THE REDUCTION OF ORGANIC COMPOUNDS OF SULFUR BY
METALS IN LIQUID AMMONIA

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I

INTRODUCTION

Anhydrous liquid ammonia has a combination of properties which permit the realization of experimental conditions not obtainable with other solvents. Tremendous possibilities are foreseen for the utilization of this solvent in synthesis and in the study of reaction mechanisms.

One particularly outstanding application of ammonia as a solvent lies in the field of chemical reduction of organic compounds. High hydrogenation temperatures and special catalysts are entirely avoided by the use of a metal-ammonia system for reduction. Moreover, many metals which normally decompose water with the liberation of hydrogen dissolve quietly in liquid ammonia.

Another paramount advantage realized in the properties of liquid ammonia is its unusual solvent characteristics at low temperatures, especially in regard to the alkali and alkaline earth metals and many organic compounds which are insoluble or unstable in other media. A great number of these substances are soluble in liquid ammonia without decomposition over a very broad range of temperatures and concentrations. The fact that the solvent capacity of liquid ammonia for organic compounds approaches that of the common organic solvents, while its freezing point is far below that of water, suggests that ammonia, upon occasion, would provide an

ideal medium for carrying out reactions where the reaction intermediates or final products are unstable at the higher temperatures.

This investigation comprised a study of the reduction of several representative compounds containing only sulfur, hydrogen, and carbon. The fate of the carbon-sulfur bond in these compounds in the presence of different metallic reducing agents in liquid ammonia was ascertained at varying concentrations of ammonium ion as a proton donor.

Saturated aliphatic sulfides, allyl sulfide, allyl and propyl mercaptans, and thiophene were investigated. Each compound was studied as indicated, the extent and course of reduction being determined by systematic analyses developed specifically for each type of compound.

The direct purpose of this work was to investigate the extent and course of reduction as related to the half-cell potential of the metal and concentration of proton donor employed. Different sulfur compounds were utilized in order to obtain data which would show how molecular structure affects the stability of the carbon-sulfur bond in the said reducing system.

Prior to this investigation, no attempt to correlate all these factors has been reported.

The ultimate aim was to learn how reduction had taken place in the metal-proton donor-ammonia system by designing appropriate experiments and studying the resultant data.

It is hoped that the information revealed will find new application for the metal-ammonium ion-ammonia system as a tool for selective reduction.

II

LITERATURE REVIEW

The following is not intended to be a complete resumé of the research in the field of reactions of metals in liquid ammonia, but is designed to shed some light on the nature of the subject by the presentation of specific reactions typical of various classes of organic substances. These data precede a review of the metal-ammonia system as a reductant for the sulfur containing compounds of the type employed in this investigation.

General Background.--Kraus³⁰ asserted that a metal dissolves in liquid ammonia to reach the equilibrium

His conductance studies gave evidence that the electron was solvated, or associated with ammonia molecules, the extent of solvolysis varying directly as the concentration of the metal.

Weyl⁵⁵ observed the high solubility of the alkali metals in liquid ammonia. Moissan³⁹ indicated the ability of cesium, calcium, barium, and strontium to dissolve in ammonia. Manganese and amalgamated aluminum were found to be soluble in the ammonium ion-ammonia system at room temperature², and recently, the solubility of pure aluminum in anhydrous ammonia has been reported²⁰.

One description of the composition of the metal-ammonia system embodies an approach based upon the assumption that the alkali metals exist as colloidal particles, denying the presence of free or solvated electrons⁴¹.

Kruger³³ theorized that the color of liquid ammonia solutions of sodium was due to the formation of a colloidal suspension of sodium. He based his conclusions on observations through the ultramicroscope and filtration through an ultrafilter. The filtration removed the sodium and blue color, causing a large increase in the electrical resistance of the solution.

Later researchers, Freed and Thode²⁵, said that the color was not caused by the colloidal sodium but by a minute suspension of the sodium amide and hydroxide. The hydroxide was said to be formed from the reaction of sodium with small amounts of water absorbed by ammonia, and consequently, partly decomposed the ammonia. The bulk of the sodium in solution, however, was considered to be made up of independent atomic or electronic magnets.

In this connection, the magnetic susceptibilities of solutions of sodium in liquid ammonia were observed to be a function of concentration, varying from a weak paramagnetism in concentrated solutions to a strong paramagnetism in dilute solutions²⁴.

Amide formation is not appreciable in liquid ammonia at temperatures below $-33.5^{\circ}\text{C}.$, the boiling point of ammonia at atmospheric pressure⁵².

In many cases the use of diluents or co-solvents reduces the reaction time and facilitates complete conversion of the reactants⁵⁰. The course of reaction has been shown to be subject to change in the presence of an "inert" diluent, i.e., a saturated hydrocarbon, particularly where coupling and condensation reactions normally are apparent⁵⁶. When sodium was added to chlorobenzene in liquid ammonia with petroleum ether as a co-solvent, only triphenylamine was obtained. A measurable amount of the diamine was found in the products, however, when the petroleum solvent was omitted.

In general, however, the role of the co-solvent in altering the course of reactions is unpredictable in view of the present state of knowledge of the subject.

A great many reactions of organic compounds with metal ammonia solutions are carried out with the displacement of an active hydrogen by a metal, leading to salt formation⁵¹. Hydrogen liberated in situ has often been reported to reduce the initial compound. In this instance, one is confronted with a choice of several reaction paths; namely, active hydrogen addition, electron addition, or both.

In many cases, proton donors, such as ammonium salts and alcohols, have been utilized to assist the reduction, the effect of which has not definitely been established. Krug and Hsieh³², in studying the stability of a single compound, methyl ethyl ketone, in the presence of various metals and different concentrations of ammonium ion, have illustrated that a high concentration of this proton donor favors the formation of hydrogen and decreases the reduction of the organic substance. It was also pointed out in this work that the extent of reduction depended primarily upon the half-cell potential of the metal, a greater potential causing more reduction.

Henne and Greenlee²⁶ have found that monoalkyl acetylenes can be reduced quantitatively to the corresponding olefin by the theoretical amount of sodium in liquid ammonia containing ammonium sulfate, with no evolution of hydrogen. It was also pointed out in this investigation that dialkyl acetylenes were incompletely reduced, more than the theoretical amount of sodium being consumed. When ammonium chloride was used as the proton donor, some hydrogen was liberated and incomplete reduction noted. It was thus concluded by the investigators that hydrogen released from the acetylene molecule is more effective as a reductant than the hydrogen from the ammonium ion, and that the function of the ammonium ion was to regenerate acetylene from the sodium derivative.

On the other hand, no such clear-cut conclusion could be reached concerning the effect of methanol and ammonium bromide on the extent of reduction of nitrobenzene and 2-nitrofluorene in the sodium-ammonia system⁵³.

There is no evidence in the literature for a reaction between a metal-ammonia system and a saturated hydrocarbon. The fact that compounds of this type are ultimate reduction products of the corresponding unsaturated compounds, if complete reduction should take place, is indicative of the stability of these molecules to further reduction.

Likewise, alkenes are not reactive toward solutions of metals in liquid ammonia^{9,36}. However, the dienes reduce in an irregular manner to give products not typical of a simple hydrogenation of the multiple linkage. Sodium reacts with butadiene to give butene and octadiene²⁸.

In the reduction of phenyl substituted saturated and simple unsaturated hydrocarbons, the following modes of reaction may be expected: hydrogen displacement, double bond addition, dimerization, polymerization, cleavage of the carbon-carbon bonds and/or addition to one of two double bonds of a molecule. For example, with sodium in liquid ammonia, styrene reduces to ethyl benzene and also polymerizes^{34,37,65}. In general, however, phenyl substituted

derivatives of saturated hydrocarbons will not undergo reduction to a large extent unless the benzohydryl group is present.

2,5-Dihydrotoluene will reduce to 1-methylcyclohexene (50%) and 3-methylcyclohexene (10%)⁴. The benzene ring is usually not attacked by solutions of metals in liquid ammonia^{36,48,64}. For this reason, benzene, xylene, etc., may be used as co-solvents or diluents⁶⁶.

However, Wooster and Godfrey⁶² obtained an addition product having the properties of a cyclic olefin from a mixture of sodium, toluene, and ammonia, to which water had been added, the theoretical volume of hydrogen not being obtained. This experiment led the investigators to the conclusion that the hydrogen liberated in an ammonia solution is more effective as a reducing agent than the electron. Wooster⁶¹ further demonstrated the effect of other proton donors in promoting reduction on benzenoid compounds. Generally, these compounds are reduced to the dihydro- or tetrahydro-derivative^{3,6}.

Biphenyl will reduce to tetrahydrobiphenyl with sodium alone in anhydrous ammonia³⁶. Similarly, naphthalene reduces to tetrahydronaphthalene in ammonia solutions of sodium or potassium^{35,66}. Anthracene, under the above conditions, yields 9,10-dihydro-anthracene^{35,38}.

Halogens may be removed quantitatively from organic compounds by solutions of metals in liquid ammonia^{17,19,49}. A method of halogen determination has been realized here which has found considerable use. The status of the remainder of the molecule is usually of no interest in an analytical procedure of this type, thus accounting for the lack of complete studies concerning the effect of a halogen on the nature of reduction.

In general, monohalogen hydrocarbons yield saturated and unsaturated hydrocarbons in a metal-ammonia system, plus the metal halide and amide. Ethyl bromide⁶⁰ yields ethane, sodium amide, and sodium bromide, whereas ethyl iodide³⁷, under similar circumstances, yields ethene in addition to other unidentified products.

In the case of phenyl substituted alkyl halides, polymerization is frequently encountered. Where R represents a phenyl group, RCH_2Cl and sodium in liquid ammonia give RCH_3 , RCH_2CH_2R , and a solid hydrocarbon^{21,32}. Only RCH_2CH_2R is reported in the reduction of the bromine analogue⁶⁴. R_2CCl_2 will give a 90% yield of $R_2C:CR_2$ ^{21,22}. The halide $RC(CH_3)_2CH_2Cl$ reacts to form $RC(CH_3)_3$ ⁵⁸.

Acetylene dibromide in the sodium-ammonia system reacts to produce sodium acetylide, hydrogen, and sodium bromide³².

The literature concerning the action of liquid ammonia solutions of metals on aryl halides is highly limited. Those reactions are exemplary of free radical polymerizations and ammonolyses and,

in general, produce poor yields of the simple dehalogenated compound. Chlorobenzene or iodobenzene yields benzene, diphenylamine, triphenylamine, and the sodium halide⁵⁶.

Alcohols form alkoxides in metal ammonia systems with the evolution of hydrogen^{7,13}. An unsaturated alcohol, e.g., allyl alcohol, may, in addition undergo reduction at the hydroxyl group^{10,11,14}. Benzyl alcohol, phenylmethylcarbinol, phenyldimethylcarbinol, and phenylbutylcarbinol reduce at the hydroxyl group to the corresponding alkyl benzenes¹².

Some lower aliphatic amines react with alkali metals in liquid ammonia producing substituted metal amides, the amide being formed preferentially at elevated temperatures⁴⁴.

Since aldehydes react with liquid ammonia, it is not a suitable solvent for effecting simple reductions of this class of organic compounds. The reaction product of acetaldehyde and ammonia is said to be triethylidene thimine $(\text{CH}_3\text{CH}::\text{NH})_3 \cdot 3\text{H}_2\text{O}$. This product will react with sodium in a 1:1 ratio to yield one equivalent of hydrogen and a precipitate considered to be $\text{CH}_3\text{CH}(\text{ONa})\text{NH}_2$ ⁴⁵. Acetals generally react only to a very slight extent with metals in liquid ammonia.

Acetone will react with one gram equivalent weight of sodium with no evolution of gas³¹. The product of this reaction was not identified. Benzophenone, under the same treatment, forms a

monosodium ketyl, $(C_6H_5)_2CONa$. Two equivalents of metal give the disodium ketyl $(C_6H_5)_2CNaONa$ ^{48,63}.

Krug and Hsieh³² report the formation of 2-butanol from methyl ethyl ketone, the yield varying directly with the single electrode reduction potential of the metal and inversely with the concentration of the ammonium ion as a proton donor.

Esters of carboxylic acids have been shown to react with metals in liquid ammonia to give alcohols¹⁵.

Simple aliphatic ethers are not affected by the metal-ammonia system^{27,31}, a fact which accounts for their wide use as co-solvents^{21,50,65}. If the ether should contain one or more aromatic groups, the carbon-oxygen bond is cleaved^{29,46,54}. The reaction may be represented by the general equation

The reduction of nitrobenzene in liquid ammonia with metals has been shown to yield phenylhydroxylamines and complex unidentified products, the amount of which appears to be dependent upon the reaction conditions and amount of metal present⁵⁷. However, 1-nitronaphthalene yields 97% dihydro-1-naphthylamine at $-33.5^\circ C$ ⁵³. When ammonium bromide was used as a proton donor, the extent of reduction decreased greatly.

Phenylhydroxylamine can be reduced directly to aniline with no evolution of hydrogen by the sodium-ammonia system⁵⁷.

The Carbon-Sulfur Bond.--Only isolated or contradictory information is available describing the effect of sodium alone in ammonia, or with a single proton donor, on specific sulfur compounds. Kraus and White³¹ reported the conversion of diphenyl sulfide into benzene and sodium sulfide in a sodium-ammonia system. However, these results could not be duplicated by Williams and Gebauer-Fuelnegg⁵⁹, who obtained thiophenol and aniline but no benzene or sodium sulfide in the same system. The latter investigators gave evidence for the following generalized equations for the reactions of sulfides and disulfides in the sodium-ammonia system.

Mercaptides were the only products identified in the reduction of n-propyl and n-heptyl sulfides and n-propyl and isocamyl disulfides.

Moses and Reid⁴⁰ found that organic sulfides are stable to sodium in ether even after standing several months, indicating that sodium in liquid ammonia is more reactive than in ether.

Since mercaptans were weak acids, these sulfur compounds can react slightly with ammonia to form white crystalline ammonium mercaptides. Upon the addition of sodium to a liquid ammonia solution of the mercaptide, sodium mercaptide is found with the evolution of hydrogen.

The mercaptan 1,1-bis (mercaptomethyl) cyclohexane was obtained in 93% yield from the reaction between a solution of sodium in liquid ammonia and an ether solution of 2,3-dithiaspiro(4.5) decane¹.

Bishydroxymethyl-bismercaptomethyl methane was prepared in 87.5% yield from 4,4-bishydroxymethyl 1,2-dithiacyclopentane in the same reduction system.

Thiophene in the sodium-ammonia system containing methanol as a proton donor yields 2,3- and 2,5- dihydrothiophenes, 2-butene-1 thio, 2-butene, and hydrogen sulfide⁵. The last three products result from cleavage of the carbon-sulfur bond in thiophene.

No evidence has been reported concerning the effects of different metal-ammonia systems, as such, upon the carbon-sulfur bond, or with a proton donor present. Moreover, there are no data available in the literature concerning the reactivity of unsaturated sulfides in any metal-ammonia system.

The present investigation was directed toward acquiring this information, and thereby accumulating sufficient data to postulate a mechanism of reduction.

III

EXPERIMENTAL

PRELIMINARY REMARKS

The relative quantity of metal and organic sulfur compound employed in an experiment was chosen on the basis of the following reaction⁵⁹:

where two gram equivalent weights of a metal reduce one molecular weight of the sulfide. Also, one equivalent weight of metal would be consumed, theoretically, in the competitive reaction with an equivalent weight of ammonium ion proton donor present.

It should be understood that equations (1) and (2) are of value in this investigation only for the purpose of justifying the otherwise arbitrary selection of the relative quantities of reactants. Since maximum yield was not a goal and minimizing the number of variables simplified the study, this ratio was observed in all runs undertaken.

The concentration of ammonium ion in ammonia was changed simply by the utilization of three ammonium salts, ammonium chloride, ammonium bromide, and ammonium sulfate, which differ appreciably in regard to their solubilities in liquid ammonia,

as given on page 40. In any event, a sufficient reservoir of ammonium ion was always available to completely decompose all metal.

The volume of ammonia was based upon the amount of metal employed, the ratio selected being 500 ml. of ammonia to one equivalent weight of metal, i.e., approximately a 2 N solution. Since the capacity of the reduction flask was one liter, the weight of metal never exceeded 0.4 equivalent, which required 200 ml. of ammonia according to the above ratio.

The rate of stirring, which ranged between 125 and 150 r.p.m., appeared to have no effect upon the extent of reduction as observed in identical runs using lithium metal, propyl sulfide, and ammonium sulfate. However, the rate of reaction was found to vary directly with the speed of stirring within the range of velocities utilized.

A higher stirring velocity would have been used had the rubber seal on the stirrer shaft been able to withstand the additional heat of friction. The mercury type seal could not be of service because internal gas pressure could easily displace the mercury. Further, the use of mercury in the presence of ammonia constitutes a safety hazard.

The time required for a run depended also upon the solubility of the metal and ammonium salt in liquid ammonia, the reaction time ranging from 20 minutes for a lithium run to eight hours for that of beryllium.

APPARATUS

The liquid ammonia reactor system, illustrated in Figure 1, employed a one liter, round bottom, three neck flask, one neck of which was connected to a dry ice-ethanol cooled condenser. A rubber sealed glass stirrer was attached to the middle neck of the flask, while the third neck was available for the addition of reagents. The gas train leading from the condenser consisted of a trap, two acid scrubbers for ammonia, and a Wet Test Meter for the measurement of the volume of gas evolved in the reaction.

The fractionating column employed for the fractionation of products which distill at temperatures below 80°C. was a vacuum jacketed, silvered column 24" x 1/2", packed with 1/8" glass helices. It could not be utilized for materials which boil above 100°C. without flooding. Using a test mixture of benzene and carbon tetrachloride, this column was rated at 15 theoretical plates under total reflux. An additional electrically heated column was constructed for the fractionation of substances and compounds which boil above 80°C. It was 31" x 1/2", packed also with 1/8" glass helices. An outer glass tube was wired throughout its length with Chromel-A wire of 30 ohms total resistance. The current for this adiabatic jacket was supplied from a Powerstat.

A modified 125 ml. Claisen flask was also utilized for the rapid fractionation of relatively unstable liquids at atmospheric

or reduced pressures. The arm containing the delivery tube was lengthened by the insertion of a 6 1/2" glass section which was indented so as to increase the refluxing area.

Allyl mercaptan was characterized by its absorption spectrum (Figure 2) obtained from a model DU Beckman quartz spectrophotometer.

MATERIALS

The anhydrous ammonia was supplied by the du Pont Company. It was used directly from the 52 pound cylinder.

All organic sulfides and propyl mercaptan were "Eastman" grade, obtained from the Eastman Kodak Company. The allyl mercaptan was C.P. grade.

Crude thiophene was generously supplied through the courtesy of the Socony Vacuum Oil Co., Inc. This compound was purified by fractional distillation, the fraction distilling at 82°C. under 712 mm. pressure being employed in the investigation.

The sodium was C.P. grade metal stored under oil and cut as needed. Petroleum ether was used to dissolve the oil coating. The residual petroleum ether was evaporated in a stream of nitrogen. Lithium, C.P., was treated in a similar manner.

Beryllium spheres of 97% minimum purity were acquired from the Beryllium Corporation. The metal was shattered by a heavy hammer, washed in petroleum ether, and dried in a stream of nitrogen prior to use.

The ammonium chloride, ammonium sulfate, and ammonium bromide were C.P. grade.

SATURATED ALIPHATIC SULFIDES

General Procedure.--After the system was opened between the first trap and the charged dry ice-ethanol condenser, ammonia was run into the reduction flask. The ammonium salt and organic sulfide were then added in that order, and the contents stirred for several minutes. A 125 ml. Erlenmeyer flask containing pieces of metal having a volume of no greater than three cubic millimeters was attached to a neck of the reduction flask by means of Gooch tubing. The system was then closed and the metal added slowly to the reactor while stirring the contents at a constant rate. An effort was made to regulate the addition of metal so as to insure the smooth gas flow necessary for an accurate gas volume reading on the Wet Test Meter. A blue color, which disappeared with stirring, appeared around the sodium or lithium metal floating on the surface of the ammonia solution. No color was noted in the beryllium experiments. When the reaction had terminated, as indicated by the cessation of gas evolution after all metal was added, the system was opened.

In lengthy beryllium runs where gas evolution had diminished and unreacted metal was present, the stirring rate was periodically increased to about 250 r.p.m. for a few seconds.

The Development of a Method of Recovery for Alkyl Sulfide

Runs.--A photometric method of analysis was attempted which relied upon the extraction of all organic material with isooctane and subsequent measurement of the per cent ultra violet transmission of the hydrocarbon solution. The procedure failed principally because of the high solubility of organic material in the ammonia or aqueous ammonia phase, and difficulty of obtaining a satisfactory blank.

The two major techniques utilized with success were based upon (1) addition of water to the reaction product mixture and (2) allowing the ammonia to evaporate after a run, supposedly leaving the other materials in the flask.

A study of procedure (1) showed that at least one volume of water is required to dilute the ammonia mixture sufficiently to minimize the loss of organic material which may separate as a second phase. As more water is added, the mixture tends to become less effervescent because of the solubility of ammonia in water.

It was also noted that the sulfides and mercaptans found in the reactor after a run were more soluble in a basic than a neutral or weakly acidic solution. Since only 70% of the sulfide, at best, could be accounted for by the simple separation of the organic material from the aqueous phase, the adverse effect of this solubility factor upon recovery was apparent. It was

observed that the recovery of organic material varied within limits in this instance with the amount of excess ammonium salt present, with no recovery being less than 70% when ammonium chloride was added to the reaction products originally for the purpose of decomposing residual metal.

Acidification of the aqueous phase, so as to bring about the separation of additional dissolved organic material, was found to be extremely tedious and wasteful because of (1) the difficulty of dissipating the heat of neutralization, (2) the large amount of acid required, and (3) the relatively large resultant volumes, which impeded extraction.

The continuous ether extractor, employing the principle of concentrating organic material by continuously recycling ether through the aqueous solution, was found to be useless because of the time required for this method of extraction and the necessity of heat, both of which are factors which favor oxidation and/or decomposition of the mercaptan.

Technique (2) was found to be relatively simple but unrewarding when the organic contents of the reduction flask contained low molecular weight sulfides. The method was modified so as to minimize the removal of organic material upon evaporation of ammonia by controlling the rate of evaporation and the addition of 50 ml. of a 20% solution of sodium hydroxide immediately after a run. The ammonia was permitted to weather off through the condenser,

the reactor being surrounded by asbestos powder. Addition of the alkaline solution had the dual effect of preventing the ammonia from boiling off, as opposed to a slow evaporation, and of converting the mercaptan to the nonvolatile mercaptide, thus preventing recovery losses through evaporation of mercaptan. It was realized that some organic sulfide could be lost through vaporization with ammonia, but the loss is small relative to that incurred when no effort is made to control the rate of evaporation. One hundred milliliters of water were added to the contents of the reactor just before all ammonia had been evaporated, and the mixture was stirred under reflux conditions until all solid material dissolved. Upon occasion, more water was added to effect solution. The organic sulfide layer was separated from the aqueous phase, the mercaptan being recovered by acidification and ether extraction of the aqueous phase. The application of this method to a butyl sulfide-lithium-ammonium sulfate run gave a recovery of 81%.

A system was arranged so that ammonia could evaporate through a water cooled condenser and sodium hydroxide trap. Since no organic material was condensed or captured in the trap, this procedure was abandoned.

It was generally observed that technique (1) was more rapid and gave the better recoveries providing the said modifications were employed. The data presented in Table 8 are based on recoveries obtained through the following procedure:

- (a) Ten grams of ammonium chloride were added to the reactor after a run.
- (b) One volume of water was then added, the system being under reflux conditions as in a run. All water soluble salts were dissolved by stirring and the use of more water, if necessary.
- (c) The resultant solution was extracted with successive 50 ml. portions of ethyl ether.
- (d) The combined ether extractions were dried and fractionally distilled, the fractions conforming to the boiling points of the sulfide and corresponding mercaptan being separated and weighed.

ALLYL SULFIDE

General Procedure.--The runs were carried out in a manner similar to that employed for the saturated aliphatic sulfides, with the exception of the technique of metal addition. Since allyl sulfide experiments were more vigorous, all metals utilized were added very slowly, whenever possible, or rapidly, if need be, to favor a constant gas flow comparable to that observed in the saturated aliphatic sulfide runs. A high gas pressure differential in the system, caused by an inconsistent rate of gas evolution, constricted the Gooch tubing through which metal was added and forced the acid scrubbing solution out of the traps.

The system was opened immediately after a run and the products recovered by the final method described in the next section.

A similar procedure was used for the single allyl mercaptan run.

The Development of a Method of Recovery for Allyl Sulfide Runs.--A preliminary run was made employing 0.2 mole of allyl sulfide, 0.4 mole of sodium, and 0.2 mole of ammonium sulfate. It was noted that no organic phase appeared when 200 ml. of water were added to the reaction products, as contrasted to similar treatment of the materials present in the reactor at the conclusion of alkyl sulfide experiments. Moreover, a piece of filter paper moistened with five per cent aqueous lead acetate solution

turned black almost immediately when exposed to the fumes of the resultant solution, indicating the presence of hydrogen sulfide.

The contents of the reactor were extracted with three successive 50 ml. portions of ether, no dissolved material being found in a subsequent fourth extraction. These ether solutions were combined, dried with anhydrous sodium sulfate, and distilled in the modified Claisen flask from 55-140°C. after first stripping off the ether in the 15 plate vacuum jacketed column at 34°C. An attempt to obtain specific fractions in the distillation failed primarily because of the thermal decomposition of the material. The dark brown polymer remaining in the flask closely resembled in appearance and odor that resulting from refluxing allyl mercaptan for 10 minutes.

A vacuum distillation of the products from a similar run at 20 mm. pressure, using the modified Claisen flask, failed to yield but a single fraction distilling continuously over the range 20-42°C. Likewise, distillations at progressively higher pressures failed to yield a satisfactory separation of the products.

Since hydrogen sulfide was detected when water was added to the open reduction flask, it was surmised that a new analytical procedure was desirable for a determination of the products of reduction. The quantitative determination of sulfide ion was believed to be impractical in aqueous ammonia solution because

of possible loss of hydrogen sulfide and oxidation of sulfide to sulfate ion.

The same ammonia weathering procedures applied to the saturated sulfide runs were even less successful with allyl sulfide-sodium-ammonium sulfate runs. It is believed that the evaporating ammonia had entrained most of the reduction products.

1-Decene, a high boiling hydrocarbon, was added to the reduction products after a similar run in an attempt to prevent the loss of sulfur compounds in the weathering procedure by their being extracted into a separate lower hydrocarbon phase. Upon distillation of the decene phase at atmospheric pressure, no organic material save decene was found in the distillate. Extensive polymerization was noted with the progression of distillation. A subsequent vacuum distillation from an identical run failed to yield but one fraction, all material distilling continuously between 53 and 60°C. at 20 mm. pressure.

Similarly, the addition of an even higher boiling hydrocarbon, tetrahydronaphthalene, failed in the same manner as 1-decene as a solution to the recovery problem.

The solid materials, in each of the above runs employing a high boiling additive, was separated from the hydrocarbon phase by vacuum filtration from a Buchner funnel. Without attempting to completely dry the solids, they were placed in a distilling flask fitted with a separatory funnel containing 6 N hydrochloric

acid. The delivery tube led into a flask containing 250 ml. of an aqueous solution of five grams of iodine and enough potassium iodide to permit complete solution of the iodine. Several other similar iodine solutions were held in reserve.

Hydrochloric acid was added slowly, with periodic shaking of the distillation flask, until the evolution of all gas had ceased. The iodine solution was titrated with 1.0 N sodium thiosulfate solution, using starch as an indicator, and the gram ions of sulfide ion formed in the ammonia reactor calculated.

Although the sulfide ion determined by the previous method for one run was added to the best recovery obtained by the ether extraction method for an identical run, the total material balance was only about 60%. This study illustrated the difficulty in obtaining a picture of the extent and type of reduction even when separate identical runs were carried out, the products being recovered specifically for either organic material or sulfide ion.

Two hundred milliliters of ether were added slowly to the reactor immediately after a run and stirred rapidly for ten minutes. An attempt was made to separate the top ether phase from the ammonia phase with the aid of a siphon. The ether phase, containing a large amount of dissolved ammonia, erupted when poured into a graduated cylinder. When most of the ammonia had escaped from this phase, fractional distillation of the ether

revealed but an insignificant amount of organic material, which readily polymerized with further attempts at distillation.

Trial distillations of various mixtures of ether and the expected organic contents of the reactor after a run, allyl sulfide and allyl mercaptan, indicated the following: (1) ether could not be separated from allyl mercaptan at reduced pressure with a standard or modified Claisen distilling flask; (2) the stripping off of ether at 34°C. and atmospheric pressure caused some polymerization of the mercaptan. This difficulty was minimized by using the lowest possible distilling temperature and discontinuing the operation immediately after all ether had been stripped off; (3) fractionation of a pure commercial sample of allyl mercaptan in the modified Claisen flask or vacuum jacketed column gave only 30-40% of a distillate having the boiling point of the monomeric substance (67-68°C.). This sample of allyl mercaptan at one time distilled sharply at 67°C.

The above experiments vividly illustrated the difficulty encountered in attempting to obtain pure allyl mercaptan by fractionation.

It was thus evident from all experimental information that a method of recovery or determination was required which involved neither distillation or a mercaptan phase nor addition of water to the reactor after a run.

A trap was designed whereby gaseous ammonia contaminated with the volatile products of reduction had to pass through an inert upper solvent phase in weathering. Two hundred milliliters of ether were added to the reduction flask after a run, the ammonia being allowed to evaporate slowly, without violent ebullition. The extent of packing of the asbestos around the reduction flask was an excellent regulator of the rate of ammonia evaporation.

After the ammonia had been evaporated, an ether phase and caked solid phase were observed. The two phases were separated, the solid material being subsequently broken up and extracted twice with 25 ml. portions of anhydrous ether. These ether solutions were then combined and divided into several 10 ml. portions for tests.

One portion was treated with 50 ml. of a 10% aqueous lead nitrate solution in an attempt to learn if a lead mercaptide could be precipitated which would be useful for a quantitative determination of the mercaptan present. A yellow precipitate formed instantly which turned grey with the addition of more lead nitrate solution.

Another portion was washed first with 6 N hydrochloric acid solution in order to remove residual ammonia and hydrogen sulfide prior to the addition of lead nitrate solution. A bright yellow coagulate formed, which gradually turned brown in spots when an effort was made to isolate the water-insoluble material by vacuum

filtration from a Büchner funnel. Attempts to dissolve the coagulate in 50 ml. portions of benzene, acetone, ethyl ether, petroleum ether, and ethanol failed. The ease of oxidation of heavy metal mercaptides also seemed to be evident for this presumed lead allyl mercaptide, as indicated by the color shift which took place spontaneously. Hydrogen peroxide caused the color shift to occur immediately.

The dried lead derivative, after having been washed with acetone, decomposed at 65°C. when an effort was made to obtain a melting point.

Because of the difficulties encountered in attempting to quantitatively isolate allyl mercaptan in this investigation, an iodometric method of determination was considered. Initial experiments showed that a five per cent aqueous iodine solution containing potassium iodide would oxidize allyl mercaptan quantitatively without effecting allyl sulfide.

Other trial experiments proved that hydrogen sulfide could be removed quantitatively from a mercaptan by the addition of ethyl ether and subsequent fractional distillation of the ether phase only at 34-36°C. The hydrogen sulfide can be determined iodometrically by passing the ether distillate into a stirred iodine-potassium iodide solution and titrating with sodium thiosulfate, using starch as an indicator. Fractionation without the

prior addition and subsequent stripping off of ether did not yield a hydrogen sulfide-free mercaptan. Other contaminants, such as benzene and a high boiling petroleum ether fraction, did not hinder the extractive distillation procedure.

The iodometric methods were applied in the following manner with relatively good results:

- (a) Two hundred milliliters of dried ether were added to the material in the reactor after a run and the ammonia allowed to evaporate through a drying tube.
- (b) The supernatant liquid and subsequent ether extractions of the solid material were combined and stoppered.
- (c) The solid materials in the cooled reactor were slowly acidified and the evolved hydrogen sulfide led into a standardized iodine solution.
- (d) Organic phases of (b) and that which separated out upon the acidification in (c) were combined. Ether was stripped off into the iodine solution of (c), which was subsequently titrated with standard thiosulfate solution for the iodometric determination of hydrogen sulfide.

- (e) The liquid remaining in the still pot was extracted with three 20 ml. portions of 40% potassium hydroxide, which dissolved the mercaptan by forming the water soluble mercaptide. The residual organic phase (principally allyl sulfide), if any, was fractionated.
- (f) Potassium hydroxide extractions of (e) were slowly acidified at 25°C. the aqueous and resultant organic phase (allyl mercaptan) poured into a standard iodine solution. This solution was titrated with standardized sodium thiosulfate solution for the determination of mercaptan.

In the allyl mercaptan run, only steps (a) to (d), inclusive, were necessitated.

THIOPHENE

General Information.--Hydrogen sulfide was detected by the lead acetate test in the products of a preliminary sodium-ammonium sulfate run carried out in the same manner as in the case of the other sulfur compounds investigated. It was therefore postulated that unsaturated compounds were also by-products of the reductive-cleavage of the carbon-sulfur bond in the thiophene molecule.

All runs were carried out exactly as indicated previously for allyl sulfide. The reaction rate here was also more violent than that observed in alkyl sulfide experiments.

Recovery of Products from Thiophene Runs.--The following procedure was found to give satisfactory recoveries:

- (a) Two hundred milliliters of sodium sulfate dried ether were added to the reduction products immediately after a run, the ammonia being subsequently allowed to weather off through a drying tube.
- (b) The ether phase remaining in the reactor was decanted off and the residual solid material extracted with dried ether.
- (c) The solid material was acidified and the evolved hydrogen sulfide passed through a known iodine-potassium iodide solution.

- (d) The combined organic phases were fractionated at 34°C. into the iodine solution of (c), and the hydrogen sulfide thus determined iodometrically after titration with sodium thiosulfate solution. (An examination of the residual material in the still pot at this point showed that if a viscous material were present, it could not be fractionated without complete decomposition. In this instance (e) was observed.)
- (e) The material in the still pot was weighed and oxidized with a known iodine-potassium iodide solution for the determination of what was believed to be crotyl mercaptan⁵.
- (f) If the material in the still pot were non-viscous, distillation was carried out from a 50 ml. flask, the fractions being identified by their refractive indices and boiling points.

IV

DISCUSSION

The working hypothesis which guided this investigation is that the reduction of organic compounds at a given temperature and solute-solvent ratio is dependent upon the half-cell potential of the metal and the concentration of the proton donor. The three metals studied were lithium, sodium, and beryllium having standard half-cell potentials in liquid ammonia at -50°C . of 3.0, 2.6, and 1.2 volts, respectively. The values for sodium and lithium are those of Pleskov^{42,43}, while the value for beryllium is an estimate based on that of calcium and sodium. Ammonium salts used in this work were the sulfate, chloride, and bromide, whose solubilities in ammonia are 0.0, 1.4, and 2.0 moles/liter, respectively⁴⁷. Since two equivalents of ammonium salt are employed for each liter of ammonia, the solubilities of the sulfate and chloride being exceeded, initial concentrations of these salts were the same as the solubilities. A reservoir of ammonium ions was available from the undissolved solid in the reactor in the case of these two proton donors, as contrasted to ammonium bromide which dissolved completely in ammonia to give a concentration of two moles per liter.

In Table 1 are presented, according to class, the organic compounds of sulfur studied in this investigation.

Table 1
Compounds Investigated

Sulfides	Mercaptans	Heterocyclic Compound
$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{S}$ $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{S}$ $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{S}$ $(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{S}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$ $\text{CH}_2=\text{CH}-\text{CH}_2\text{SH}$

The experimental data are given in Tables 8, 9, and 10.

Saturated Sulfides.--The carbon to sulfur bond is a very stable linkage, and its bond energy value is reported by Pauling to be 54.5 kcal mole⁻¹ compared with 58.6 for the carbon to carbon bond. Using the said metals and proton donors, the stability of the saturated sulfides were determined as a function of the half-cell potential of the metal and the concentration of proton donor.

From these data presented in Table 8, several interesting trends are noted. Upon consideration of the reducing system $\text{Li}-(\text{NH}_4)_2\text{SO}_4-\text{NH}_3$, it is found that n-propyl sulfide undergoes a 13% reduction to n-propyl mercaptan, while n-butyl sulfide and n-hexyl sulfide are reduced in the order of 2-6% to the mercaptan. Thus, as the molecular weight of the sulfide increases (solubility

in ammonia decreasing), the extent of reduction decreases. The mercaptan formed is not reduced, as evidenced by the absence of hydrogen sulfide in the products. In the case of ammonium sulfate as a proton donor, lithium metal, which has the highest electrode reduction potential of the metals used, effected a 13% reduction of n-propyl sulfide, while sodium and beryllium caused no reduction.

The data from a number of experiments where no reduction of the sulfur compound had taken place are omitted since no fundamental information concerning organic product distribution is gained through their consideration. In each of these instances, the volume of hydrogen evolved approximated that calculated from the assumption that all metal was consumed in the reduction of ammonium ion, i.e.,

It was noted in the lithium runs that the volume of hydrogen evolved decreased as the extent of reduction became more pronounced.

The effects of the concentration of the proton donor on the extent of reduction of the sulfide linkage in propyl sulfide are given in Table 2.

Table 2

Propyl Sulfide and Lithium in Ammonia

Proton Donor	% Reduction
None	35
$(\text{NH}_4)_2\text{SO}_4$	13
NH_4Cl	3

As the concentration of the ammonium ions increases, it was apparent that the reduction of these ions gained preference to the competitive reduction-cleavage of the carbon-sulfur bond.

Unsaturated Sulfide.--Allyl sulfide was the only organic sulfur compound employed here. The greater reactivity of allyl sulfide as compared with the previously mentioned saturated sulfides was immediately apparent upon the addition of metal. Reactivity was not only increased, but reduction was more extensive since appreciable amounts of hydrogen sulfide were found. In the presence of ammonium sulfate as a proton donor, sodium and lithium effected 100% conversion of allyl sulfide. Beryllium metal was inert, no reduction products or hydrogen being detected.

In the case of ammonium chloride, all metals showed some reactivity. The conversion of allyl sulfide using this proton donor is given in Table 3.

Table 3

Allyl Sulfide and Ammonium Chloride in Ammonia

Metal	% Conversion
Li	100
Na	42
Be	0

With a given donor, the stronger the reducing potential of the metal, the greater is the conversion of allyl sulfide. Beryllium metal did not effect reduction of allyl sulfide although 72% of the theoretical amount of hydrogen gas was evolved. Some beryllium metal remained unreacted.

The extent of reduction of allyl sulfide under different conditions is revealed by a consideration of product distribution as presented in Table 4.

Table 4
Product Distribution

Metal	Proton Donor	Products	
		$\text{CH}_2=\text{CH}-\text{CH}_2\text{SH}$	H_2S
Li	$(\text{NH}_4)_2\text{SO}_4$	85	15
Li	NH_4Cl	88	12
Na	$(\text{NH}_4)_2\text{SO}_4$	92	8
Na	NH_4Cl	95	5
Na	NH_4Br	95	5

In Table 3 it is seen that the per cent conversion of allyl sulfide increases as the reducing power of the metal (availability of electrons) increases. The above table conclusively shows that the selection of the metal utilized has a more pronounced effect on the extent of reduction of allyl sulfide than the specific ammonium salt present, i.e., concentration of proton donor. In the presence of ammonium sulfate, the more reactive lithium yields 85% allyl mercaptan and 15% hydrogen sulfide as compared with 92% and 8%, respectively, obtained with sodium.

It should be noted at this point that from these studies has resulted a new synthesis of pure allyl mercaptan. A dried sample of the mercaptan from an allyl sulfide-sodium-ammonium sulfate run,

which experiment gave best yields of the product, had an absorption spectrum (Figure 2) and boiling point conforming with that of the pure commercial material.

The influence of the concentration of proton donor on the conversion of allyl sulfide is illustrated by the values of Table 5.

Table 5
Allyl Sulfide-Sodium Ammonia

Proton Donor	% Conversion
$(\text{NH}_4)_2\text{SO}_4$	100
NH_4Cl	42
NH_4Br	19

A comparison of the results of the reductive-cleavage of the carbon to sulfur bond in alkyl and allyl type compounds reveals the tremendous effect of the double bond. The greater reactivity of allyl sulfide is not unexpected in view of the known properties of allylic compounds. In terms of electronic theory, the relatively low -I effect of the carbon-sulfur bond is recognized, and the attacking agent (the nucleophilic solvated electron) receives little help in promoting bond cleavage. The rupture of the carbon-sulfur bond in allyl sulfide is probably facilitated by an electromeric effect induced by the approach of the nucleophilic reagent.

The allyl mercaptide ion formed as a result of the reaction given above could then undergo reduction to the sulfide and acid sulfide ion and a second molecule of propene. Under similar experimental conditions, the reduction of allyl sulfide proceeds to a greater extent than the reduction of allyl mercaptan, as illustrated in Table 6.

Sulfide and acid sulfide ion were determined as hydrogen sulfide by the analytical procedure described in section III.

Mercaptans.--n-Propyl mercaptan did not undergo reduction either in the presence or absence of a proton donor. This stability was expected in view of the experiments with propyl sulfide where propyl mercaptan was the ultimate product of reduction.

Allyl mercaptan in the presence of lithium and ammonium sulfate was converted to hydrogen sulfide in 70% yield. This experiment further demonstrated the susceptibility to cleavage of the carbon to sulfur bond in an allylic type structure. For a given metal and proton donor, the effect of the introduction of a double bond in the β,γ position is shown in Table 6. The numbers in the

second column represent relative ease of reaction as indicated by the per cent conversion under the experimental conditions.

Table 6

Reductive Cleavage of the Carbon-Sulfur Bond
in the $\text{Li}-(\text{NH}_4)_2\text{SO}_4\text{-NH}_3$ System

Compound	Reactivity
$\text{CH}_3\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_3$	1.0
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{SH}$	5.4
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{S}-\text{CH}_2-\text{CH}=\text{CH}_2$	7.8

Heterocyclic Compound.--Both lithium and sodium in the presence of different ammonium salts effected the reduction of thiophene. Beryllium caused no reduction of the organic compound, although some hydrogen was evolved during the reaction period. Data obtained in the case of lithium and sodium with different salts are presented in Table 7.

Table 7
Product Distribution for Thiophene Experiments

Metal	Proton Donor	Products		
		H ₂ S	RSH	Polymer
Li	(NH ₄) ₂ SO ₄	25	9	65
Li	NH ₄ Cl	25	6	70
Na	(NH ₄) ₂ SO ₄	4	7	90
Na	NH ₄ Cl	5	4	90

The mercaptan symbolized as RSH is believed to be crotyl mercaptan. The composition of the polymer may be (C₄H₄S)_x as indicated by the material balance of the runs producing polymer. As in the case of other sulfur compounds investigated, lithium caused the most extensive reduction, i.e., the complete rupture of the carbon to sulfur bonds of the thiophene ring. No unreacted thiophene was found in runs 1, 2, 4, and 5, given in Table 10.

Lithium in the presence of ammonium bromide effected a 53% conversion of thiophene, polymer and a trace of hydrogen sulfide being the only products identified.

Sodium with ammonium bromide caused a 42% conversion of thiophene yielding isomeric 2,3- and 2,5- dihydrothiophenes as

the principal products. A trace of hydrogen sulfide was detected, and very little polymer was obtained. On the basis of 100% conversion, the yield of the dihydrothiophenes was 84% and polymer 16%. Physical constants (boiling point, refractive index) for the dihydrothiophenes are in excellent agreement with the recently published data of Birch and McAllan⁵, who employed sodium and methanol in ammonia as the reducing system. Hydrogen sulfide, crotyl mercaptan, and 2-butene were also obtained in the latter paper. The use of ammonium bromide in the present investigation holds promise of an excellent method of synthesis of dihydrothiophenes since side reactions are minimized.

It should be noted that again the metal of greatest reducing potential effects the most extensive reduction, and the greater the concentration of ammonium ion the lower the percentage reduction of the compound. The small amount of polymer found in the case of sodium and ammonium bromide may be related to the high ammonium ion concentration. Additional information is needed to interpret this phenomenon.

The polymer formed in this investigation of thiophene was a light amber, viscous mass which became a tough solid upon standing in an open beaker for several days. No thiophene polymer of the empirical formula postulated for this resin, $(C_4H_4S)_x$, is reported in the literature.

Mechanism of Reduction.--The work presented lends additional support to the mechanism of the reducing action of metal in liquid ammonia as presented by Krug and Hsieh³². Throughout the course of the present investigation, temperature, solute-solvent ratios, and the type of proton donor were kept constant. A study of the effect of these variables is beyond the scope of the present paper.

It is postulated that the metals dissolve in the reaction media as follows^{23,30}:

The solvated electron may then react with the organic sulfur compound, e.g.,

The proton donor subsequently reacts as follows:

Following the rupture of the first carbon-sulfur bond in allyl sulfide, as in equation (2), the allyl mercaptide ion may then have been reduced according to the following equation:

The acid sulfide ion can then participate in the reaction

The solvated electrons formed in the reaction illustrated by equation (1) can also reduce ammonium ions to yield hydrogen and ammonia.

Thus, equation (7) competes for the electrons with equation (2). The greater the concentration of the ammonium ions, the more predominant becomes equation (7), as clearly shown in the experimental data. Similarly, it was evident from the volume of hydrogen produced in specific runs that more weight can be placed on equation (7) as the organic sulfur compound becomes more difficult to reduce.

The greater the electron release of the metal, i.e., availability of solvated electrons for reaction (2), the greater will be the reduction of the sulfur compound.

The experimental evidence in this work is in opposition to the concept of reduction by active or "nascent" hydrogen. In the study of alkyl sulfides, the data reveal in several instances that beryllium and sodium effect no reduction of the organic compound, although the yield of hydrogen approaches the theoretical value, i.e., where it was assumed that only reaction (7) had occurred.

Further, the attack by a solvated electron as postulated in equation (2) very nicely interprets the reduction of alkynes to yield exclusively trans olefins^{8,18}.

The large ammonia molecule could easily prevent a cis attack at the triple bond. It is highly doubtful that the unsolvated electron or atomic hydrogen could accomplish the same results.

V

SUMMARY

1. A systematic study of the reduction of organic sulfur compounds by different metals in liquid ammonia is reported for the first time.
2. A metal with a high half-cell potential favors a greater extent of reduction than a lower potential metal.
3. The greater the concentration of ammonium ion as a proton donor, the greater will be the evolution of hydrogen, and the lower will be the extent of reduction.
4. A mechanism for the reduction of organic sulfur compounds by metals in ammonia is presented.
5. A new procedure for the quantitative removal and determination of hydrogen sulfide in mercaptans was developed.
6. A new synthesis for allyl mercaptan was found.
7. The formation of a resin believed to be a thiophene polymer of the formula $(C_4H_4S)_x$ is reported.

VI

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VII

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IX

APPENDIX

This appendix contains tables of experimental data and illustrations not included in the text.

Table

8. Reduction of Saturated Sulfides
9. Reduction of Allyl Sulfide
10. Reduction of Thiophene

Figure

1. Liquid Ammonia Reactor System
2. Allyl Mercaptan - Per Cent Transmission vs. Wave Length
3. Allyl Sulfide Experiments - Product Distribution Based on
100 % Recovery

Table 8
Reduction of Saturated Aliphatic Sulfides

Experiment No.		1	2	3	4	5	6	7	8	9	10	11	12	13	14
Saturated Sulfide (R-S-R) R=alkyl group	Form.	$C_6H_{14}S$								$C_8H_{18}S$			$C_{12}H_{26}S$		
	Grams	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	20.0	20.0	20.0
	Moles	0.212	0.212	0.212	0.212	0.212	0.212	0.212	0.212	0.171	0.171	0.171	0.100	0.100	0.100
Metal	Symbol	Na	Na	Li	Li	Be	Be	Li	Na	Li	Li	Na	Li	Na	Li
	Grams	9.8	9.8	2.9	2.9	1.9	1.9	2.9	9.8	2.4	2.4	7.9	1.4	4.6	1.4
	Moles	0.424	0.424	0.424	0.424	0.212	0.212	0.424	0.424	0.342	0.342	0.342	0.200	0.200	0.200
Ammonium Salt Proton Donor	Anion	Cl ⁻	SO ₄ ⁼	Cl ⁻	SO ₄ ⁼	Cl ⁻	SO ₄ ⁼	--	--	SO ₄ ⁼	Cl ⁻	SO ₄ ⁼	SO ₄ ⁼	SO ₄ ⁼	Cl ⁻
	Grams	22.7	28.0	22.7	28.0	22.7	28.0	--	--	22.6	18.3	22.6	13.2	13.2	10.67
	Moles	0.424	0.212	0.424	0.212	0.424	0.212	--	--	0.171	0.342	0.171	0.100	0.100	0.200
Unchanged R-S-R	Grams	23.0	22.5	21.3	19.0	22.8	23.0	13.5	14.3	19.5	23.0	22.3	16.8	18.5	18.2
	Moles	0.195	0.190	0.180	0.161	0.193	0.195	0.114	0.121	0.133	0.157	0.152	0.083	0.091	0.090
Products	RSH	Grams	0.0	0.0	0.4	1.9	0.0	0.0	4.8	4.0	0.3	0.0	0.0	0.6	0.0
		Moles	0.0	0.0	0.005	0.025	0.0	0.0	0.063	0.053	0.0033	0.0	0.0	0.005	0.0
	Mole % Recovery		92	90	87	88	91	92	84	82	79.5	92	89	88	91
	Gas	Gas, Liters(STP)	5.13	4.88	4.48	3.52	4.85	4.52	2.09	4.07	3.62	3.98	3.80	1.86	2.16
		Theo. Volume	4.75	4.75	4.75	4.75	4.75	4.75	4.75	4.75	3.83	3.83	3.83	2.24	2.24
		% Theo. Vol.	100*	100*	95	74	100*	95	44	86	95	100*	100*	83	96.5
	%*		100	100	97	87	0	0	65	69	0	0	0	35	31
		R-S-H	0	0	3	13	0	0	35	31	0	0	0	0	0

* These values are based on 100% recovery.

** No proton donor was used in the run.

Table 9
Reduction of Allyl Sulfide

Experiment No.			1	2	3	4	5	6	7*	8			
Allyl Sulfide R-S-R			Grams	22.8	22.8	22.8	22.8	22.8	22.8	22.8			
			Moles	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200		
Metal			Symbol	Na	Na	Li	Li	Be	Be	Li	Na		
			Grams	9.2	9.2	2.8	2.8	1.8	1.8	2.8	9.2		
			Moles	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40		
Ammonium Salt Proton Donor			Anion	SO ₄ ⁼	Cl ⁻	SO ₄ ⁼	Cl ⁻	Cl ⁻	SO ₄ ⁼	SO ₄ ⁼	Br ⁻		
			Grams	26.2	21.4	26.2	21.4	21.4	26.5	26.5	39.2		
			Moles	0.200	0.400	0.200	0.400	0.400	0.200	0.200	0.400		
Products			RSR ⁽¹⁾		Grams	0.0	11.0	0.0	0.0	21.3	19.2	-	15.8
					Moles	0.0	0.097	0.0	0.0	0.187	0.166	-	0.138
			RSH		Grams	11.0	4.94	10.20	10.50	0.0	0.0	3.60	2.21
					Moles	0.148	0.06	0.138	0.142	0.0	0.0	0.049	0.030
			H ₂ S		Grams	0.4	0.1	0.80	0.67	0.0	0.0	4.0	0.03
					Moles	0.135	0.0034	0.024	0.020	0.0	0.0	0.120	0.001?
			Mole % Recov.		81	83	81	81	94	83	85	85	
			Gas		Liters (STP)	4.60	4.70	4.25	4.42	3.26	-	-	-
					Liters, Theo.	4.48	4.48	4.48	4.48	4.48	4.48	4.48	4.48
					% Theo. (2)	100 ⁺	100 ⁺	95	98	72	-	-	-
% Conversion of R-S-R			100	42	100	100	0	0	71	19			
Based on 100% Recov.			RSR		Moles	0.0	0.116	0.0	0.0	0.0	0.200	-	0.163
					%	0.0	58	0.0	0.0	100	100	-	81
			RSH		Moles	0.183	0.080	0.170	0.175	0.0	0.0	0.058	0.035
					%	92	40	85	88	0	0	29	18
			H ₂ S		Moles	0.017	0.004	0.029	0.024	0.0	0.0	0.14	0.0012
					%	8	2	15	12	0	0	71	1

* Allyl mercaptan.

(1) The letter R represents an allyl group.

(2) This figure is based on the reaction of metal with ammonium ion only.

Table 10
Reduction of Thiophene

Experiment No.		1	2	3	4	5	6	7	8
Thiophene	Grams	16.8	16.8	16.8	16.8	16.8	16.8	16.8	16.8
	Moles	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200
Metal	Symbol	Li	Li	Li	Na	Na	Na	Be	Be
	Grams	2.8	2.8	2.8	2.8	9.2	9.2	1.8	1.8
	Moles	0.40	0.40	0.40	0.40	0.40	0.40	0.20	0.20
Ammonium Salt Proton Donor	Anion	SO ₄ ⁼	Cl ⁻	Br ⁻	SO ₄ ⁼	Cl ⁻	Br ⁻	SO ₄ ⁼	Cl ⁻
	Grams	26.5	21.4	39.2	26.5	21.4	39.2	26.5	21.4
	Moles	0.200	0.400	0.400	0.200	0.400	0.400	0.200	0.400
Unreacted Thiophene	Grams	0.0	0.0	6.8	0.0	0.0	7.6	13.9	14.2
	Moles	0.0	0.0	0.084	0.0	0.0	0.090	0.166	0.169
Products	H ₂ S	Grams	1.43	1.40	0.0	0.40	0.30	0.0	0.0
		Moles	0.042	0.041	0.0	0.012	0.009	0.0	0.0
	RSH C ₄ H ₈ S (?)	Grams	1.32	0.90	0.0	0.60	0.60	0.0	0.0
		Moles	0.015	0.010	0.0	0.007	0.007	0.0	0.0
	Dihydro-Thiophenes	Grams	0.0	0.0	0.0	0.0	0.0	5.0	0.0
		Moles	0.0	0.0	0.0	0.0	0.0	0.058	0.0
	Polymer (C ₄ H ₄ S) _x (?)	Grams	9.3	9.6	7.6	13.0	13.4	0.8	0.0
		Moles	0.11	0.11	0.09	0.16	0.16	0.01	0.0
	Mole % Recovery		84	71	87	90	88	79	85
	Gas, Liters (STP)		1.59	1.86	3.89	2.57	1.39	4.15	0.692
	%		3.30						
% Thiophene Conv.			100	100	52	100	100	49	0
Based on 100% Recovery	Thiophene	Moles	0.0	0.0	0.097	0.0	0.0	0.11	0.20
		%	0	0	47	0	0	55	100
	H ₂ S	Moles	0.051	0.051	0.0	0.008	0.010	0.0	
		%	25	25	0	4	5	0	
	RSH	Moles	0.018	0.012	0.0	0.014	0.008	0.0	
		%	9	6	0	7	4	0	
	Dihydro-Thiophenes	Moles	0.0	0.0	0.0	0.0	0.0	0.073	
		%	0	0	0	0	0	38 ⁺	
	Polymer	Moles	0.13	0.14	0.10	0.18	0.18	0.013	
		%	65	70	52	90	90	7	

Figure 1

LIQUID AMMONIA REACTOR SYSTEM

Figure 2

(0.5 GRAM ALLYL MERCAPTAN DILUTED TO 100 MILLILITERS WITH
ISOÖCTANE)

Figure 3

ALLYL SULFIDE EXPERIMENTS

PRODUCT DISTRIBUTION BASED ON 100 % RECOVERY