mixture of products was obtained. A sufficient amount of the white salt was produced, however, to identify. The orange-yellow product was observed to be soluble in liquid ammonia, and thus by repeatedly condensing ammonia in the reaction chamber and forcing the solution through a sintered glass filter located in the bottom of the reactor, the insoluble solid was washed free of soluble compounds. Analysis of the white salt which was left gave results in agreement with the expected ammonium amidosulfite.

Calculated value for $2NH_3SO_2$: sulfur 32.7%

Experimental values for $2NH_3SO_2$: sulfur 32.5%

Reaction of liquid ammonia solutions of sodium with gaseous sulfur dioxide: A series of nine experiments was carried out to study the reduction of sulfur dioxide by sodium. Although some of these involve variations in procedures and experimental conditions, the general procedure will be described here in detail and reference will be made to significant modifications where necessary.

Ammonia was condensed in the reactor shown in Figure 3 until about 30 ml. of liquid had been collected. A weighed amount of sodium, usually 0.5 to 1.0 grams, was added by means of the introduction tube to the liquid ammonia, where it dissolved to give a deep blue solution.

Sulfur dioxide from the commercial storage cylinder was admitted to the gas burette and from there forced into the solution. In this way the amount of gas used could be measured and the rate of delivery controlled. The first attempts to introduce the sulfur dioxide directly into the liquid ammonia were not very successful because of the combination of gaseous ammonia with sulfur dioxide in the inlet tube. Later experiments employed an arrangement whereby a stream of dry nitrogen gas could be used to dilute the sulfur dioxide and sweep back the ammonia from the gas entry tube. This proved to be reasonably successful although some ammonia still diffused into this gas stream and reacted with the sulfur dioxide. An additional function of the nitrogen was to keep the mixture stirred effectively.

Sulfur dioxide was admitted very slowly into the solution until the blue color of the sodium was gone and a white precipitate remained. By this method small amounts of the solid product could be prepared.

It was found to be advantageous, however, to add the sodium in small amounts and discharge the blue color almost completely with sulfur dioxide between successive additions. In some of the experiments (noted in Table I) a slight excess of sodium was permitted to remain in solution after the sulfur dioxide addition had been stopped. This excess sodium was separated from the insoluble solid by filtration through the sintered glass filter and the product thoroughly washed with fresh portions of liquid ammonia several times. The washings were discarded.

The product was allowed to remain in the reaction chamber until all of the remaining liquid ammonia had evaporated. The cell was then detached from the rest of the apparatus and the product shaken loose from the bottom into a collector tube which had been substituted for the introduction tube. This consisted of a piece of glass tubing about one inch in diameter sealed to a 20/40 standard-taper glass joint at one end and having the other end sealed to a small stopcock. The collector was removed from the apparatus and immediately stoppered. After being placed in a vacuum desiccator with the stopcock open, the tube was evacuated through the desiccator for at least 24 hours on a good oil pump to free the product of the bulk of the adsorbed ammonia before analysis. The results of the chemical analyses are presented in Table I.

Reaction of liquid ammonia solutions of sodium with ammonium amidosulfite: Approximately 0.3-0.4 grams of finely crystalline ammonium amidosulfite was packed into a small specially constructed weighing bottle. The bottle was built with loops of glass to which strings or small wires were attached to permit the bottle to be tilted and the lid removed. After about 50 ml. of ammonia had been condensed in the large reactor shown in Figure 2, the upper half of the reactor was opened at the ground glass joint and the weighing bottle lowered into the reaction chamber. By removing the lid and tilting the bottle, the contents were shaken out. The bottle was then withdrawn and reweighed to determine the amount of amidosulfite added. In this way the water picked up by the very hygroscopic salt was minimized and the transfer into the ammonia made quantitative.

Sodium, previously prepared in small pieces and placed in the introduction tube, was now gradually added to the reaction mixture. A vigorous reaction was observed to take place, and the blue color of the sodium solution disappeared almost as fast as it was formed. As the addition continued the rate of reaction slowed considerably, and the blue color persisted for longer periods of time. It was noticed that the insoluble solid had changed to a light yellow color from the original white. The solution, containing a trace of excess sodium, was allowed to stand for about a half hour before final washing. The amount of sodium required by the reaction was determined by reweighing the addition tube and its contents.

The technique mentioned previously for recovering the product was followed. After the excess ammonia solution was drawn off through a filter and the product dried, it was shaken into a collector tube and evacuated. It was observed that after drying the product had lost its yellow color and become white again.

The gas evolved during the reaction was collected over water and measured in the gas burette. It was assumed that this gas was entirely hydrogen.

Results obtained from these experiments are found in Table II.

PREPARATION OF SILVER SALT: Experiments were conducted with the view of preparing the corresponding silver salts of the sodium derivatives obtained from the reaction of sodium with both sulfur dioxide and ammonium amidosulfite. It was hoped that these could be shown to be identical.

Silver nitrate was dried and an amount weighed out slightly in excess over that calculated to replace with silver all the sodium present in the salts. The silver nitrate was placed in the introduction tube and added slowly with stirring to the sodium compounds suspended in approximately 50 ml. of ammonia. Upon the addition of the first few crystals, the whole mixture turned a deep chocolate brown. After all the silver nitrate had been added, the mixture was allowed to stand for at least 15 minutes. Excess silver nitrate then was washed out by repeatedly condensing ammonia in the reaction chamber and forcing out the wash liquid through the filter. After the ammonia had been allowed to evaporate, the dry salt was shaken into a collector tube and evacuated.

The results of analyses for silver are shown below. Experiment I refers to the salt prepared from sodium, ammonium amidosulfite, and silver nitrate while experiment II refers to the salt made from sodium, sulfur dioxide, and silver nitrate.

Experiment	Percent Silver
I	25
II	34.8

TABLE I

Reaction of Sulfur Dioxide with Sodium

Experiment No.	Na used, moles	SO_2 used, moles	Analysis of insoluble products		
			Na, %	S, %	N, %
4*	0.0011	0.0037	---	12.9	---
6*	0.0015	0.0013	---	14.5	---
7†‡	0.0020	0.0018	35	24.3	
8†‡	0.0060	0.0039	27.9	15.	
11	0.0136	0.0032	58.2	---	13.2
12	0.0254	0.0354	18.9	---	4.8
13‡	0.0226	0.0515	32.4	22.5	21.03
14*‡	0.0123	0.0230	37.3	14.5	4.3
18†‡	0.027	------	42.0	24.1	----

* S analysis by iodine titration

† Trace of sulfide present

‡ Slight excess of sodium used

TABLE II

Reaction of Ammonium Amidosulfite with Sodium

Experiment No.	$NH_4SO_2NH_2$, moles	Na, moles	H_2, moles	Analysis of insoluble products		
				Na, %	S, %	N, %
15	0.0067	0.0151	——	33.8	21.8	——
16	0.0057	0.0128	0.0086	39.6	24.9	11.0
17	0.0071	0.0158	0.015	34.2	23.4	12.4

DISCUSSION

In studying the reaction between sulfur dioxide and liquid ammonia solutions of sodium, the possibility of a reaction with the solvent could not be overlooked; therefore, a series of experiments were carried out to investigate the nature of the products of such a reaction. The results obtained from these experiments were qualitatively in agreement with those expected by analogy to the compounds reported in the literature for the combination of these substances in the gaseous phase.

Experimental difficulties such as those encountered in the plugging of the tubes of the apparatus, resulting from the combination of the gaseous sulfur dioxide and ammonia, made it almost impossible to maintain a reproducible set of conditions. When the ammonia was present in large excess, as it was when sulfur dioxide gas was bubbled into liquid ammonia, the product was white and consisted principally of ammonium amidosulfite. If the sulfur dioxide was introduced too rapidly, it did not completely react with the liquid ammonia and would combine with gaseous ammonia toward the top of the apparatus. On the other hand, if the rate of introduction was decreased or if a gas dispersion tube were used to increase the possibility of absorption, extensive combination occurred in the inlet tube yielding a mixture of solids which effectively blocked the gas entrance.

In an effort to further identify the product formed in liquid ammonia, liquid sulfur dioxide was allowed to react with the ammonia. Although the yields of insoluble solids were increased, an obvious mixture resulted. The white product upon isolation and purification was identified by analysis as ammonium amidosulfite, and the colored materials were doubtless the compounds described by Ephriam and Piotrowski.

It was concluded from this set of experiments that if the sulfur dioxide were to react with a liquid ammonia solution of sodium so as to give a single identifiable product, the rate of reaction must greatly exceed the rate of combination of sulfur dioxide with ammonia.

<u>The reaction of sulfur dioxide with liquid ammonia solutions of sodium</u>: In accordance with the currently accepted views regarding the nature of a liquid ammonia solution of an alkali metal such as sodium, (17) sulfur dioxide might be expected to be readily reduced by ammoniated electrons according to one of the following schemes:

$$2e(NH_2)_x^- + SO_2 \longrightarrow SO_2^{--} + 2xNH_3$$

$$2e(NH_3)_x^- + 2SO_2 \longrightarrow S_2O_4^{--} + 2xNH_3$$

$$4Na^+ + 4e^-(NH_3)_x + SO_2 \longrightarrow S^{--} + 2Na_2O + 4xNH_3$$

This is by analogy to the reduction of carbon monoxide and nitric oxide to form ionic carbonyls and nitrosyls, in which the negative ions are derived from these oxides:

$$e(NH_3)_x^- + CO \longrightarrow CO^- + xNH_3$$

$$e(NH_3)_x^- + NO \longrightarrow NO^- + xNH_3$$

The overall results point, however, to an entirely different course for the reaction analogous to the primary reduction of carbon dioxide to sodium carbamate:

$$Na^+ + e(NH_3)_x^- + CO_2 \longrightarrow Na^+(CO_2NH_2)^- + \tfrac{1}{2}H_2 + (x-1)NH_3$$

The problem of determining the course of the reaction was attacked by: (1) attempting to determine the relative proportions of reactants taking part and (2) analyzing the solid residues remaining after the reaction. The second precedure assumed that a single pure compound was formed or that a quantitative separation could be effected.

From the data of Table I it can be seen that there is apparently no constant relation between the quantity of sodium used and the quantity of sulfur dioxide added to the system. This is readily explained, however, by the extensive and uncontrollable combination of sulfur dioxide and ammonia in the tubes of the apparatus. For example, the ratio of the number of moles of sulfur dioxide to sodium was found to vary from 1 to 0.2. Consequently, little useful information could be derived from these measurements. In subsequent experiments no attempt was made to measure sulfur dioxide used.

The results obtained by analysis of the solid product are not very satisfying. If the sole product of the reaction is assumed to be the salt represented by the formula Na_2SO_2NH, the calculated percentages of the constituents are as follows: sulfur 25.6, sodium 36.8, and nitrogen 11.2. Reference to Table I shows that although considerable deviation from these values was found in some experiments, the analytical data are generally in agreement with this formulation.

The values for the percent of nitrogen were found to be most variable. This may be due in part to an indefinite amount of ammonia adsorbed on the product and not removed by evacuation. Some justification for this interpretation is found in the number of experiments in which the nitrogen content exceeded the theoretical amount.

Considerable analytical difficulties were encountered throughout the course of the experimental work. Since the yield of solid product in each experiment was small, there was generally insufficient material to run enough duplicate analyses to determine if the apparent discrepancies between the results of successive experiments were the result of faulty analyses or different products. Unfortunately, however, the checks between the analyses made on a particular experiment were often not very good either. When efforts were made to use micro techniques in order to conserve the amount of product, the results were not greatly imporved, probably because of lack of homogeneity in the samples taken for analysis.

As noted also in Table I several values for the sulfur content of the product are exceptionally low. This can be attributed directly to the use of iodine in the volumetric determination of sulfurous acid. The volumetric determination is carried out in acid solution, and there is a possible loss of sulfur dioxide from the solution which makes the analysis low. More nearly consistent results were obtained by precipitation of the sulfur as barium sulfate.

As is well known, the determination of sodium is frequently not very accurate. In this case, the use of the micro method for sodium gave erratic results, undoubtedly due partly to the heterogeneous nature of the sample and to the variability in the amount of surface oxidation of the sodium.

It was believed that some of the difficulties might possibly have been the result of using an excess of sulfur dioxide which might then react with the ammonia to contaminate the sodium salt. Several experiments were therefore run in which a slight excess of sodium was allowed to remain in solution after the addition of sulfur dioxide had been stopped. No significant differences in results were obtained in these experiments. It was noted, however, that a trace of sulfide was formed in those cases where an excess of sodium was used.

Reaction of liquid ammonia solutions of sodium with ammonium amidosulfite: The experiments involving the reaction of sulfur dioxide with sodium in ammonia indicated that little or no reduction was occuring and that the sodium was merely being used to form a sodium salt of amidosulfurous acid. Ammonium amidosulfite was assumed to be formed as an intermediate by the combination of sulfur dioxide and ammonia. Since the sodium salt has not been reported previously, an attempt was made to prepare it in liquid ammonia by the reaction of ammonium amidosulfite with sodium under much the same conditions existing in the other type of experiment.

From the data of Table II it can be seen that the number of equivalents of sodium used corresponded reasonably well with the number of equivalents of hydrogen produced. This number was two equivalents per mole of ammonium amidosulfite. The analytical data were less satisfactory, although somewhat more consistently close to the calculated values for Na_2SO_2NH than those obtained from the reaction of sodium with sulfur dioxide. There seems to be no reason for doubting that the disodium salt obtained in this manner was identical with that produced from sodium and sulfur dioxide in ammonia.

A definite end point to the reaction could be detected by the appearence of the characteristic blue color of sodium in liquid ammonia. The addition of more sodium did not appear to result in the formation of more hydrogen, and the solution remained permanently blue. This indicated that the second hydrogen attached to the amido group could not be displaced under these conditions. Since this seemed to be the case, no more than two sodium atoms would be expected in the product obtained from the reaction of sulfur dioxide with sodium solutions where excess sodium was constantly present during the course of the reaction.

The conclusions reached from these experiments can be summarized by the following two equations:

$$2Na^{+} + 2e^{-}(NH_3)_x + SO_2 \longrightarrow Na_2^{+}(SO_2NH)^{=} + H_2 + (2x-1)NH_3 \quad (1)$$

$$NH_4(SO_2NH_2) + 2Na^{+} + 2e^{-}(NH_3)_x \longrightarrow Na_2^{+}(SO_2NH)^{=} + H_2 + (2x+1)NH_3 \quad (2)$$

<u>Preparation of the silver salt:</u> Since only two experiments were run in an effort to prepare silver salts by metathesis, this work must be regarded as incomplete. Although reaction apparently occurred rapidly in both experiments, the silver analyses do not correspond to any possible pure silver salt or mixed silver-sodium salt. This is shown by the following comparison of calculated and experimental values for the present silver:

Calc'd. for Ag_2SO_2NH.	73.0%
Calc'd. for $AgNaSO_2NH$	51.5%
Experiment I.	25%
Experiment II	34.8%

The only conclusion, therefore, is that reaction was incomplete. An explanation for this might be the mechanical interference of the silver salt in preventing more silver nitrate from contacting the unreacted compound. All of these reactions were complicated by being heterogeneous, although the success of Watt and Davies (18) in the quantitative metathesis of the potassium salt of aquoammonomolybdic acid to the silver salt suggest that it might reasonably have been expected to occur in this reaction also.

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BIOGRAPHY

Max Dwain Adams, son of R. Glen Adams and Elva Penry Adams, was born in Red Oak, Iowa, on May 23, 1926. He attended the Red Oak public schools and high school and received his diploma in 1943. He then entered Tarkio College at Tarkio, Missouri in the fall of 1943. After one year of college he went to the army for a period of two years. Most of this time was spent in the military police in the Philippine Islands.

Returning from the army in October of 1946 he returned to Tarkio College where he received the B. A. degree in July, 1948. He enrolled at Oklahoma A. and M. College in September, 1948 where he served one year as a graduate fellow in the Department of Chemistry while completing requirements for his Master of Science degree.

He was married in July of 1947 to Jeanne Beatty of Beatrice, Nebraska.

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