

THE REDUCING ACTION OF DIFFERENT METALS

IN LIQUID AMMONIA

by

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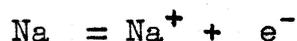
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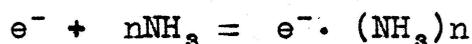
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I. INTRODUCTION

Kraus³⁵ in 1908 studied the conductivities of solutions of alkali metals in liquid ammonia. His work showed that the conduction process was ionic. On the basis of this evidence, Kraus postulated that sodium dissolves in liquid ammonia as follows:



Further, the electron was solvated in the ammonia.



Since Kraus' article, voluminous work has been done in the field of reduction of organic compounds in liquid ammonia. While reduction in ammonia is not new, there has been little work done on reaction mechanisms, identification of by-products, or the nature of the effect of process variables.⁵⁷ Most of the work has been directed toward the development of new synthetic methods. To understand these new methods then, it is important to know more about the reactions in liquid ammonia themselves.

Most of the work has been done using sodium metal and relatively little using other metals such as potassium, calcium, and beryllium. Williams⁶³ reduced 2-acetylthiophene in ammonia using sodium, calcium, and beryllium. He found that sodium effected a more extensive reduction of 2-acetylthiophene than did beryllium. This would seem to indicate that the amount of reduction caused by each metal was in some

way related to the electrode potential of the metal used. This forms the basis of this investigation, i.e., to study the reducing action of the metals sodium, lithium, aluminum, and beryllium on a single organic compound methyl ethyl ketone. It is hoped that the study of simple molecules might eventually lead to the selective reduction of poly-functional molecules once the effects of various metals and proton donors have been ascertained.

The use of proton donors to assist reduction has been long practiced by many investigators but the effect in each case has been unpredictable. In this investigation, the effect of a single type of proton donor, namely ammonium salts, is to be studied. The extent and type of reduction brought about by different metals will be evaluated. On the basis of these studies it may then be possible to describe the mechanism of the reducing action of the system metal-ammonium ion-ammonia on methyl ethyl ketone.

By the study of the effect of different metals and various ammonium ion concentrations on simple molecules such as nitriles, ketones, sulfides, and alkynes, it may then be possible to bring about the selective reduction of poly-functional molecules by the appropriate choice of metal and proton donor.

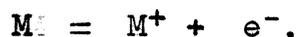
II. HISTORICAL

Soon after the discovery of metallic sodium and potassium by Davy¹⁴ in 1807, Gay-Lussac and Thénard²³, during the course of their examination of the properties of the newly found metals studied the reaction of these metals with ammonia. They were the first to prepare the amides of sodium and potassium and assigned the formula NaNH_2 and KNH_2 to the new compounds²⁴. In the years that followed, a great amount of work was done by many investigators on the properties and reactions of the alkali amides.

Weyl⁶¹ studied solutions of alkali metals in liquid ammonia and observed the formation of highly colored solutions. Recently, Krüger⁴⁰ suggested that the color was due to colloidal particles in the solution. After Weyl's work, Seely^{53,54,55} reported that solutions were formed between metal and ammonia with little tendency for the formation of amides. This has been substantiated by the work of Johnson and Meyer³². Seely further found that aluminum, magnesium, thallium, indium, mercury, and copper were insoluble in liquid ammonia. Later work by Moissan⁴⁴ and Guntz^{27,28} showed cesium, calcium, barium, and strontium to be soluble in liquid ammonia. Bergstrom¹ reported the solubility of manganese and amalgamated aluminum in ammonium ion-ammonia system at room temperature. Recently, aluminum was reported to be very slightly soluble in liquid ammonia.¹³

In 1908, Kraus³⁵, by studies of conductivities of solutions of

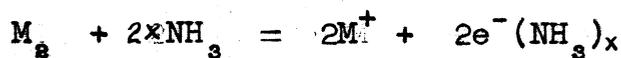
alkali metals in liquid ammonia concluded that the conduction process was ionic. He postulated that the metal ionized in liquid ammonia as follows,



and the free electron was solvated,



Recent studies²⁰ of the magnetic susceptibilities of certain metals in liquid ammonia indicate that perhaps the following equation may be preferred.



Until further evidence is presented however, the equations used in the present discussion will be those of Kraus.

It is evident that the solvated electron represents a reducing agent of great power. Thus, solutions of metals in liquid ammonia represent an unusual opportunity for the study of redox reactions. A further advantage is the fact that whereas sodium in water decomposes violently to form hydrogen and a solution of sodium hydroxide, sodium in liquid ammonia merely dissolves forming a rather stable system with relatively little compound formation³².

A study of the properties of liquid ammonia and water reveal the similarity of the two. Both have unusually high dielectric constants⁴⁶.

Liquid ammonia is an excellent solvent for a large variety of substances¹⁹, many of which are insoluble in water. The solvent powers of liquid ammonia have been compared to that of the lower alcohols^{8,18}. The tendency for solvolysis to occur is less in ammonia than in water. A disadvantage of working with liquid ammonia lies in the special apparatus and techniques necessary for handling the material.

Early workers conceived the idea of using a compound with an active hydrogen, i.e., a proton donor, to aid the reduction. Although the effects of many proton donors have been noted, relatively little is known about the cause of these effects. The effects of proton donors such as methanol and the ammonium salts upon the reduction of different compounds show marked variations. The role of co-solvents and diluents have been studied^{15,62,66}, but much work has to be done to clarify their actions.

Probably the most widely used proton donors are the ammonium salts. Watt, Knowles, and Morgan⁵⁹ have reported that the use of ammonium bromide and methanol as proton donors in the presence of sodium in ammonia increased or decreased the extent of reduction of nitrobenzene and 2-nitrofluorene in an unpredictable way. Henne and Greenlee²⁹ reported that sodium alone in ammonia is more effective in reducing acetylene than sodium and ammonium sulfate. They further state that the nascent or atomic hydrogen seemed to be the prime reducing agent.

Extensive investigations have been carried out on the reduction

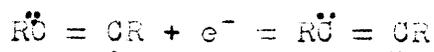
of many types of organic compounds. Among the more interesting types studied are the alkenes and alkynes. Simple ethylenic hydrocarbons are not very reactive toward solutions of metals in liquid ammonia,⁴² but butadiene has been reduced by sodium to butene and an octadiene³¹. Isoprene was reduced to 2-methyl-2butene in 60% yield⁴³ but the 2-methyl-2-butene was not further reduced by sodium in ammonia. Recently, Greenlee and Henne²⁶ reduced a whole series of 1, 3 dienes. They found only a few cases of 1, 2 addition, most of the addition being 1, 4. Many phenyl substituted ethylenic hydrocarbons have been studied wherein either reduction or polymerization occurred⁶⁶.

Solutions of alkali metals in ammonia are very important in the study of alkynes. Preparation of many substituted alkynes utilize the formation of a sodium or calcium acetylide^{44,45}.



Henne and Greenlee²⁹ have studied the reduction of a number of alkynes using sodium alone and with ammonium chloride or ammonium sulfate as proton donors. They reported that the addition of sodium followed by the addition of an ammonium salt led to complete reduction with high yields of olefin. When ammonium chloride was used, hydrogen was evolved and reduction of the alkyne was incomplete. They further reported that the use of relatively insoluble ammonium sulfate increased the efficiency of the reduction. From these facts, they reached the conclusion that the hydrogen from the alkyne was a more powerful reducing agent than the proton from the ammonium ion.

Greenlee and Fernelius²⁵ studied the reduction of dialkyl acetylenes. They obtained high yields of exclusively the trans olefin and attributed this to the formation of ionic intermediates



in which the trans isomers are produced by electrostatic repulsion leading to a configuration which is maintained during subsequent ammonolysis. Diacetylenes²⁹ have been reduced by sodium or sodium and ammonium sulfate to the corresponding trans-trans dienes. In the reduction of alkynes, at no place is there ever a complete reduction, i.e., to the alkene.

Benzene is not attacked by sodium in ammonia^{42,52,65} and may be used as co-solvent in many reactions as may xylene or toluene. Benzene is attacked however by sodium in the presence of a proton donor. Biphenyl has been reduced to the tetrahydrobiphenyl^{31,42} and naphthalene to tetrahydronaphthalene^{41,52,67} but methanol reduces the efficiency of the reduction.

Alcohols react readily with liquid ammonia and alkali metals as proton donors forming hydrogen and alkoxides^{9,38}. Unsaturated alcohols are reduced either at the primary alcohol grouping or the double bond^{10,11,12}. Phenols react with solutions of alkali metals in a manner similar to the aliphatic alcohols but naphthols are reduced

to the tetrahydronaphthol.

Aliphatic ethers are in general unreactive towards sodium in liquid ammonia and have been used extensively as solvents. However, aromatic ethers are cleaved by sodium or potassium in liquid ammonia^{21,23,34,49,60} as follows:



Birch^{3,4,5} reduced ethers by the use of sodium and ethanol or methanol in ammonia.

Aldehydes in general react very readily with liquid ammonia³⁸ so this medium is not suitable for reactions between metals and aldehydes. Relatively few ketones have been studied with solutions of metals in ammonia. Acetone has been studied but the reactions products were not fully characterized³⁹. Benzophenone plus one equivalent of sodium in liquid ammonia forms the metal ketyl while with two equivalents, the diketyl is formed. The diketyl gives the corresponding alcohol when treated with water or ammonium chloride as proton donor³⁹.

Carbohydrates and cellulose derivatives have been reacted with solutions of sodium in liquid ammonia. Cellulose amines have been prepared from cellulose nitrate⁵¹.

Carboxylic acids and esters have been studied⁵⁷. Nitroparaffins are not reduced by sodium plus ammonium bromide⁵⁸, but are slowly and incompletely reduced to corresponding alkyl hydroxylamines by sodium in ammonia alone. The reduction of nitrobenzene with sodium in liquid

ammonia yields varied and complex products⁶². However, with either ammonium bromide or methanol as a proton donor, greater reduction is effected and higher yields of aniline are found⁵⁹.

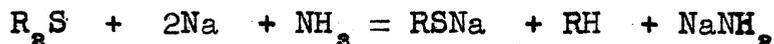
1 - Nitronaphthalene is reduced to dihydro-1-naphthylamine in 97% yield by sodium alone but is a slow reaction because of insolubility of the 1-nitronaphthalene in ammonia⁵⁹. If ammonium bromide is used however, the reduction product is 1-naphthylamine in low yields which may be improved by the use of toluene as co-solvent. If methanol is used in place of ammonium bromide, the dihydro-and tetrahydro-naphthylamines are isolated.

2 - Nitrofluorene is reduced to tetrahydro-2-aminofluorene in 89% yield by sodium in ammonia. With ammonium bromide as a proton donor, there is no reaction. The tetrahydro-and hexahydro-2-aminofluorenes are found if methanol is the proton donor.

Azoxybenzene can be reduced by sodium in liquid ammonia to azobenzene which can be further reduced to the disodium salt of hydrazobenzene⁶². Azobenzene is reduced to aniline by sodium and ammonium bromide in ammonia.

Considerable work has been done with heterocyclic compounds, especially by Fernelius and Cappel^{7,16,17}. Benzoxazole and benzothiazole have been reduced by sodium in ammonia with ring cleavage in the heterocyclic ring. More extensive reduction is reported with ammonium bromide as proton donor. Alkyl mercaptans and phenyl

mercaptans react with liquid ammonia to form ammonium salts which in turn react with sodium to form the corresponding sodium mercaptides^{37,38}. Aliphatic sulfides react with sodium in ammonia chiefly according to the following equation.



From the above survey of reactions in liquid ammonia, it can be seen that most of the work is apparently unrelated, and for the most part with but one purpose, i.e., synthesis.

One can conclude then, that a systematic study of the redox reaction in ammonia is highly desirable. From a study of the effect of different metals and ammonium salts, the nature of the mechanism of the reaction may be revealed. Such information may then be applied to the preparation of organic compounds by selective reduction.

III. EXPERIMENTAL

MATERIALS

The ammonia was National Anhydrous Ammonia supplied by the duPont Company. It was used directly from the 52 pound cylinder.

The methyl ethyl ketone was Eastman Kodak No. 383 bp 79-80° C., dried over CaCl_2 prior to use.

The sodium was c. p. grade metal stored under oil and cut as needed. The bright metal, in cubes of about 5 mm. in length, was washed with petroleum ether to remove the heavy oil coating. Residual petroleum ether was removed in a stream of nitrogen. Lithium (c. p.) was handled in a similar manner although it was extremely difficult to keep the metal free of an oxide film.

Beryllium spheres of 97% minimum purity were supplied by the Beryllium Corporation. The metal was shattered with a heavy hammer to give small pieces which could be conveniently handled. The metal was washed with petroleum ether and dried in a stream of nitrogen.

Manganese flakes (carbide free) were obtained from the Coleman and Bell Company. A microscopic examination of the surface of these flakes revealed a very dull appearance. In order to present a clean surface for reaction in the reduction experiments the manganese was treated with dilute hydrochloric acid, water washed, and then washed in benzene. The metal was then washed with petroleum ether and dried in a nitrogen atmosphere. The metallic surface appeared exceedingly

bright under the microscope. The ammonium chloride, ammonium sulfate, and ammonium bromide were c. p. grade dried prior to use.

APPARATUS

The liquid ammonia reactor system is illustrated in Figure 3. A round bottom, 3-neck flask protected by asbestos insulation is connected to a dry ice-ethanol cooled condenser. A rubber sealed stirrer is attached to the middle neck of the flask while the third neck is available for addition of reagents. The gas train leading from the condenser consists of an activated Al_2O_3 drying tube to protect the contents of the reactor, a safety bottle, an acid scrubber for ammonia, and a gas holder. The liquid in the gas holder is saturated sodium chloride solution, which is displaced if there is a positive gas flow in the system.

To determine the temperature in the flask at given intervals, a Rubicon Company potentiometer serial No. 56334 using a copper-constantan couple was employed. Temperatures were recorded ranging from -35°C . to -40°C .

The continuous ether extractor used in this work is shown in Figure 4.

The fractionating column employed to separate the ether, ketone, and alcohol was a vacuum jacketed, silvered column 24" x $\frac{1}{2}$ " packed with $\frac{1}{8}$ " glass helices. Using a test mixture of benzene and carbon tetrachloride, this column was rated at 15 theoretical plates under total reflux.

REDUCTION OF METHYL ETHYL KETONE

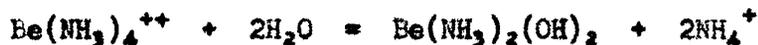
Sodium-Ammonium Sulfate. - - Into the three neck flask was run a total of 500 ml. of ammonia and to this was added 66.1 g. (0.50 mole) ammonium sulfate (c. p.) and 36.0 g. (0.50 mole) methyl ethyl ketone. Attached to the neck of the reactor flask by means of Gooch tubing was an Erlenmeyer flask containing 23.0 g. (1.0 mole) of cubed sodium. With constant stirring of the contents of the flask, sodium was slowly added to the reactor and the gas (hydrogen) evolved was collected by the displacement of a saturated sodium chloride solution. A blue color which disappears with stirring, appears around the sodium metal in the reaction flask. The reaction mixture was stirred for several hours, after which 1.5 liters of water was slowly added to the mixture. The aqueous phase was extracted with 100 ml. of ethyl ether. This extract was saved and the aqueous layer was saturated with sodium chloride. This solution was then subjected to continuous extraction with ethyl ether for 48 hours. The original ether extract and this latter extract were combined, dried over sodium sulfate and subjected to fractionation.

Sodium-Ammonium Bromide or Chloride. - - Reduction using these more soluble proton donors was carried out in a manner similar to the above described experiment. It should be noted that several experiments were performed in which the ammonia was allowed to weather overnight and the residue was extracted with ethyl ether. This method was abandoned because of the poor recovery of materials. The addition of

water and subsequent continuous extraction with ethyl ether proved to be the better procedure.

Beryllium-Ammonium Sulfate. - - As in the above cases 0.50 mole of ketone, 0.5 mole of ammonium sulfate were used with 500 ml. of ammonia. To this was added 4.5 g. (0.50 mole) beryllium. The mixture was stirred for 12 hours but no gas was evolved. After the addition of water to the reaction mixture, the beryllium was recovered unchanged.

Beryllium-Ammonium Chloride. - - In the reactor were placed 500 ml. of ammonia, 53.5 g. (1.0 mole) ammonium chloride, 36.0 g. (0.50 mole) methyl ethyl ketone. To this was added 4.5 g. (0.50 mole) beryllium and the reaction mixture was stirred for a period of 12 hours. A total of 7.2 liters (STP) of gas was collected. Water was then added to the reaction mixture, about one volume of water to one-half volume of ammonia. The water phase contained a light grey, translucent, gelatinous solid, perhaps a hydroxide of beryllium. The following equation may represent the formation of this substance.



It was not possible to effect a good recovery of organic products by continuous ether extraction in the presence of this solid. Apparently both the ketone and the 2-butanol are strongly sorbed by the gel. It was necessary to acidify the aqueous layer, thus dissolving the solid in order to obtain a high recovery of materials.

Beryllium-Ammonium Bromide. - - This work was performed as in the previously described experiment.

Lithium. - - Lithium runs using ammonium sulfate, ammonium chloride, and ammonium bromide were made in a manner similar to the sodium runs.

Manganese. - - The attempted use of manganese as a reducing agent was not successful with the proton donors described in this work. No gas was evolved during the contact of the metal with the other components of the systems. The metal was recovered unchanged.

Amalgamated Manganese. - - Clean manganese metal was amalgamated with dilute aqueous solution of mercuric chloride and ether washed. The reaction was performed in a manner similar to the above experiment. No gas was evolved during a reaction period of 6 hours. The manganese was recovered unchanged. Amalgamation of manganese by mercuric chloride was accomplished in the presence of benzene. This amalgam was also inert in the liquid ammonia reaction mixture. Ammonium bromide was used as proton donor in both experiments.

Other Metals. - - Zinc, aluminum, and magnesium did not react in the presence of ammonium chloride, ammonium sulfate, or ammonium bromide and ammonia under the conditions of the experiments.

Blank. - - A mixture of 500 ml. of ammonia, 36.0 g. (0.50 mole) methyl ethyl ketone and 98.0 g. (1.0 mole) NH_4Br was stirred for several hours. No metal was added. The experiment was completed by the usual

continuous ether extraction. In addition, to the ketone, 6.7 g. of higher boiling material was obtained. This fraction may contain the products of ammonolysis of the ketone. The higher boiling material was a dark brown, viscous liquid with a sharp odor not unlike pyridine.

2-Butanol. - - The alcohol resulting from the reduction of methyl ethyl ketone was characterized by its 3, 5 dinitrobenzoate mp 75-6°C. (uncorr.) as compared with 75° C. reported by Shriver and Fuson.⁵⁶

IV. DISCUSSION

The present work comprises a study of the metals lithium, sodium, beryllium, manganese, and aluminum in liquid ammonia at atmospheric pressure in presence of methyl ethyl ketone and the proton donors ammonium sulfate, ammonium chloride, and ammonium bromide. In Table 1 are presented the half-cell potentials of these metals in the water system, and in ammonia related to the normal hydrogen electrode potential in the aqueous system as zero.

Table 1

Metal	Standard Electrode Potential E°	
	H ₂ O at 25°C	NH ₃ at -50°C 47,48
Li	3.0	3.0
Ca	2.9	2.4
Na	2.7	2.6
Al	1.7	---
Be	1.7	1.2 *
Mn	1.1	---

*The value for beryllium is an estimate based upon Pleskov's value for calcium.

Little information is available on electrode potentials in liquid ammonia and most of the published data are not free from

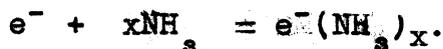
junction potentials. The values quoted in Table 1 are of importance in the light of comparison of the reducing power of those metals but the absolute numbers cannot be quantitatively interpreted.

In Table 2 are presented the solubilities of the ammonium salts at -40°C . in liquid ammonia, and the concentrations of the salts used in this work. The tabulated concentrations are initial values and in case of ammonium sulfate and ammonium chloride the amounts of salts used exceeded the solubilities at -40°C .

Table 2

Salt	Solubility ⁵⁰ (Mole/liter)	Concentration Mole/liter
$(\text{NH}_4)_2\text{SO}_4$	0.0-	0.0-
NH_4Cl	1.4	1.4
NH_4Br	5.1	2.0

Kraus³⁵ postulated that when a metal, say sodium, dissolves in ammonia the reaction may be described by the equilibria,



The metal is recovered unchanged upon the evaporation of the ammonia.

Recent studies²⁰ of the magnetic susceptibilities of certain metals

in ammonia indicate that perhaps the following equation may be preferred.



Since the problem is still unsolved, the first equation of Kraus will be used in the discussion with the understanding that the electron is solvated.

Of the metals discussed in this work aluminum and manganese failed to react under the conditions of the experiment. Bergstrom¹ reported that manganese and aluminum (amalgamated) dissolved at room temperature in ammonium salts in ammonia with the evolution of hydrogen. In the present investigation, amalgamated manganese also failed to react at $-40^{\circ}C$. Lithium and sodium reacted under all the experimental conditions. Beryllium did not undergo reaction in the presence of ammonium sulfate, but did react in the presence of the chloride and bromide, thus, data on the ease of reduction of methyl ethyl ketone are presented for the metals lithium, sodium, and beryllium having standard half-cell potentials in ammonia as shown in Table 1. Bergstrom² reported that beryllium dissolved, with the evolution of hydrogen, in ammonia, in the presence of ammonium chloride, ammonium iodide, ammonium cyanide, and ammonium thiocyanate at room temperature. Ammonium sulfate was not included in the report of his study. A summary of the results of the experiments with lithium, sodium, beryllium, and manganese is presented in Table 3, and in part plotted in Figure 1 and 2.

Table 3

Metal	Results			
	Proton Donor	% 2-Butanol	% Others	Vol. H ₂ (STP)
Na	(NH ₄) ₂ SO ₄	54	26	1.35
	NH ₄ Cl	44	7	1.98
	NH ₄ Br	31	10	2.43
Li	(NH ₄) ₂ SO ₄	50	14	2.9*
	NH ₄ Cl	45	11	3.1
	NH ₄ Br	31	6	3.38
Be	(NH ₄) ₂ SO ₄	0.0	--	0.0
	NH ₄ Cl	8.5	--	7.2
	NH ₄ Br	2	--	9.6
Mn	(NH ₄) ₂ SO ₄	0.0	--	0.0
	NH ₄ Cl	0.0	--	0.0
	NH ₄ Br	0.0	--	0.0

*This value was taken from a duplicate lithium-ammonium sulfate run.

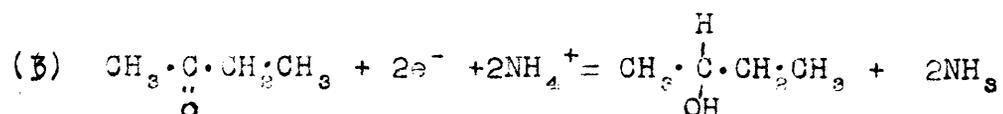
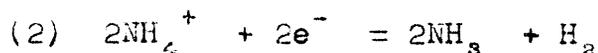
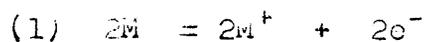
From Table 3 it is seen that the experiments employing sodium and lithium resulted in decisively greater reduction of the ketone than the use of beryllium. Reductions obtained with sodium and lithium show a high degree of similarity. Perhaps the relatively small difference in standard half-cell values (0.4 volt) is overshadowed by solu-

bility and solvation effects while beryllium is of sufficiently lower potential to reveal the difference in the reducing power of the metal. As the concentration of ammonium ion increases, the amount of hydrogen evolved increases and the reduction of the ketone decreases. Therefore, it appears that the ammonium ion competes more favorably for the electron from the metal than does the organic compound. This is readily seen to be the case at low E^0 values, i.e., with beryllium metal. In the case of lithium and sodium the decrease in the yield of 2-butanol as the more soluble ammonium salts are used as proton donors is continuous and is of the same order of magnitude for these two metals. This trend is apparent in the case of beryllium although comparison in the case of ammonium sulfate is not possible since the beryllium failed to react under the experimental conditions. The large amounts of hydrogen obtained in the reactions employing beryllium and ammonium chloride and ammonium bromide indicate a high degree of reactivity of the metal although the extent of reduction of methyl ethyl ketone was small. The reactions studied gave in addition to the 2-butanol, varying quantities of materials having a boiling range much higher than the alcohol. This higher boiling liquid appears to be in part comprised of products of the ammonolysis of the methyl ethyl ketone. This premise is in agreement with recent work reported concerning the condensation of alkyl aryl ketones in ammonia forming pyridine derivatives.

In the reduction of alkynes, Greenlee and Fernalius²⁵ postulate that the addition of two electrons to the alkyne is followed by a proton transfer, the ionic intermediate maintaining a trans configuration

during the proton transfer. (p.7) The product is exclusively the trans olefin. Henne and Greenlee²⁹ attribute the difference in ease of reduction of acetylene by sodium and by sodium and ammonium sulfate to the hypothesis that the hydrogen from the acetylene is more active than that from the ammonium ion.

The results of the present work may be interpreted on the basis of the following equations:



Equation (1) is the reducing half reaction and then equations (2) and (3) compete for the electrons from (1), i.e., they are oxidizing half reactions. In the case of beryllium, a large volume of hydrogen is obtained but reduction of ketone is slight. This is not easily explained by any concepts of "nascent" or active hydrogen but is easily correlated with the above scheme by saying equation (2) proceeds more rapidly than (3). The use of sodium or lithium, i.e., a more potent reducing half reaction brings about an increase in the reduction of methyl ethyl ketone. Thus, equation (3) which needed a stronger "force" behind it is now competing very favorably for the electrons from (1).

The half-cell potential of the reducing half reaction and the concentration of the proton donor in the oxidizing half-cell play a fundamental and prime role in the reduction of compounds in liquid ammonia. The use of other proton donors such as methanol would have to

be similarly investigated, especially in view of its role of co-solvent which may have a marked effect on the half-cell potential.

The above mechanism of reduction in ammonia may be applied to the results of other workers. Henne and Greenlee²⁹ found that sodium and ammonium sulfate is a stronger reducing system than sodium and ammonium chloride. This may be easily explained by noting that the ammonium ion concentration is greater using the ammonium chloride than ammonium sulfate hence equation (2) is favored with ammonium chloride at the expense of the main reduction reaction, i.e., equation (3). Thus sodium-ammonium sulfate reduces the alkyne studied more than sodium-ammonium chloride.

It should be pointed out that a great many reactions using ammonium bromide as proton donor were not very successful as compared to the same reactions using sodium alone with no proton donor. Since ammonium bromide is one of the most soluble ammonium salts, it is to be expected that the equation (2) will be highly favored at the expense of equation (3) since the ammonium ion concentration will be quite high.

Ammonium nitrate was not used in this investigation because of the possibility of its reduction to the ammonium nitrite thus offering numerous possibilities of side reactions and undesirable by-products which would complicate the interpretation of the mechanism of the reaction.

That the results reported for the various metals are reproducible may be seen from an examination of Table 4. Experiments 2 and 3, 5 and 6

are duplicate runs. More than twenty-five runs have been made. Those not included in the table usually involved mechanical difficulties such as maintaining a tight seal at the stirrer shaft and sudden evolution of large amounts of gas due to too rapid addition of the metal. The products isolated from some of these experiments were in agreement with the experiments shown in Table 4.

It is emphasized that the work reported was not directed toward maximum yield, although the yields reported are in fair agreement with the work of Boord and co-workers⁶ who reported yields of about 60% for simple ketones. In that work sodium was added to the ketone in liquid ammonia and the proton donor subsequently added. Such a procedure does not lend itself conveniently to a study of different metals since side reactions may invalidate the correlations of the metals themselves.

At the present stage of development of the study of reducing action in liquid ammonia, it is possible to suggest that if after the reducing action of several metals on monofunctional substances are studied, it may be possible to selectively reduce a polyfunctional molecule. The reduction of an alkyl ketone has already been described. At present, work is under way on the investigation of reduction of organic sulfides by various metals. It can be seen that when more data is found concerning the reduction of sulfides, it may be possible to study the reduction of a more complex molecule such as 2-acetyl thiophene, and perhaps selectively reduce, let us say the carbonyl group without breaking the ring or break the ring without reducing the

carbonyl group. Other groups such as acids, nitriles, nitro-compounds and alkynes may be studied with selective reduction as goal.

V. SUMMARY

1. A systematic investigation of the reducing action of different metals on an organic compound in liquid ammonia is reported for the first time.
2. The greater the half-cell potential of the metal, the greater the extent of reduction effected by that metal.
3. A high concentration of the ammonium salt as a proton donor favors the formation of hydrogen and decreases the reduction of methyl ethyl ketone.
4. A mechanism of the reducing action of the system metal-ammonium ion-ammonia on methyl ethyl ketone is presented.
5. The possibility of selective reduction of polyfunctional molecules is mentioned.

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Table 4

Reduction of Methyl Ethyl Ketone

Experiment No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Methyl Ethyl Ketone	Grams	36.0	36.0	36.0	36.0	36.0	36.0	36.0	36.0	36.0	36.0	36.0	36.0	36.0
	Moles	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Metal	Subst.	-----	Na	Na	Na	Na	Na	Be	Be	Be	Li	Li	Li	Na
	Grams	-----	23.0	23.0	23.0	23.0	23.0	4.5	4.5	4.5	6.9	6.9	6.9	23.0
Ammonium Salt	Moles	-----	1.0	1.0	1.0	1.0	1.0	0.50	0.50	0.50	1.0	1.0	1.0	1.0
	Subst.	Br ⁻	SO ₄ ²⁻	SO ₄ ²⁻	Cl ⁻	Cl ⁻	Cl ⁻	Br ⁻	Cl ⁻	Br ⁻	SO ₄ ²⁻	Cl ⁻	Br ⁻	Cl ⁻
Products	Grams Form. Hts.	98.0	66.1	66.1	53.5	53.5	98.0	66.1	53.5	98.0	66.1	53.5	98.0	53.5
	Liters STP	-----	1.35	-----	1.20	1.98	2.43	0.0	7.2	9.6	2.9	3.1	3.38	2.41
2-Butanol	Moles	-----	0.06	-----	0.05	0.088	0.11	0.0	0.32	0.43	0.13	0.14	0.15	0.11
	Grams	-----	16.0	14.7	10.3	13.6	15.1	10.2	2.9	0.7	16.2	16.2	9.3	11.2
Others	Moles	-----	0.22	0.20	0.14	0.18	0.14	-----	0.039	0.009	0.22	0.22	0.13	0.15
	Grams	6.7	8.0	4.8	4.7	2.3	2.3	3.1	-----	5.0	1.0	4.0	1.8	1.9
Recovered MEK	Grams	25.2	5.6	4.0	8.7	15.1	13.6	19.7	25.4	28.7	10.3	15.6	18.7	10.4
	Grams	31.9	29.6	23.5	23.7	31.0	31.0	33.0	33.3	30.4	31.6	35.8	29.8	23.5
Conversion	%	88	82	65	66	87	87	91	92	84	88	99	83	65
	%	19	66	53	41	44	48	37	22	5	58	56	31	35
Field	%	0.0	44	40	28	38	42	28	7.8	2	44	45	26	30
	%	19	22	13	13	6	6	9	14	3	14	11	5	5
No. Loss	%	22	80	80	62	51	55	41	24	6	66	57	37	54
	%	0.0	54	62	42	44	48	31	8.5	2	50	45	31	46
No. Loss	%	22	26	18	20	7	7	10	15	4	16	11	6	8

(1) The rubber seal at the stirrer shaft leaked slightly.

(2) Methyl ethyl ketone.

(3) This value was obtained in a duplicate experiment.

Figure 1

Percent 2-Butanol vs. Standard Half Cell Potentials

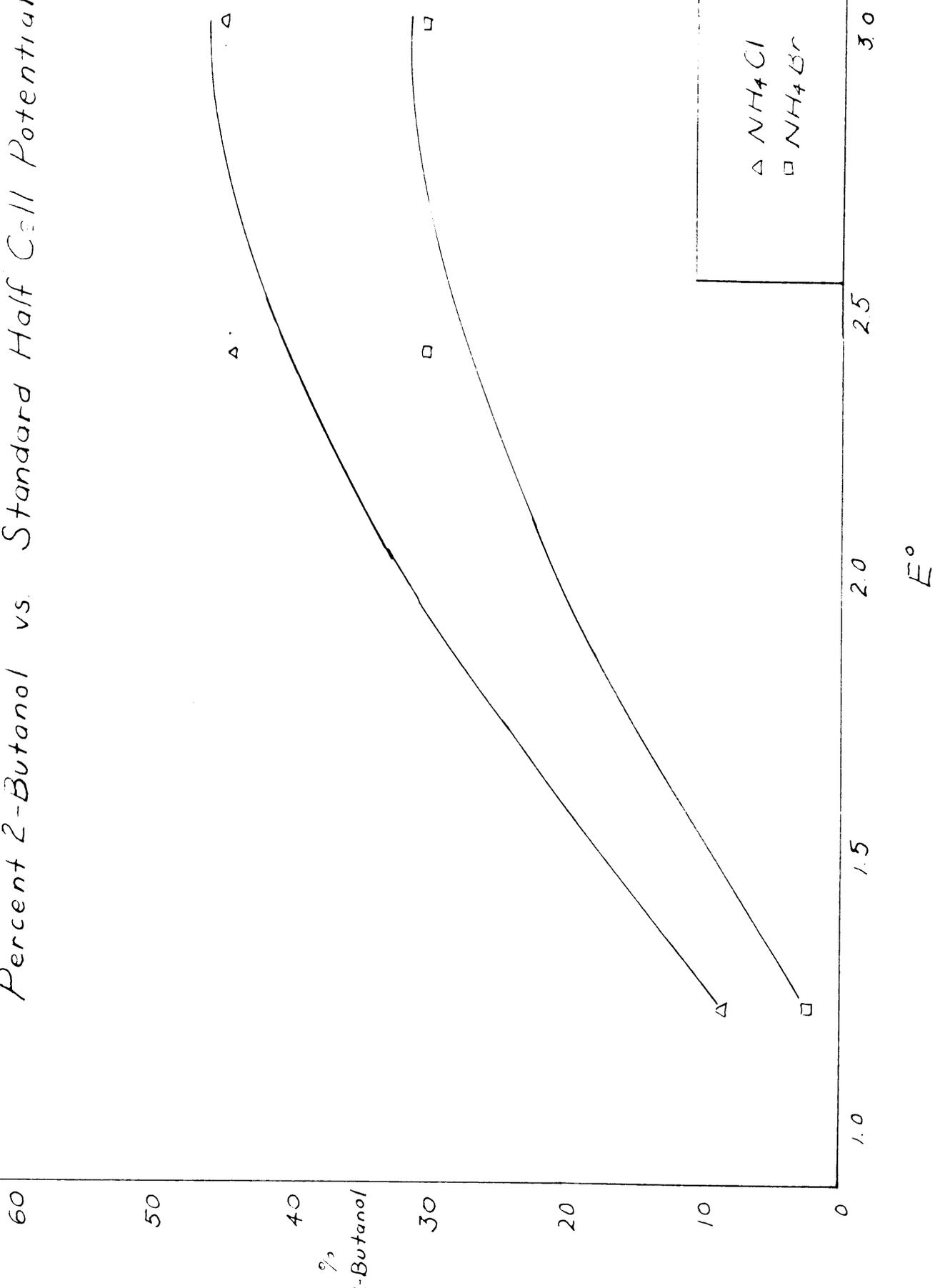
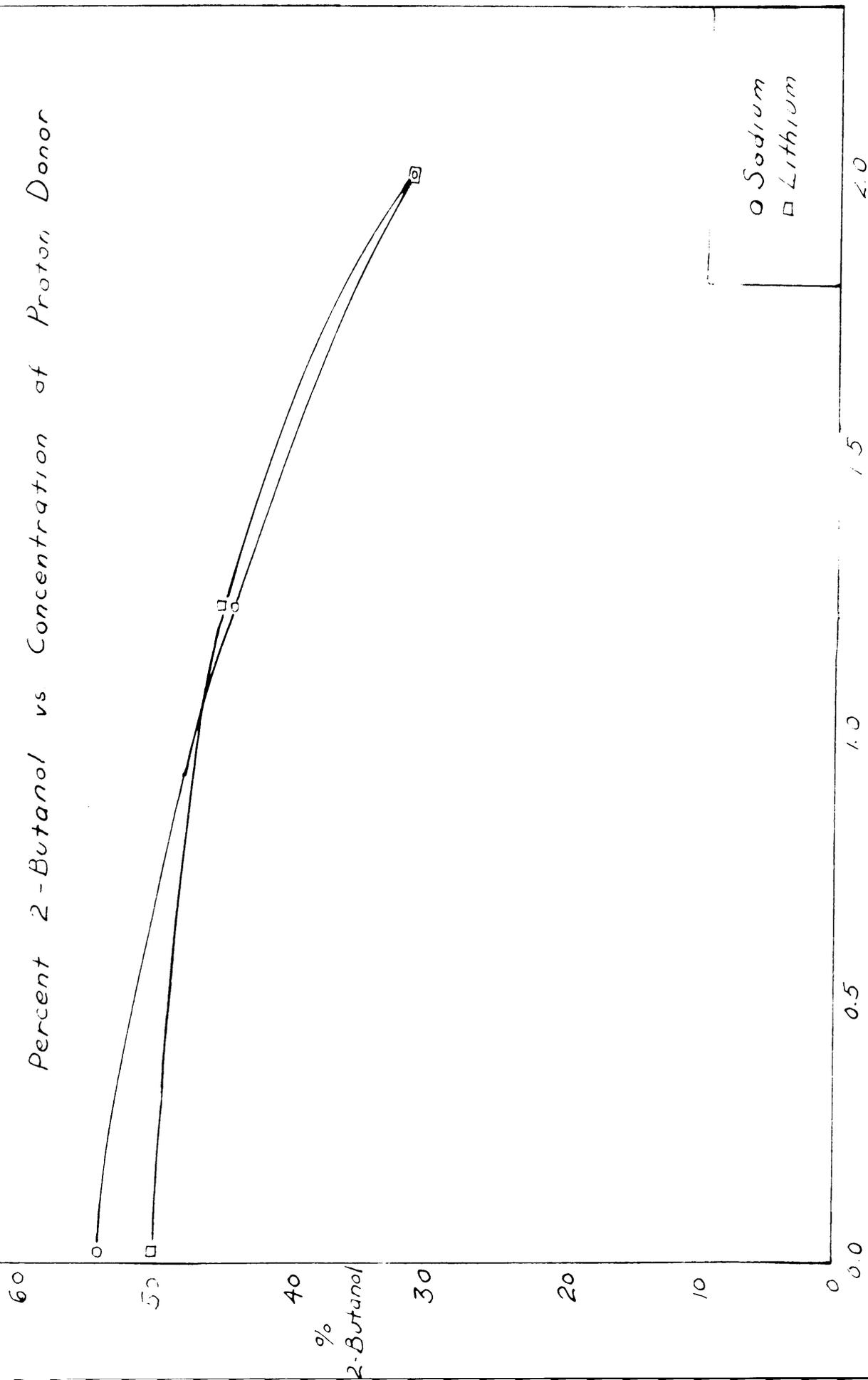


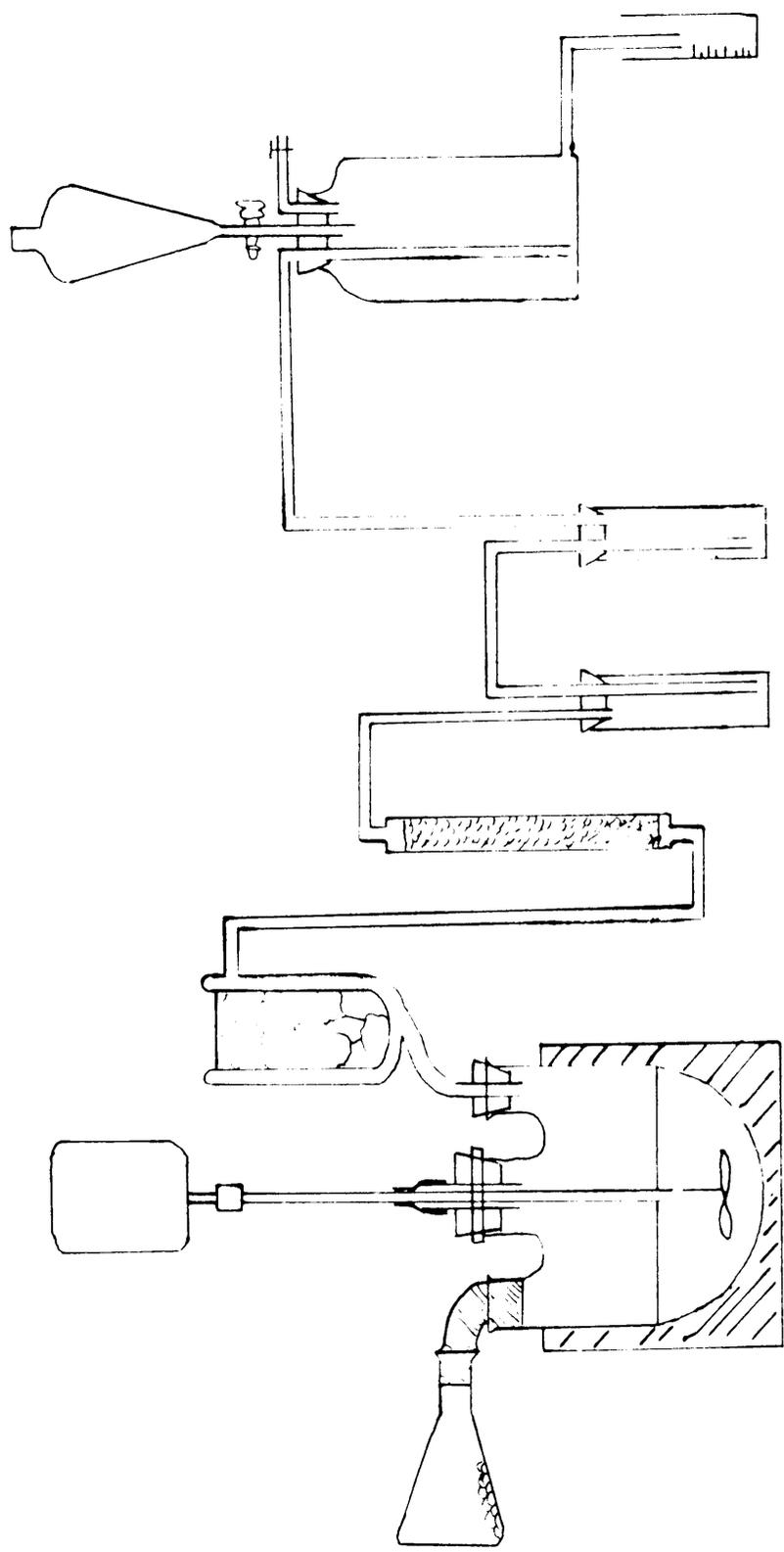
Figure 2

Percent 2-Butanol vs Concentration of Proton Donor



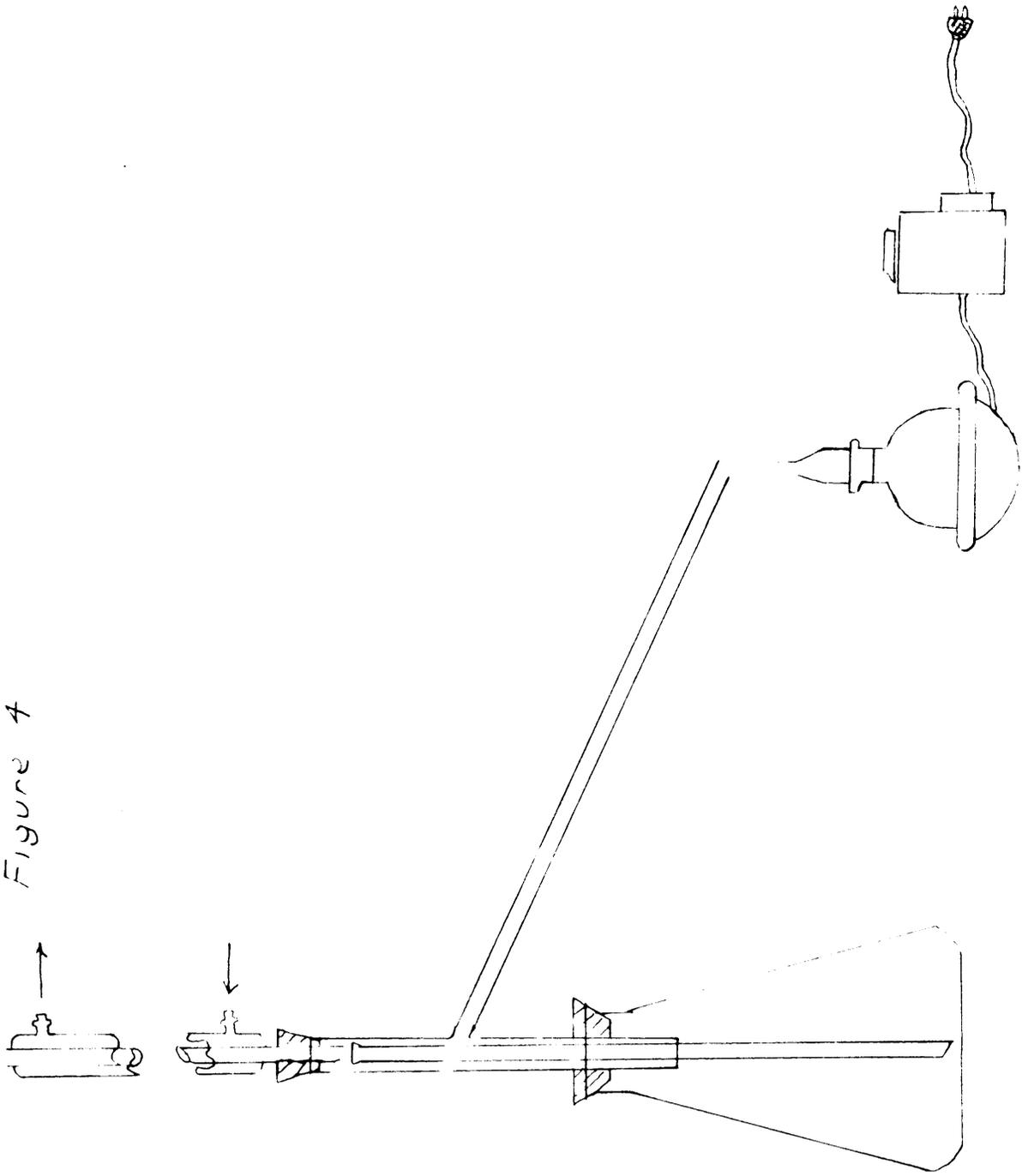
NH_4^+ Concentration in Moles per Liter

Figure 3



LIQUID AMMONIA REACTOR SYSTEM

Figure 4



CONTINUOUS ETHER EXTRACTOR