



Theses and Dissertations

1957-09-01

The preparation and catalytic properties of rhenium blacks obtained by reduction of Re(VII) in anhydrous ammonia and amines with alkali metals

David William Seegmiller
Brigham Young University - Provo

Follow this and additional works at: <https://scholarsarchive.byu.edu/etd>



Part of the [Chemistry Commons](#)

BYU ScholarsArchive Citation

Seegmiller, David William, "The preparation and catalytic properties of rhenium blacks obtained by reduction of Re(VII) in anhydrous ammonia and amines with alkali metals" (1957). *Theses and Dissertations*. 8349.

<https://scholarsarchive.byu.edu/etd/8349>

This Thesis is brought to you for free and open access by BYU ScholarsArchive. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of BYU ScholarsArchive. For more information, please contact scholarsarchive@byu.edu, ellen_amatangelo@byu.edu.

XD 5-102
.02
S42
957

THE PREPARATION AND CATALYTIC PROPERTIES OF RHENIUM BLACKS
OBTAINED BY REDUCTION OF RE(VII) IN ANHYDROUS
AMMONIA AND AMINES WITH ALKALI METALS

A Thesis
Submitted to the Department of Chemistry
Brigham Young University
Provo, Utah

In Partial Fulfillment
of the Requirements for the Degree of
Master of Science

225788

by
David W. Seegmiller

September, 1957

BYU
LIBRARY
PROVO, UTAH

This thesis by David W. Seegmiller is accepted in its present form by the Department of Chemistry of the Brigham Young University as satisfying the thesis requirements for the degree of Master of Science.

ACKNOWLEDGEMENT AND DEDICATION

The author wishes to express his sincere appreciation and deep indebtedness to all those who have aided in the compilation and publication of this work. Particularly, an expression of gratitude is extended to Dr. H. Smith Broadbent under whose guidance this work was accomplished.

To my wife, Jean, goes my love and thanks for her understanding and patience. To her this work is dedicated.

Gratitude is expressed to the author's parents, Mr. and Mrs. Glen W. Seegmiller, whose encouragement and support have been undeviating.

Appreciation is extended to both the Air Force and the Brigham Young University which provided financial aid in the form of a research fellowship and an academic scholarship.

TABLE OF CONTENTS

	page
LIST OF TABLES AND FIGURES	vii-viii
I. INTRODUCTION	1
II. LITERATURE REVIEW	2
A. Rhenium	2
1. History and Production	2
2. Physical Properties	4
3. Chemical Properties	6
4. The Rhenide Ion	9
5. Catalytic Activity	15
B. The Nature and Advantages of the Alkali Metal-Liquid Ammonia System	18
C. Reduction of Inorganic Compounds in Liquid Ammonia	21
1. The Theory of Liquid Ammonia Reductions	21
2. The Mechanisms of Reduction	22
3. The Reduction of Oxides	23
4. The Reduction of Sulfides	25
5. Reduction of Metallic Halides	25
6. Reduction of Cyanides, Cyanates, and Thiocyanates	28
7. Reduction of Nitrates	29
8. Reductions which yield Intermetallic Compounds	29
D. The Catalytic Activity and General Characteristics of Alkali Metal-Liquid Ammonia Reduction Products	30
III. EXPERIMENTAL	35
A. Liquid Ammonia Apparatus, and the Determination of the Solubility of Rhenium Salts in Liquid Ammonia	35
B. Catalysts, General	37
1. Catalyst Code	37
2. Catalyst Preparation	38
3. Analysis	39
C. Catalysts, Preparations and Analyses	40
1. Sodium-Ammonia Catalysts	40
2. Lithium-Ammonia Catalysts	46
3. Lithium-Ethylamine Catalysts	48
4. Miscellaneous Catalysts	50
D. Hydrogenations: General	52
1. Procedure	52
2. Analysis of Products	53
E. Hydrogenations: Summary of Individual Experiments	55
1. Sodium-Ammonia Catalysts	55
(a) Acetone	55
(b) Butanone	56
(c) 3-methyl-2-butanone	58
(d) 2,3-butanedione	58
(e) 2-Pentanone	58
(f) 3-Pentanone	58
(g) 4-methyl-2-pentanone	59
(h) 2,4-Pentanedione	59
(i) Cyclopentanone	59
(j) 2-Hexanone	60

	page
(k) 2,5-Hexanedione	60
(l) Cyclohexanone	60
(m) 2-Heptanone	61
(n) 3-Heptanone	61
(o) 4-Heptanone	61
(p) Cycloheptanone	61
(q) 2-Octanone	62
(r) 2-Nonanone	62
(s) Phenyl-2-propanone	62
(t) Acetophenone	62
(u) Hexene-1	63
(v) Hexene-2	63
(w) Cyclohexene	64
(x) Styrene	64
(y) Benzene	65
(z) Nitrobenzene	66
(aa) Acetic Acid	67
(bb) Allylacetone	68
2. Lithium-Ammonia Catalysts	68
(a) Acetone	68
(b) Butanone	68
(c) Cyclohexanone	69
(d) Acetophenone	69
(e) Hexene-1	69
(f) Isooctene	70
(g) Styrene	70
(h) p-Chlorostyrene	70
(i) Cyclohexene	70
(j) Benzene	70
(k) Nitrobenzene	71
(l) Nitropropane	71
(m) Capronitrile	72
(n) Acetic Acid	72
(o) Allylacetone	72
(p) 2-Allylcyclohexanone	72
(q) o-Phenylenediamine	73
3. Lithium-Ethylamine Catalysts	73
(a) Acetone	73
(b) Butanone	73
(c) Cyclohexanone	74
(d) Hexene-1	75
(e) Isooctene	75
(f) Cyclohexene	75
(g) Styrene	75
(h) 1-Phenylbutene-2	76
(i) Benzene	76
(j) Toluene	76
(k) Allyl bromide	77
(l) Nitrobenzene	77
(m) 1-Nitropropane	77
(n) Pyridine	77
(o) Acetic Acid	78
(p) Propionic Acid	78
(q) Isobutyric Acid	79
(r) Valeric Acid	79
(s) Caproic Acid	79
(t) Caprylic Acid	80
(u) Capric Acid	80

	page
(v) Lauric Acid	80
(w) Benzoic Acid	80
(x) Nitrocyclohexane	80
(y) Capronitrile	81
(z) Allylacetone	81
(aa) 2-Allylcyclohexanone	82
(bb) Crotonaldehyde	82
(cc) <u>m</u> -Nitroacetophenone	83
(dd) <u>p</u> -Nitrophenylacetic Acid	83
(ee) Nitrophenylmethane	84
(ff) <u>m</u> -Nitrostyrene.	84
(gg) <u>m</u> -Nitrobenzaldehyde	84
(hh) Propargyl Alcohol	85
4. Miscellaneous Catalysts	85
(a) Butanone	85
(b) Hexene-1	86
(c) Benzene	87
(d) Nitrobenzene	87
5. Standard Catalysts	87
(a) Butanone	87
(b) Hexene-1	88
(c) Cyclohexene	88
(d) Styrene	88
(e) Nitrobenzene	89
(f) Allylacetone	89
(g) 2-Allylcyclohexanone	89
(h) Crotonaldehyde	89
D. Determination of Valence State of Rhenium in Catalysts	89
IV. DISCUSSION	91
A. Catalyst Preparation	91
B. Analysis of Catalysts	94
C. Hydrogenations	95
1. Sodium-Ammonia Catalysts	95
2. Lithium-Ammonia Catalysts	100
3. Lithium-Ethylamine Catalysts	102
4. Miscellaneous Catalysts	107
D. A Comparison of the Catalysts Prepared in this Investigation	108
E. A Comparison of Previously Studied Rhenium Catalysts with Metal-Ammonia(Amine) Types	111
F. A Comparison of the Activity of the Catalysts Prepared in this Investigation with Several "Standard" Catalysts	114
V. SUMMARY	117
VI. BIBLIOGRAPHY	118

LIST OF TABLES

	page
1. Oxidation Potentials of Rhenium Couples	11
2. Surface Area and Catalytic Activity of Nickel Produced by Reduction in Liquid Ammonia	31
3. Solubility of Rhenium Salts in Liquid Ammonia	37
4. Selected Functional Groups and the Columns and Temperatures which were Found Best for their Identification and the Identification of their Reduction Products by Gas Chromatography	54
5. Selected Substrates and the Columns and Temperatures Used for the Analysis of their Reduction Products	54
6. A Comparison of the Catalytic Activity of Several Catalysts on Different Substrates Illustrating the Effect of Acid Extraction of the Catalyst	93
7. Hydrogenations Performed Using Sodium-Ammonia Catalysts	97
8. Hydrogenations Performed Using Lithium-Ammonia Catalysts	101
9. Hydrogenations Performed Using Lithium-Ethylamine Catalysts	103
10. Hydrogenations Performed Using Miscellaneous Rhenium Catalysts	105
11. A Comparison of the Catalytic Activity of Sodium-Ammonia, Lithium-Ammonia, and Lithium-Ethylamine Catalysts for the Reduction of Various Selected Substrates	109
12. A Comparison of Rhenium Catalysts of Different Types in the Reduction of Some Selected Substrates	112
13. A Comparison of the Catalytic Activity of Catalysts Prepared in this Investigation with Several "Standard" Catalysts on Selected Substrates	115

LIST OF FIGURES

	page
1. Rhenium Oxidation Potential Diagram	7
2. Rhenide Absorption Spectra	12
3. Comparative Activity of Nickel Catalysts for Hydrogenation of Allyl Alcohol	32
4. Comparative Activity of Nickel Catalysts for Hydrogenation of Allyl Alcohol	32
5. Comparative Activity of Cobalt Catalysts for Hydrogenation of Allyl Alcohol	34
6. Comparative Activity of Platinum Catalysts for Hydrogenation of Allyl Alcohol	34
7. Liquid Ammonia Apparatus	36
8. Temperatures Necessary for Reduction of Various Ketones Using Sodium-Ammonia Catalysts	96

I. INTRODUCTION

Work done in recent years at Brigham Young University has shown that the element rhenium, and some of its compounds, exhibit good catalytic activity in liquid-phase hydrogenation reactions. Catalysts prepared in a variety of ways have been used on numerous substrates, and while in general their activity is somewhat less than that of "standard" catalysts, such as Adam's catalyst and Raney nickel, some very distinct advantages are apparent. These rhenium catalysts have been shown to be good in general hydrogenation reactions and outstanding for some substrates.

Rhenium sesquioxide has been shown to reduce styrene at room temperature and nitrobenzene at 65-70°C.⁹⁴ It has also been shown capable of reducing bromobenzene without session of the carbon-bromine bond.⁹⁴

Rhenium heptasulfide and heptaselenide have been used in the reduction of allyl phenyl sulfide to n-propyl sulfide without carbon-sulfur bond hydrogenolysis.^{92,93} These catalysts are also very resistant to poisoning.

A tetrahydropyran-rhenium heptoxide catalyst has catalyzed the reduction of benzene at 150-160°C., while requiring temperatures of 200-250°C. for the reduction of the nitro group. Attempts to selectively reduce the phenyl group in the presence of the nitro group, however, were unsuccessful. The catalyst also induces the reduction of chlorobenzene without accompanying carbon-chlorine bond scission.⁹⁴

Another very important reaction is the reduction of carboxylic acids to alcohols by Re_2O_7 , in situ. The conditions necessary for this type of reduction are the mildest yet reported.⁹¹

Previous investigators (cf. literature review) have shown that the product obtained from the reduction of metal salts in liquid ammonia with alkali metals is in most cases the free metal. The metal so obtained is usually very finely divided and in a highly reactive state, often pyrophoric. These products are often highly efficient as hydrogenation catalysts, in some cases approaching Raney nickel in effectiveness.

The purpose of the present investigation was to determine the activity of rhenium blacks prepared in an analogous manner.

Various catalysts were prepared using ethylamine as well as ammonia as a solvent and various alkali metals as reducing agents. The activity of the catalysts so prepared was comparable with that of most rhenium catalysts heretofore studied. These catalysts exhibited a very high activity toward reduction of the carboxyl group, and also indicated that a possibility of selective reduction exists in the case of the carbonyl and olefinic groups. An interesting phenonemn was observed in the reduction of a homologous series of ketones. All of these observations are treated in detail in the Discussion part of this thesis.

II. LITERATURE REVIEW

A. Rhenium¹

1. History² and Production

Rhenium, one of the last discovered of the naturally occurring elements, has a rather brief but highly interesting history. Although the bulk of printed material dealing with rhenium is still comparatively small, it is rather certain that a great amount more will appear, principally because of the rather unusual characteristics and properties of the metal. In searching the literature it has been found that information of the chemical properties of rhenium is abundant, but as of yet extensive work has not been done on the physical metallurgy and physical constants of rhenium.

The discovery of rhenium itself illustrates the great amount of interest which lies in the element. Its discovery was announced almost simultaneously by three independent groups of workers. W. Noddack, I. Tacke, and O. Berg.^{3,4} were first claimants. They claimed to have separated the element from platinum bearing ores such as columbite. They also estimated the abundance of rhenium in the earth's crust to be 10^{-12} parts. In addition they coined the name "rhenium" in honor of the German Rhineland.

F. Loring and J. Druce⁵ next claimed to have separated rhenium from crude manganese compounds. They predicted that the highest oxide would have the formula M_2O_7 .⁶

At about the same time V. Dolejsek and J. Heyrovosky⁷ announced the discovery of rhenium. They claimed to have detected it by the electrolysis of manganous sulfate solutions with a dropping mercury cathode. They later however refuted their own claim, stating that they had mistaken other elements for rhenium.⁸

¹Sims, C.T., Wyler, E.N., Gaines, G.B., and Rosenbaum, D.M., A Survey of the Literature on Rhenium, WADC Technical Report 56-319, ASTIA Document No. AD 110596, Battelle Memorial Institute to Aeronautical Research Laboratory, Wright-Patterson Air Force Base, Ohio (June 1956).

²Hund, J., Chem. Education, 10, 605 (1933).

³Noddack, W., Tacke, I., and Berg, O., Naturwissenschaften, 13, 567 - 71 (1925), [Sims, op. cit., p. 2].

⁴Noddack, W., and Tacke, I., Oesterr. Chem. - Ztg., 28, 127 (1925) [Sims, op. cit., p. 2].

⁵Druce, J., Chem. News, 131, 273 (1925), [Sims, op. cit., p.2].

⁶Loring, F., Chem. News, 132, 407 (1926), [Sims, op. cit., p.2].

⁷Dolejsek, V., and Heyrovosky, J., Nature, 116, 782 (1925) .

⁸Heyrovosky, J., Nature, 135, 870 (1935).

Whether the Noddacks had actually separated rhenium at the time of their first announcement is still unknown, they are, however, credited with its discovery and the name they coined is the one in general use.⁹

The Noddacks³ originally estimated the concentration of rhenium in the earth to be 10^{-12} parts. This value was later revised upwards to 10^{-9} parts. This value places rhenium as being 10 times more rare than iridium and 1000 times more rare than molybdenum.^{10,11} It is this rareness of the element, along with its separation that has caused the cost to remain high.

Rather recent work by Brown and Goldberg¹² on meteorites indicates that the rhenium content may lie as high as 0.28×10^{-6} to 1.45×10^{-6} parts. If this is the case, rhenium is possibly 50 times more abundant than the Noddacks thought it to be.

Rhenium production in the world has been very erratic.¹ The present production centers are Mansfeld, Germany (Russian dominated); Balkhash, Kazakh (Russia); France; Great Britain; University of Tennessee; and the Kennecott Copper Company. B. Gonser¹³ has indicated that the U.S. production potential is of the order of 20,000 to 30,000 pounds per year, however at present, production is only 75 to 100 pounds per year.

The processes for the recovery and isolation of rhenium are numerous and varied. Most of them, however, depend upon one of the following characteristics or properties of rhenium compounds: (a) insolubility of rhenium disulfide or heptasulfide, (b) high volatility of rhenium heptoxide, (c) high solubility of rhenium heptoxide, or (d) temperature dependence of the solubility of potassium perrhenate. The first recovery process developed by the Noddacks¹⁴ depended upon the insolubility of the sulfide. They later developed another process which depended upon the solubility of the high oxides in mineral acids and also on water soluble salts of the type X_2ReO_4 .^{15,16,17,18}

⁹Weeks, E., J. Chem. Education, 22, 519 (1935).

¹⁰Suess, H., Z. Naturforsch., 2a, 604 (1947), [Sims, op.cit., p.4].

¹¹Frank, F., Proc. Phys. Soc. (London), 60, 211 (1948) [Sims, op. cit., p. 4].

¹²Brown, H., and Goldberg, E., Phys. Rev., 76, 1260 (1949).

¹³Gonser, B., Resources for Freedom, IV, A Report to the President by the President's Materials Policy Commission, p. 109, U.S. Government Printing Office, Washington (June, 1952), [Sims, op. cit., p. 7].

¹⁴Bertolus, M., U.S. Pat. 2,579,107 (December 18, 1951) [Sims, op.cit., p. 13].

¹⁵Noddack, I. and W., Z. anorg. allgem. Chem., 183, 353 (1929) [Sims, op. cit., p. 13].

¹⁶Noddack, I. and W., Brit. Pat. 317,035 (July 28, 1930) [Sims, op. cit., p. 10].

¹⁷Noddack, I. and W., Metallbörse, 21, 603, 650 (1931) [Sims, op.cit., p.10].

¹⁸Noddack, I. and W., Ger.Pat. 606,488 (December 3, 1934) [Sims, op. cit., p.10].

F. Driggs¹⁹ obtained the first American patent for the commercial separation of rhenium. His process depended upon the volatilization of Re_2O_7 and its subsequent reduction to the metal. The most important American process at present is that used at the University of Tennessee.²⁰ This process depends upon the solubility of rhenium heptoxide which is contained in flue dust and its subsequent precipitation with potassium chloride.

2. Physical Properties

Rhenium has two naturally occurring isotopes. These isotopes have the atomic wts. of 185 and 187 and occur in the ratio of 1:1.62.^{21,22} It would therefore be expected that Re would have an atomic wt. between 185 and 187. The Noddacks²³ performed the first experimental atomic wt. determination for Re and obtained a value of 188.71 ± 0.15 . This value was later shown to be slightly in error and the presently accepted value of 186.31 ± 0.02 was determined by Hönigschmid and Sachtleben.²⁴ Recently this value has come under criticism and will likely be changed. The Commission on Atomic Weights in 1955 at the 18th Conference of the International Union of Pure and Applied Chemistry recommended that the value be changed to 186.22.²⁵

Agte^{26,27} in 1931 calculated the density of Re to be 20.53. Experimentally he found a value of 20.9. The calculated value is the presently accepted value. Recent work at Battelle, however, may alter this value. These workers^{28,29} calculated the density of rhenium from lattice constants and obtained a value of 21.02 ± 0.01 . These values establish rhenium as the 4th most dense element.

¹⁹Driggs, F. (To Westinghouse Elec. Co.), U.S. Pat. 1,911,943 (May 30, 1933), [Sims, op. cit., p. 11].

²⁰Melaven, A., and Bacon, J. (To Univ. of Tennessee Research Corp.) U.S. Pat. 2,414,965 (January 28, 1957), [Sims, op. cit., p. 13].

²¹Aston, F., Nature, 127, 591 (1931).

²²Manescu, I., Compt. rend., 226, 1010 (1948), [Sims, op. cit., p. 32].

²³Noddack, I., Z. Electrochem., 34, 629 (1929), [Sims, op. cit., p. 21].

²⁴Hönigschmid, O., and Sachtleben, R., Z. anorg. allgem. Chem., 191, 309 (1930), [Sims, op. cit., p. 21].

²⁵No author, Chem. and Eng. News, 33 (52), 5578 (1955).

²⁶Agte, C., Alterthum, H., Becker, K., Heyne, G., and Moers, K., Z. anorg. allgem. Chem., 196, 129 (1931), [Sims, op. cit., p. 22].

²⁷Agte, C., Alterthum, H., Becker, K., Heyne, G., and Moers, K., Naturwissenschaften, 19, 108 (1931), [Sims, op. cit., p. 22].

²⁸Investigations of Rhenium, Wright Air Development Center Tr 54-371, Battelle Memorial Institute to Aeronautical Research Laboratory, Wright-Patterson Air Force Base, Ohio (June, 1954), [Sims, op. cit., p. 169].

²⁹Sims, C., Craighead, C., and Jaffee, R., Journal of Metals (Transactions), pp. 168 (January, 1955), [Sims, op. cit., p. 169].

The one property of rhenium which probably has stirred scientists more than any other is its melting point. The melting point of rhenium is second only to tungsten. Agte and coworkers^{26,27} obtained a value of $3167 \pm 60^\circ\text{C}$. Jaeger and Rosenbohm³⁰ have reported a value of 3160°C . which is identical within the limits of accuracy.

The boiling point of Re like the melting point is extremely high. Richardson³¹ has given a value of 5900°C . The boiling point of tungsten is accepted as 5930°C .³² More recently Rosenbaum, Sherwood, and Campbell²⁸ have estimated the boiling point from vapor pressures to be 5630°C .

Mellor³³ measured the standard electrode potential of rhenium against the normal calomel in 2 N sulfuric acid and obtained a value of 0.6 volts. This indicates that rhenium is a mildly noble metal lying between copper and thallium in the electromotive series.

One of the two naturally occurring isotopes of Re (at.wt. 187) is radioactive. This isotope has a half life of $(4 \pm 1) \times 10^{12}$ years and decays by beta emission.^{34,35,36} ^{187}Re also possesses a short-lived nuclear isomer, (i.e. same charge and mass numbers with different decay characteristics), a comparatively rare occurrence among atomic nuclei. This isomer was found to have a half life of 0.65×10^{-6} seconds.^{37,38}

Eight artificial isotopes of rhenium are now known; their atomic numbers are 182, 183, 184, 186, 188, 189, 191, and 194. Of all these, atomic numbers 186 and 188 are by far the most common.

³⁰Jaeger, F., and Rosenbohm, E., Proc. Acad. Sci. Amsterdam, 36, 786 (1933), [Sims, op. cit., p. 22].

³¹Richardson, D., Proc. of the 5th Summer Conference (at MIT) on Spectroscopy and Applications, 1937, pp. 64-70 (Published 1938) [Sims, op. cit., p. 22].

³²Metals Handbook, p. 20, The American Society for Metals Cleveland, Ohio, 1948 [Sims, op. cit., p. 22].

³³Mellor, J., "The Physical Properties of Manganese and Rhenium", A Comprehensive Treatise on Inorganic Chemistry, 12, p. 469, [Sims, op. cit., p. 27].

³⁴"Minor Metals-Rhenium", Minerals Yearbook, U.S. Gov't Printing Office, 1948, [Sims, op. cit., p. 32]

³⁵Naldrett, S., and Libby, W., Phys. Rev., 73, 487, 929 (1948).

³⁶Seliger, H., and Bradt, H., Phys. Rev., 73, 1408 (1948).

³⁷De Benedetti, S., and McGowan, F., Phys. Rev., 71, 380 (1947).

³⁸De Benedetti, S., and McGowan, F., Phys. Rev., 74, 728 (1948).

One of the greatest uses for rhenium may come through its resistance to corrosion.³⁹ Agte²⁶ has studied the corrosion of rhenium in air and found that when heated to 1000°C. it oxidizes at about the same rate as tungsten. However, when only 10 per cent oxygen is present no attack occurs below 1600°C., and above 1600°C. it oxidizes only 1/3 as fast as tungsten. Water and carbon dioxide speed the oxidation. In general rhenium is more resistant to oxidation than tungsten and less so than osmium. Agte²⁶ also experimented in an atmosphere of hydrogen and claimed that rhenium is not attacked by moist hydrogen at any temperature, although tungsten is susceptible. Moist nitrogen however attacked Re above 1900°C.

Rhenium has a very high resistance to corrosion by hydrochloric acid. Samples tested in hydrochloric acid show no effect of corrosion or attack even after several days.⁴⁰ Sulfuric acid also has little or no effect, even at elevated temperatures.^{41,42} Nitric acid on the other hand dissolves rhenium readily. Netherton⁴³ has done work on codeposited nickel-rhenium platings and has observed that the platings show more resistance to conc. HCl than even pure Re. The plate, however, was attacked by 6 N. HCl. Alkalies⁴¹ attack Re, especially if fused.

3. Chemical Properties

The chemical properties of rhenium are highly varied and extremely interesting. Much study has been made and in general the chemical properties are quite well known. The wide variance in properties of rhenium may be attributed principally to its valence states which include all the oxidation states between a (-I) and (VII). In general rhenium behaves as an element between tungsten and osmium. It is attacked by oxidizing acids but is almost inert to halogen acids. According to Pauling⁴⁴ the single-bond radius for rhenium is 1.283 Å.

³⁹Kates, L. W., Materials and Methods, 39, No. 3, 88 (1954)
[C.A., 48: 4398i].

⁴⁰Fink, C. G., and Deren, P., Bull. Amer. Electrochem. Soc., 66, 381 (1934), [Sims, op. cit., p. 51].

⁴¹Druce, J., Rhenium, pp 12-15, University Press, Cambridge, 1948
[Sims, op. cit., p. 51].

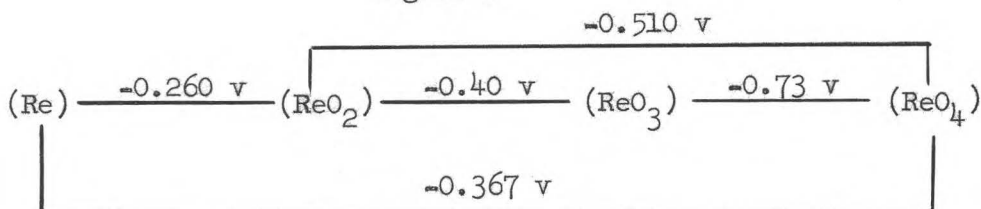
⁴²Netherton, L., and Holt, M., J. Electrochem. Soc., 95, 324 (1949)
[Sims, op. cit., p. 51].

⁴³Netherton, L., and Holt, M., J. Electrochem. Soc., 98, 106 (1951)
[Sims, op. cit., p. 51].

⁴⁴Pauling, L., Proc. Royal Soc. (London), A196, 343 (1942)
[Sims, op. cit., p. 52].

A revised oxidation-reduction potential diagram for rhenium in acid solution has recently been proposed by G. Boyd⁴⁵ and coworkers.

Figure 1



Rhenium (-I) is the most recent valence of rhenium observed. The rhenide ion is dealt with in more detail in a later section of this thesis, and will not be discussed here.

Rhenium (I) and rhenium (II) were prepared by Young and Irvine⁴⁶ as the hydrated oxides. They were prepared by the reduction of perrhenic acid. Schacherl⁴⁷ claimed to have produced ReCl₂ but evidently it does not exist. Recently Searcy and McNees⁴⁸ have prepared rhenium monosilicide, ReSi, and Hahn and Konrad⁴⁹ have prepared rhenium nitride. X-ray studies indicate the nitride to lie between Re₃N and Re₂N.

Rhenium (III) compounds are among the more common of rhenium compounds, however, oxidation to higher valence states occurs very readily.⁵⁰ Compounds such as ReBr₃ and ReCl₃ are common, and Re₂O₃ is a well known oxide.

Rhenium (IV) was one of the first known valences of Re. Turkiewicz⁵² produced this oxidation state by the reduction of perrhenate by chromium with an iodine catalyst. Sn(II), Cr(II), Ti(III), and V(III) have also been used

⁴⁵Boyd, G., Cobble, J., and Smith, W., J. Am. Chem. Soc., 75, 5783 (1953).

⁴⁶Young, R., and Irvine, J., J. Am. Chem. Soc., 59, 2648 (1937).

⁴⁷Schacherl, F., Chem. Listy, 28, 623 (1929), [Sims, op. cit., p. 70].

⁴⁸Searcy, A., and McNees, R., J. Am. Chem. Soc., 75, 1578 (1953).

⁴⁹Hahn, H., and Konrad, A., Z. anorg. allgem. Chem., 264, 174 (1952), [Sims, op. cit., p. 205].

⁵⁰Manchot, W., and Düsing, J., Z. anorg. allgem. Chem., 212, 21 [Sims, op. cit., p. 56].

⁵²Turkiewicz, E., Roczniki Chem., 12, 589 (1932) [Sims, op. cit., p. 56].

for the reduction⁵³. Some of the more common tetravalent compounds are rhenium dioxide, rhenium disulfide, rhenium tetrafluoride, and double salts such as K_2ReCl_6 . The Noddacks^{54,55} produced the dioxide by merely heating a perrhenate salt in the presence of hydrogen. The dioxide is a brown or black solid which reduces easily to the free metal. Oxidation to the perrhenate also occurs readily. A selenide which is analogous to the sulfide has also been prepared.⁵⁶

The perrhenate ion is reduced easily in acid solution by electrolysis to Re(V). Rhenium (V), however, hydrolyzes readily and is usually an intermediate in the formation of Re(IV).⁵¹ The (V) state is a rather uncommon valence for rhenium although compounds such as $ReCl_5$, X_2ReOCl_5 ,⁵⁷ and the penta carbonyl are known. Briscoe⁵⁸ and Roth⁵⁹ have both prepared the oxide.

The Noddacks were also the first to observe the (VI) valence state for rhenium.^{60,55} They prepared the oxide by reduction of the perrhenate ion. The trioxide is commonly known as rhenium blue. Numerous compounds of the type ReX_6 where X is a halide ion are known. The oxyfluoride has also been prepared.⁶¹

Rhenium (VII) is the highest and by far the most common oxidation state of rhenium. Re_2O_7 and the salts of perrhenic acid are very well known and characterized. It is upon the properties of these compounds that most of the recovery procedures are based. The heptoxide is easily prepared by simply heating the metal in moist air. Oxidation of any of the lower oxides also yields the heptoxide.⁶² The yellow, crystalline heptoxide is a very hygroscopic substance,

⁵³Tribalat, S., Compt. rend., 222, 1388 (1946), [Sims, op. cit., p. 56].

⁵⁴Noddack, K. and W., Naturwissenschaften, 17, 93 (1929), [Sims, op. cit., p. 56].

⁵⁵Noddack, K. and W., Z. anorg. allgem. Chem., 181, 1-37 (1929) [Sims, op. cit., p. 56].

⁵⁶Briscoe, H., Robinson, P., and Stoddart, E., J. Chem. Soc., 1931, 1439-43.

⁵⁷Jakob, W., and Jezowska, B., Z. anorg. allgem. Chem., 220, 16 (1934), [Sims, op. cit., p. 56].

⁵⁸Briscoe, H., Robinson, P., and Rudge, A., J. Chem. Soc., 1931, 3087.

⁵⁹Roth, W., and Becker, G., Ber., 65B, 373 (1932), [Sims, op. cit., p. 59].

⁶⁰Noddack, W., Z. Electrochem., 34, 627 (1928), [Sims, op. cit., p. 56].

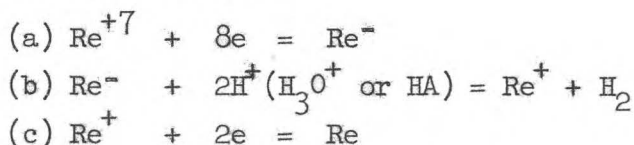
⁶¹Noddack, W., and I., Z. anorg. allgem. Chem., 181, 1-37 (1929) [Sims, op. cit., p. 56].

⁶²Nechamkin, H., Melaven, A., et al., Inorganic Synthesis, 49, 50, McGraw-Hill Book Co., New York (1950) [Sims, op. cit., p. 60].

picking up water readily from the air. It is soluble in alcohol and acetone but not in ether, and it is precipitated from acid solution by hydrogen sulfide as the heptasulfide. Also one of the most satisfactory methods of analysis is based upon the insolubility of AsReO_4 .

4. The Rhenide Ion

The most recent oxidation state of rhenium to be discovered is the uninegative species or rhenide ion. In 1937 Lundell and Knowles⁶⁵ reduced perrhenic acid in a Jones reductor and claimed the formation of the rhenide ion. The solutions they used were 0.00009 to 0.00018 F KReO_4 in 0.9 F sulfuric acid. The oxidation number was established by titration to Re(VII). The oxidation number was substantiated by Tomicek and Tomicek⁶⁶, and by Lingane⁶⁷. Lingane after producing the rhenide ion then attempted to study the polarography of the ion. The evidence he obtained indicated that the perrhenate ion is reduced all the way to rhenide ion at potentials of about -1.4 volts. His experiments agreed closely with those of Knowles⁶⁵ in that he found the rhenide ion to be a strong and rapid reducing agent, being easily oxidized to the (I) state (Probably as hyporhenous acid, HReO). He proposed the following mechanism for the reactions he observed:



Lingane⁶⁸ also titrated solutions supposed to contain rhenide ion. He used Ce(IV) as the oxidizing agent. He obtained an experimental value of 7.9 equivalents of ceric ion required to oxidize the reduced Re solutions up to the perrhenate state. His work therefore confirms that of Lundell, Knowles,⁶⁵ and Tomicek⁶⁶. He made no attempt to postulate the ionic or molecular state of the ion, but he did observe that the rhenide ion will reduce the hydrogen ion at the surface of a platinum electrode. Lingane⁶⁸ on the other hand did postulate as to the electronic configuration of the ion. In the rhenium atom itself the first four quantum levels are completely filled, and the configuration of the outer fifth and sixth levels is $5s^25p^65d^56s^2$. Hence the addition of an electron to produce the rhenide ion could lead to either (a) $5s^25p^65d^66s^2$ or (b) $5s^25p^66s^26p^6$. Because all other elements with negative oxidation states stabilize by the formation of s^2p^6 octets, Lingane postulated that configuration (b) was probably the more likely correct. This configuration requires the promotion of all of the original 5d electrons to the 6p level. This promotion would account for the marked instability and strong reducing character

⁶⁵Lundell, G. E. F., and Knowles, H. B., Bur. Standards J. Research, 18, 629 (1937), [C.A., 31: 7779⁶].

⁶⁶Tomicek, O. and F., Coll. Czech. Commun, 11, 626 (1939) [Griswold, E., op. cit., p. 375].

⁶⁷Lingane, J. J., J. Am. Chem. Soc., 64, 1001 (1942).

⁶⁸Lingane, J. J., J. Am. Chem. Soc., 64, 2182 (1942).

of Re^{III} . Lingane also showed that polarograms of solutions of (-I) rhenium in 1 to 2 N sulfuric acid at 0°C display three anodic waves, and that in 1 N perchloric acid one of the waves is resolved into two separate waves. He concluded that the waves indicated the oxidation from (-I) rhenium to (II), (III), (V), and (VII) respectively. This conclusion was also confirmed by means of amperometric titrations. He also showed that although partially oxidized solutions obtained by warming dilute sulfuric acid solutions of $\text{Re}(-\text{I})$ show an average oxidation state of (I) that $\text{Re}(\text{I})$ is not present as was indicated by previous workers including himself.⁶⁵ Actually the polarogram of such a solution indicates that the rhenium is not actually present in the (I) state, but as a mixture of $\text{Re}(-\text{I})$ and higher states in proportions that are equivalent to an average oxidation state of (I).

The rhenide ion is the only known occurrence of a metal with a negative oxidation state⁶⁹, although compounds of metals with an oxidation state of zero, such as nickel cyanide complex, $\text{Ni}(\text{CN})_4^{\text{II}}$, have been made. In 1947 Pauling⁶⁹ postulated as to the structure of the rhenide ion. Although admitting it was only a theory, Pauling's explanation was that the existence of rhenium in the negative state was based upon the fact that the ion must be able to exist with an electronic structure similar to that of bipoisitive platinum, which is isoelectronic with uninegative rhenium. Bipoisitive platinum exists only in complexes in which it forms four covalent bonds with four groups arranged in a coplanar square about it. It is possible that rhenium exists in the same state with four waters coordinating about it at the corners of a square.

In 1950 Maun and Davidson⁷⁰ performed experiments in which they attempted to prepare rhenide solutions of higher concentration than those previously prepared. They like their predecessors, employed a Jones Reductor. With the various experimental conditions they tried, it was impossible to quantitatively reduce $\text{Re}(\text{VII})$ to $\text{Re}(-\text{I})$ if the initial $\text{Re}(\text{VII})$ concentration was greater than 0.001 F. They also found that no specific effect of the concentration of the acid was observed from 2-6 F, but reduction was far from complete in 0.1 to 0.5 F acid. They observed that some of the solutions with a $\text{Re}(\text{VII})$ concentration greater than 0.001 F yielded brown solutions from the reductor. The color was either due to suspended solid matter or to colored ions in solution, and the solutions typically had oxidation numbers from 2 to 4. At lower concentrations in which the reduction was complete the solutions were colorless. They, however, became brown on standing in air. The most characteristic test found for the rhenide ion was titration with copper sulfate. Solutions containing $\text{Re}(-\text{I})$ immediately precipitated metallic copper. The reduced solutions developed very little color when standing if air was excluded, however, added perrhenate caused the color to appear.

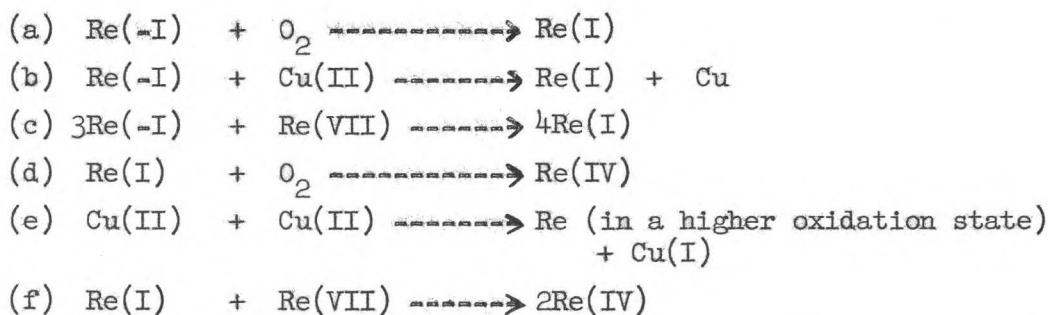
Maun and Davidson⁷⁰ have also presented evidence dealing with the oxidation of $\text{Re}(-\text{I})$ to intermediate oxidation states. Rhenium (-I) in 4 F hydrochloric acid is oxidized to a yellow-brown material by either oxygen or $\text{Cu}(\text{II})$. The yellow-brown material was identified as $\text{Re}(\text{I})$. The $\text{Re}(\text{I})$ is easily

⁶⁹Pauling, L., Chem. Eng. News, 25, 2970 (1947).

⁷⁰Maun, E. K., and Davidson, N., J. Am. Chem. Soc., 72, 3509 (1950).

oxidized up to Re (IV) by excess oxygen or Re (VII). This work substantiates that of Knowles⁶⁵ and Lingane⁶⁸ who likewise found an oxidation state of (I) upon such treatment. Lingane, however, later concluded that the (I) state was due to a mixture of higher oxides and the rhenide ion. The compound $\text{Re}_2\text{O}_3 \cdot \text{H}_2\text{O}$ has been reported⁷¹, and it is possible that the solutions considered may contain Re(I) in this form.

On the basis of their work Maun and Davidson⁷⁰ postulated that the following reactions occur:



Maun and Davidson also attempted to prepare a solid rhenide by the reaction of K_2ReCl_6 . This attempt was without success.

Rulfs and Elving^{71A} repeated the polarographic studies of Lingane.⁷⁰ While obtaining the same cathodic waves their interpretation is different. They studied the polarographic oxidation of rhenide in various acids. In sulfuric, methanesulfonic, perchloric or phosphoric acid the waves are all fundamentally the same. However, in hydrohalic acids the waves are less defined. They interpreted the waves in dilute sulfuric acid as involving the (-I) to (I) oxidation at 0.50 volts, the (I) to (II) oxidation at -0.27 v., and the (II) to (III) oxidation at -0.02 v. vs. the standard calomel electrode. They also presented evidence that the wave at +0.17 v. may involve oxidation of the (III) state and that the presence of a free (V) species results in a wave at ca. +0.09 v. They summarized the various rhenium couples in the following Table.

Table 1

Oxidation Potentials of Rhenium Couples

<u>Couple</u>	<u>E(N.H.E.)^a v</u>
$\text{Re}^- = \text{Re}^+ + 2e$	+ 0.230
$(2\text{Re}^- + \text{H}_2\text{O} = \text{Re}_2\text{O} + 2\text{H}^+ + 4e$	+ .13
$\text{Re}^+ = \text{Re}^{+2} + e$	+ .02
$\text{Re}^{+2} = \text{Re}^{+3} + e$	- .23
(Re^{+3} oxidation)	- .42, or more neg.)
(Re^{+5} oxidation)	- .34, approx.)

⁷¹Noddack, W. and I., Z. anorg. Chem., 215, 129 (1933)

[Sims, op. cit., p. 57].

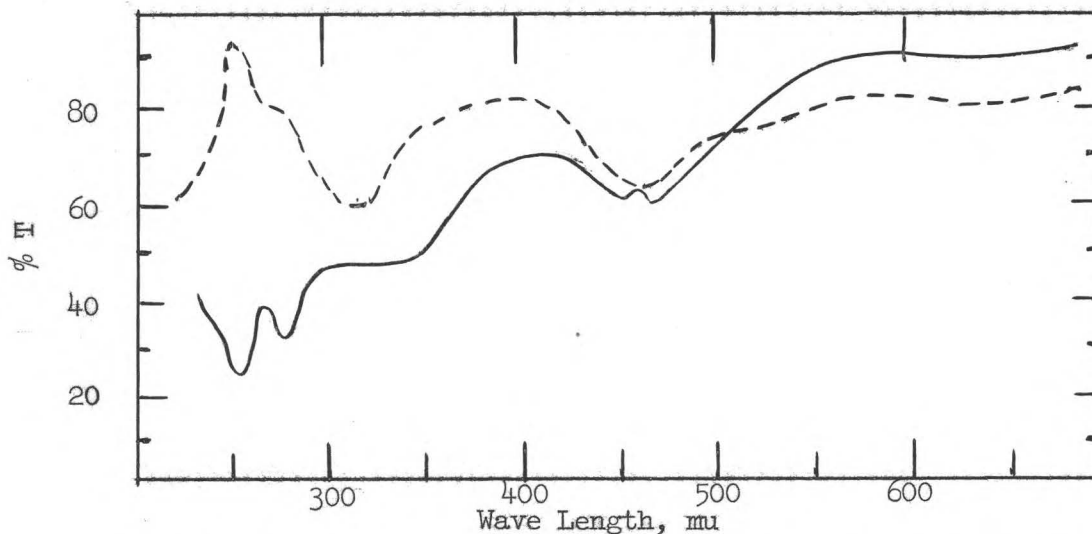
^{71A}Rulfs, C., and Elving, P.J., J. Am. Chem. Soc., 73, 3287 (1951).

a. Potentials, other than the first given, apply specifically to 0.4 mM rhenide in 2 N H_2SO_4 at 15°.

Rulfs and Elving^{71A} also pointed out that a distinction between the behavior of rhenide solutions in hydrochloric acid as compared to those in sulfuric acid exists. In 0.7 to 7 N sulfuric acid, the maximum concentration of potassium perrhenate which they were able to quantitatively reduce was 0.024 g. per 100 ml. or ca. 0.83 mM. In contrast, in hydrochloric acid of 1.2 N concentration, perrhenate concentrations of at least 1.3 mM were quantitatively reduced, and in the presence of pyridinium chloride concentrations of 2.6 mM are attainable. They interpreted this on the basis of a complex formation of the general type $\text{ReCl}_x^{-(x-1)}$ instead of the Re_2O_7 formed in sulfuric acid. They observed similar cathodic waves in solutions of other hydrohalic acids indicating the presence of comparable rhenium complexes. Also of interest is the fact that solutions of rhenide ion in hydrochloric acid, when exposed to the air, do not undergo the usual change of color to yellow-brown, and separation of dark solid that comparable sulfuric acid solutions do.

In an effort to substantiate their claim of complexation, Rulfs and Elving^{71A} also measured the absorption spectrum of sulfuric and hydrochloric acid solutions of the rhenide ion. The absorption curves (see below) indicated quite significant differences between the near ultra-violet absorption spectra of rhenide in the sulfuric acid solution and the hydrochloric acid solution.

Figure 2



Rhenide absorption in two media: absorption spectra of 0.5 mM rhenide in 2 N sulfuric acid (dashed line) and 2 N hydrochloric acid (solid line) at 25°, 1 cm. path

In 1952 Griswold, Kleinberg, and Bravo⁷² announced the preparation of the first solid rhenide. Prior to this time the rhenide ion had been produced only by means of a Jones reductor or cathodically, and a maximum concentration of only about 0.001 M could be obtained. Griswold and coworkers successfully

⁷²Griswold, E., Kleinberg, J., and Bravo, J.B., *Science*, **115**, 375 (1952).

produced a mixture containing potassium hydroxide and potassium rhenide by the reaction of potassium perrhenate in ethylenediamine-water solutions with potassium metal. They carried out the reaction in a closed system under nitrogen, and the valence number of the rhenium was established by determining the rhenium content and the reducing power of the solid material. Typical values obtained for the valence number of the solid are -0.97, -1.06, -1.00, and -0.81.

Griswold and coworkers listed the following as the optimum conditions for the conversion of the perrhenate ion to the solid rhenide:

- (a) Composition of solvent, 9.8 g. of water/100 ml. ethylenediamine-water solution.
- (b) Initial concentration of potassium perrhenate, 3mM/l.
- (c) Potassium requirement, 4 g/100 ml. solution.
- (d) Initial temp., room temperature. (The solution warms up to about 60° in the course of the reaction.)

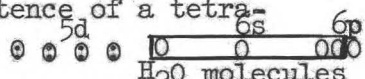
Under the conditions described the authors obtained a conversion of approximately 55% of the perrhenate to the solid rhenide. Another interesting observation they made was that treatment of an aqueous solution of the solid mixture of potassium hydroxide and rhenide compound with thallos nitrate solution yields first a white precipitate, presumably thallos rhenide, which rapidly undergoes reaction to yield finely divided thallium metal and the perrhenate ion.

In 1954 Bravo, Griswold, and Kleinberg⁷³ announced further work on the solid rhenide they had previously prepared.⁷² The potassium rhenide-potassium hydroxide mixture was prepared in the same manner as before and then the potassium hydroxide was fractionally extracted. Various solvents were tried, among them were liquid ammonia, ethyl alcohol, dioxane, cellosolve, n-amyl alcohol, n-butyl alcohol, and isopropyl alcohol. The isopropyl alcohol was found to be the most satisfactory. This solvent dissolves potassium hydroxide and has practically no solvent action on the rhenide. By repeated extractions they were able to isolate potassium rhenide of greater than 95% purity. They also established the fact that under optimum conditions of reduction, conversion of Re(VII) to Re(-I) of up to 90% is possible. Analysis of the grey material obtained after the isopropyl alcohol extractions indicated the presence of about 5 per cent potassium hydroxide and apparently four molecules of water per rhenide ion. More recent work⁷⁴ indicates the water may be an inseparable part of the ion.

After the isolation of the relatively pure KRe the authors⁷³ attempted to measure its magnetic susceptibility. The measurements indicated that the material was slightly paramagnetic. Values of 254×10^{-6} and 223×10^{-6} c.g.s respectively for two different samples after correction for the KOH present were obtained. This amount of paramagnetism is even less than that required for a substance with one unpaired electron. Inasmuch as rhenium itself possesses five unpaired electrons, the evidence indicates that the formation of the

⁷³Bravo, J. B., Griswold, E., and Kleinberg, J., J. Am. Chem. Soc., 58, 18 (1954).

⁷⁴Cobble, J.W., "On the Structure of the Rhenide Ion", Dept. of Chem. University of Purdue to Chemistry Division, Air Force Office of Scientific Research, TN-56-348, July 26, 1956.

rhenide ion involves a considerable modification in electronic configuration. Previously Lingane⁶⁸ suggested the possible structures: (a) $5s^2 5p^6 5d^6 6s^2$ and (b) $5s^2 5p^6 6s^2 6p^6$. Bravo and coworkers⁷³ state that on the basis of their work the structure $5s^2 5p^6 5d^8$ must also be considered. In addition as previously stated, Pauling⁶⁹ has suggested the likelihood of the existence of a tetrahydrate of a square planar structure, involving dsp^2 bonds 

The magnetic evidence presented definitely eliminates the possibility of structures (a) and (c) being correct since they possess four and two unpaired electrons respectively. Structure (b) which requires promotion of the $5d$ electrons to $6p$ orbitals is unreasonable in that there is a large amount of promotion energy involved. The possibility that the rhenide exists in a hydrated complex having four water molecules coordinated at the corners of a square is consistent with energy considerations, and also with the magnetic data the authors produced.

Grosse^{74A} has also prepared a solid rhenide compound. He obtained a 10 to 20% yield of $LiRe$ by the reduction of aqueous potassium perrhenate with lithium. The compound was isolated from the lithium hydroxide by fractional crystallization from water, or from a mixture of ethanol and water with a recovery efficiency of 90 percent. The compound like those previously prepared had attached water.

The most recent and final information dealing with the rhenide ion to come forth was presented by J. W. Cobble at Purdue University.⁷⁴ The work of Cobble attempts to arrive at a solution for the nature of the rhenide ion by means of thermodynamical considerations. Several other important considerations have also come out of this work. Cobble estimated the ionic radii of the rhenide ion in the following manner: The difference between the covalent and univalent radii of the halogens Cl, Br, and I is 0.83, 0.84, and 0.88 Å respectively; Cobble therefore assumed that the difference between the covalent radius of Re and Re^- would be of the same order of magnitude or about 0.88 Å. The covalent radius of rhenium would appear to be almost the same as the observed metallic radius of 1.37 Å, and thus the radius of Re^- is probably about 2.3 Å.

The attempt to prove the structure of the rhenide ion was made by means of a Born cycle. By this means Cobble was able to show that the rhenide ion is not halogen-like, i.e., Re^- . However, he was able to show that a structure of the type suggested first by Pauling⁶⁹ with four water molecules located at the corners of a square would be feasible energywise. The previous work of Griswold and coworkers⁷³ also substantiates this analysis. It is significant that the only stable rhenides prepared to date appear to be hydrates. Cobble makes the further assertion that the hydrated solid species is not stable because of any simple hydration phenomena but because the four water molecules are built into and are an integral part of the rhenide ion. If this is the case, then the rhenide does not exist as $Re(-I)$ but rather as the oxygenated complex $H_8ReO_4^-$.

^{74A}Grosse, A.V., Z. Naturforsch., 8b, 533 (1953), [C.A., 48:4347d].

5. Catalytic Activity

The Noddacks in 1929 suggested the use of rhenium as a catalyst^{75,76} They found that rhenium catalyzes the oxidation of sulfites to sulfates, nitrites to nitrates, aniline to aniline black and the oxidation of ammonia.⁷⁷

Platonov has probably done as much work as anyone on the catalytic properties of rhenium and rhenium compounds. He⁷⁸ and his coworkers found that a rhenium catalyst prepared by the methods of the Noddacks would catalyze the decomposition of formaldehyde into carbon dioxide and water. Also that the decomposition of ethanol on a rhenium catalyst takes place in two ways: (a) $\text{EtOH} \rightarrow \text{AcH} + \text{H}_2\text{O}$ and (b) $\text{EtOH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$. The first reaction predominates. The ethanol decomposition was studied in the temperature range of 250° to 500°C. and the effect of traces of H_2S and As_2O_3 was studied. It was found that these impurities increased the activity of the catalyst.

Platonov⁷⁹ performed similar experiments using methanol and found that when methanol is passed over ordinary Re catalyst it is completely decomposed and almost no CH_2O results. However, if the catalyst is partially poisoned by H_2S or As_2O_3 good yields of CH_2O are obtained. BuOH ⁸⁰ at 350° to 450°C splits easily to the aldehyde with almost no side reaction.

When using cyclohexanol,⁸¹ Platonov found that in the temperature range of 250° to 500°C good yields of cyclohexanone were obtained. Traces of phenol were also present. Traces of ReS_2 sharply increased the yields of the ketone.

⁷⁵Noddack, W. and I., (to Siemens and Halske A.G.), Brit. Pat. 346,652 (October 8, 1929), [Sims, op. cit., p. 104].

⁷⁶(to N.-V. de Bataafsche Petroleum Maatschappij), Brit. Pat. 358,180 (July 29, 1930), [Sims, op. cit., p. 104].

⁷⁷(to Siebert Ges.m.b.H.), Brit. Pat. 385,859 (June 8, 1932), [Sims, op. cit., p. 104].

⁷⁸Platonov, M.S., and Tomilov, V.I., J. Gen. Chem. (U.S.S.R.), 7, 788 (1937), [C.A., 31: 6189⁷].

⁷⁹Platonov, M.S., and Tomilov, V.K., and Tur, E.V., J. Gen. Chem. (U.S.S.R.), 7, 1803 (1937), [C.A., 31: 8341⁷].

⁸⁰Platonov, M.S., and Anisimov, S. B., J. Gen. Chem. (U.S.S.R.), 7, 1360 (1937), [C.A., 31: 8503³].

⁸¹Tur, E.V., Anisimov, S.B., and Platonov, M.S., J. Gen. Chem. (U.S.S.R.), 7, 2895 (1937), [C.A., 32: 5383⁴].

Although Platonov⁸² actually did very little work using rhenium as a hydrogenation catalyst he concluded that metallic rhenium is a relatively weak catalyst for catalytic hydrogenation. He reduced cyclohexene, benzene and nitrobenzene in the temperature range of 200 to 400°C. These conditions have been greatly improved upon in these laboratories at Brigham Young University.

A considerable amount of Platonov's work has been with various alcohols. He⁸³ found that a purified ReS_2 catalyst would dehydrogenate methyl, ethyl, and isopropyl alcohol to give good yields of the corresponding aldehydes or ketones and very small amounts of by-products at 400 to 550°C. Cyclohexanol at 550°C gives 78 to 80% yields of phenol and only small amounts of cyclohexane, cyclohexene, and benzene.

Siemens and coworkers^{84,85,86} have done work on the catalytic properties of rhenium and have obtained several patents for such processes as the production of SO_3 from SO_2 , nitrates from nitrites, and the conversion of aniline to aniline black. They also found that rhenium would catalyze the reduction of carbon monoxide to methane and the reduction of ethylene to ethane.

Patents^{87,88} have also been granted for the use of rhenium in destructive hydrogenation, refining, or desulfurization, and like treatments of carbonaceous materials.

Zenghelis and coworkers^{89,90} have used rhenium catalysts in the synthesis of ammonia. In their experiments they found that a mixture of 3 volumes of hydrogen

⁸²Platonov, M. S., Anisimov, S.B., and Krashenennikova, V. M., Ber. 68B, 761 (1935), [C.A., 29: 5005²].

⁸³Platonov, M. S., J. Gen. Chem. (U.S.S.R.), 11, 683 (1941), [C.A., 36: 397⁷].

⁸⁴Siemens, A., Halske, G., Noddack, W., and Noddack, I., British Pat. 346,652, (October 8, 1929), [C.A., P26: 569²].

⁸⁵Tropsch, H., and Kassler, R., Ber. 63.B, 2149 (1930), [C.A., 25:22²].

⁸⁶Siemens, A., and Halske, G., France Pat. 658,446 (September 30, 1929), [C.A., 24: P4362⁵].

⁸⁷N.-V. de Bataafsche Petroleum Maatschappij, British Pat. 358,180 (July 29, 1930), [C.A., 26: P4924⁷].

⁸⁸N.-V. de Bataafsche Petroleum Maatschappij, German Pat. 393,707 (June 20, 1940), [C.A., 35: P4941²].

⁸⁹Zenghelis, C., and Stathis, K., Atti. X^o Congr. intern. chim., 2, 821 (1938), [C.A., 33: 8081²].

⁹⁰Zenghelis, C., and Stathis, K., " Osterr. Chem. Ztg., 40, 80 (1937), [C.A., 34: 5383⁴].

and 1 volume of nitrogen when passed at 85° over metallic rhenium moistened with dilute sulfuric acid reacted to give ammonia. The yield was slight, a good yield, however, was obtained when the hydrogen was first passed through a solution of ammonium chloride and sodium nitrate, that is with the nitrogen in a nascent state. Metallic rhenium catalyzed the reaction strongly, and the catalysis was increased by the addition of iron to the rhenium.

Recent work^{91,92,93,94} in these laboratories indicates that rhenium is superior to the commonly used catalysts (PtO₂, Raney nickel, copper chromite, etc.) on some substrates and comparable on many others. It has been found that rhenium heptoxide reduced in situ is the best reported catalyst for the reduction of carboxylic acids. A rhenium sesquioxide catalyst will reduce styrene at room temperature and benzene at ca. 150°. A heptasulfide catalyst was found to be resistant to poisoning and to be capable of catalyzing the reduction of allyl phenyl sulfide to n-propyl phenyl sulfide without accompanying carbon-sulfur bond hydrogenation. These and other catalysts have reduced such substrates as 2-butanone, cyclohexanone, nitrobenzene, and hexene-1 with relative ease.

Although the evaluation of rhenium as a catalyst is at present rather disputed, it is surely not erroneous to say that while rhenium has not proved to be unique as a catalyst, it shows definite catalytic activity and can be classed as good.

⁹¹Shaw, "Liquid-Phase Catalytic Hydrogenations with Rhenium Heptoxide Derived Catalysts", Unpublished Master's Thesis, Department of Chemistry, Brigham Young University, 1955.

⁹²Whittle, "Rhenium Heptaselenide as a Hydrogenation Catalyst", Unpublished Master's Theses, Department of Chemistry, Brigham Young University, 1956.

⁹³Hsu, "A Correlation of the Catalytic Activity of Various Mixtures of Rhenium and Molybdenum Sulfides in Liquid-Phase Hydrogenations of Certain Reducible Organic Groups," Unpublished Master's Thesis, Department of Chemistry, Brigham Young University, 1956.

⁹⁴Johnson, "The Catalytic Hydrogenation Activity of Rhenium Blacks Produced by the Action of Sodium Borohydride on Ammonium Perrhenate and of Tetrahydropyran on Rhenium Heptoxide," Unpublished Master's Thesis, Department of Chemistry, Brigham Young University, 1956.

B. The Nature and Advantages of the Alkali Metal-Liquid Ammonia System⁹⁵

Solutions of the alkali metals in liquid ammonia were first investigated by Weyl⁹⁶ in 1864. He observed that sodium and potassium were soluble in this medium, producing highly colored solutions. A few years later, Seely^{97,98,99} reported his observations on the solutions of alkali metals in liquid ammonia.

While water is well adapted as a medium in which to carry out reactions with strong oxidizing agents, it is not well adapted to carrying out reactions involving strong reducing agents. The reducing power of reductants in water is limited by the fact that stronger reducing agents than hydrogen liberate hydrogen from water. Liquid ammonia suffers no such handicap, since the strongest reducing agents, the alkali metals, form stable solutions in this solvent. Thus ammonia (and the simple amines) becomes the ideal medium for the study of reduction reactions involving strong reducing agents.¹⁰⁰

One of the outstanding properties of a solution of an alkali metal in liquid ammonia is its powerful reducing action. This property is attributed to solvated electrons.^{96,101} It is believed that a solution of an alkali metal in liquid ammonia contains positively charged metal ions and negative electrons. Depending upon the concentration, the electrons may be relatively free, or associated with molecules of the solvent, ammonia.¹⁰² Many facts substantiate this theory. One is that on electrolysis of a solution of an alkali metal in ammonia, while the metal is plated at the cathode, no material is formed at the anode. Another interesting fact is that the absorption spectra of all the alkali metal solutions are the same. This interesting situation is interpreted as an indication that the colored component of all these dilute solutions is the solvated electron.¹⁰³

⁹⁵Johnson, W. C. and Meyer, A.W., Chem. Rev., 8, 272 (1931).

⁹⁶Weyl, Ann. Physik, 121, 601 (1864), [Johnson, op. cit., p. 272].

⁹⁷Seely, Chem. News, 22, 117 (1870), [Johnson, op. cit., p. 272].

⁹⁸Seely, Chem. News, 23, 169 (1871), [Johnson, op. cit., p. 272].

⁹⁹Seely, J. Franklin Inst., 61, 110 (187), [Johnson, op. cit., p. 272].

¹⁰⁰Fernelius, Conard, W., and Watt, G.W., Chem. Revs., 20, 195 (1937).

¹⁰¹Franklin and Kraus, Am. Chem. J., 21, 8 (1899), [Fernelius, Conard W., and Watt, G.W., op. cit., p. 204].

¹⁰²Cappel, N.O., and Watt, G.W., J. Chem. Education, 14, 174 (1937).

¹⁰³Chittum, J. R., and Hunt, H., J. Phys. Chem., 40, 581 (1936).

Kraus and Schmidt¹⁰⁴ have measured the heat of solution of metallic sodium in liquid ammonia and found it to be negative to the extent of 1385 cal. The heats of solution of potassium, rubidium and cesium have also been measured¹⁰⁵ and found to be almost negligible. The atomic heat of solution of lithium is negative.¹⁰⁵

Not only is liquid ammonia an excellent solvent but many of its solutions are conductors of electricity. The conductivities of liquid ammonia solutions have been studied extensively. Such studies have shown that although there are some extraordinary phenomena requiring special explanation, the conductivities of ammonia solutions are essentially similar to those of aqueous solutions and our familiar ideas of conductivity and dissociation can be extended in their entirety to the ammonia system.¹⁰⁶

The conduction process in solutions of the alkali metals is ionic. The positive ion in these solutions is identical with the positive ion of a salt of the same metal, while the negative ion is apparently the negative electron. At low concentrations the negative electron is associated with ammonia, as a consequence its speed is of the order of magnitude of normal ions. At higher concentrations, however, the carrying capacity of the negative ion increases. This is due to an increase in the speed of this ion in consequence of its loss of associated ammonia. At very high concentrations the speed of the negative ion in ammonia is comparable with that of electrons in metals. In saturated solutions the specific conduction reaches values of 5.047×10^7 and 4.567×10^7 for sodium and potassium, respectively.¹⁰⁷ Calculations of the ratio of the transference numbers of negative to positive ions in liquid ammonia solutions of sodium show that near saturation the negative ion has a mean speed some 280 times that of the positive ion.¹⁰⁸ This ratio diminishes with decreasing concentration until the relative carrying capacity becomes seven in the most dilute solutions.¹⁰⁵

In many respects the properties of solutions of alkali metals are intermediate in character between those of metals and those of electrolytic solutions. Thus at high concentrations the atomic conductance of solutions of these metals compares favorably with that of such metals as iron and strontium. Also electrical conductance data shows that the conductance of dilute solutions of sodium and potassium and of sodium and lithium are practically additive.¹⁰⁸

It has been shown for methylamine that the metals are less ionized in this solvent than in ammonia and that the minimum in the molecular conductivity occurs at a somewhat higher concentration. Further, the solvation of electrons in methylamine is not as complete as in liquid ammonia, and diminishes as the

¹⁰⁴Kraus, C.A., and Piddlerhof, J. A., J. Am. Chem. Soc., 56, 79 (1934).

¹⁰⁵Schmidt, F.C., Studer, F.J., and Sottysiak, J., J. Am. Chem. Soc., 60, 2780 (1938).

¹⁰⁶Fernelius, W.C., and Johnson, W.C., J. Chem. Education, 5, 664 (1928).

¹⁰⁷Kraus, C.A., and Lucasse, J. Am. Chem. Soc., 43, 2529 (1921).

¹⁰⁸Kriengl, F., Stupkol, F., and Stupkol, K., Monatsh. 63, 394 (1933), [Fernelius, Conard, W., and Watt, G.W., op. cit., p. 199].

temperature is increased.¹⁰⁹

When metallic sodium is added to liquid ammonia one of the first things that is noticed is the tremendous volume increase in the resulting solution.¹¹⁰ In saturated solution (93 g. NH_3 /gram-atom sodium), the volume of the mixture is markedly higher than one would expect. One gram-atom of sodium occupies approximately 23 ml. and 93 gm. of liquid ammonia about 137 ml. at -33°C . If no volume change occurred, the total volume of the solution would be about 160 ml. However, the calculated volume from the measured density of the saturated solution is slightly more than 200 ml. which represents a volume increase of 41 ml. or approximately 25 percent. This striking property of these solutions may be explained by considering the condition of the sodium in solution. If we bear in mind that in these solutions, sodium is present as a normal sodium ion, we must ascribe the volume change chiefly to the electron, which freed from the constraints under which it exists in the solid metal, occupies a relatively large volume in solution.¹⁰⁹

The high solubility of the alkali metals in liquid ammonia at its normal boiling point is truly remarkable. Lithium is soluble to the extent of 11.3 g./100 g. NH_3 , sodium 24.6 g./100 g. NH_3 , and potassium 49.0 g./100 g. NH_3 . It is seen that these solubilities are rather great when it is recalled that at 180 C. only 11.1 grams of sodium sulfate dissolve in 100 g. of water.¹¹⁰

Metals are also soluble in some of the amines of low molecular weight; lithium, sodium, and potassium^{111,112} and cesium^{111,113} are soluble in methylamine; lithium is less soluble in ethylamine than in methylamine¹¹⁴, cesium¹¹³ is soluble in ethylamine; sodium^{113,114} and potassium¹¹⁴ are insoluble in ethylamine; lithium is insoluble in propylamine;¹¹⁴ lithium, sodium,¹¹⁵ potassium¹¹⁴, and cesium¹¹⁵ are soluble in ethylenediamine; in hydrazine lithium is slightly soluble, sodium is soluble by reaction, potassium is too reactive to note solubility.¹¹⁶ These solutions are all more or less unstable, owing to interaction between solvent and solute to produce hydrogen and substituted amides. Each of these solutions is blue in color, closely resembling ammonia solutions.¹⁰⁸

¹⁰⁹Gibson, G.E., and Phipps, T.E., J. Am. Chem. Soc., 48, 312 (1926).

¹¹⁰Johnson, W.C., and Fernelius, C., J. Chem. Education, 6, 20 (1926).

¹¹¹Gibson, G.E., and Argo, W.L., J. Am. Chem. Soc., 40, 1327 (1918).

¹¹²Moissan, H., Compt. rend., 128, 26 (1899), [Fernelius, Conard W., and Watt, G.W., op. cit., p. 195].

¹¹³Rengade, E., Compt. rend., 140, 246 (1905), [Fernelius, Conard W., and Watt, G.W., op. cit., p. 195].

¹¹⁴Kraus, C.A., J. Am. Chem. Soc., 29, 1557 (1907)

¹¹⁵Fernelius, W. C., Unpublished observations, [Fernelius, Conard W., and Watt, G.W., op. cit., p.195].

¹¹⁶Welsch, T.W.B., J. Am. Chem. Soc., 37, 501 (1915), [Fernelius, Conard W., and Watt, G.W., op. cit., p. 195].

It is perhaps significant that ammonia solutions of strong electrolytes conform more nearly to the law of mass-action at low concentrations than do similar water solutions. A rather remarkable fact is that the ions travel faster in ammonia than in water. The cause of this phenomenon can be attributed to the low viscosity of liquid ammonia. Because ammonia is less viscous and is a weaker dissociating agent than water, dilute solutions in ammonia are better conductors than dilute aqueous solutions, while water solutions excel when concentrated.¹¹⁷

Of all known liquids, ammonia most closely approaches water in all those properties which give to water its conspicuous position among solvents. In its capacity as a general solvent for salts it is secondary to water, but superior to all other solvents. It closely approaches water in its power to dissociate electrolytes; some salts conduct electricity even better in ammonia solution than they do in water solution. It even plays a part in many compounds analogous to that occupied by water in salts containing water of hydration or crystallization.¹⁰⁶

Many of the solubility relationships of substances in liquid ammonia are extremely interesting and often times completely at variance with the solubilities in water. Ammonia differs from water in its inability to dissolve the sulfates and sulfites, the alkaline carbonates, phosphates, and oxalates, the hydroxides of the alkali and alkaline earth metals, and the facility with which it dissolves many organic substances.¹¹⁷ The solubilities of the silver halides is the inverse of that in water; silver chloride is slightly soluble, silver bromide is much more soluble than the chloride, while silver iodide is extremely soluble. The unusual solubility of these halides is doubtlessly due to the formation of a complex silver ion.¹¹⁷

C. Reduction of Inorganic Compounds in Liquid Ammonia

1. The Theory of Liquid Ammonia Reductions

The strongest reducing agents known to chemistry are the solutions of alkali metals in liquid ammonia. These metals in ammonia solution dissociate into normal positive ions and electrons. The reducing power of these solutions is due to the electron and is practically identical for all solutions of all these metals.¹¹⁸ The process of reduction by means of metals in liquid ammonia consists essentially in the combination of an electron with a positive ion. The positive ions of the alkali metals are, of course, also present, but they take no part in the reduction process. These positive ions possess no metallic properties, and they are concerned in the process of reduction only to the extent of supplying the counterbalancing electrical charge for the negative electrons.¹¹⁹ With the above picture of the nature of metal solutions in mind, one can easily see that this type of situation eliminates one of the very serious limitations in the use of alkali metals as reducing agents, i.e., surface area, by making it effectively infinite. Add to this factor the marked solvent power of liquid ammonia for a great variety of substances and the normally low reactivity of the solvent toward the dissolved metal, and it can

¹¹⁷Fernelius, W.C., and Johnson, W.C., op. cit., p. 667.

¹¹⁸Kraus, C.A., Chem. Revs., 26, 95 (1940).

¹¹⁹Fernelius, Conard W., and Watt, G.W., op. cit., p. 204.

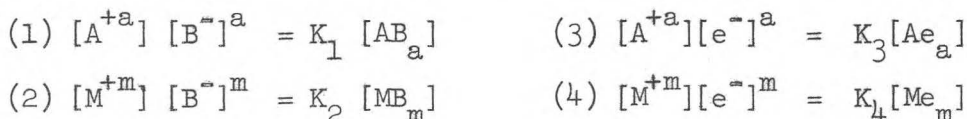
easily be seen why so many reductions take place readily and rapidly in liquid ammonia. Indeed, the use of an excess of the reducing agent is the exception rather than the rule and, because of the high tinctorial power of dissolved metal, most reactions can be titrated to a definite endpoint.¹⁰⁸

2. The Mechanisms of Reduction

Assuming the above concept of reduction to be correct, if we reduce the salt AB_a of metallic element A whose positive valence is a, by means of another metal M of positive valence m, then the problem presented is similar to that of a solution of two salts without a common ion, the ionic constituents being A^a , M^m , B^- , and e^- , we have, then the reaction equations:



Corresponding to these reaction equations we have the equilibrium equations:



Here K_1 , K_2 , K_3 , and K_4 represent the mass-action functions of the reactions in question. These mass action functions have definite values for definite conditions of the system, but vary as a function of the concentration of the various constituents present, approaching definite limiting values at low concentration. The reaction taking place in the solution will depend upon the values of the mass-action functions and the solubilities of the constituents AB_a , MB_m , Ae_a , and Me_m . A number of different cases, depending upon the relative values of the mass action functions and the solubilities of the various constituents, may be distinguished.¹²⁰

(a) The mass-action functions have approximately the same value for all constituents and the solubility of these constituents is high and of the same order of magnitude.¹²⁰ In this case interaction will take place between the salt AB_a and the reducing metal Me_m but, because of the high value of the solubility of the products of metathesis, precipitation will not occur. The solution, however, will contain both the salts AB_a and MB_m and the neutral metal atoms Ae_a and Me_m . The extent to which metathesis occurs will depend upon the relative values of the mass-action functions under the conditions of the system. An example of a system of this type is found in a solution of sodium iodide to which metallic potassium has been added. Here metathesis takes place with the formation of potassium iodide and metallic sodium, but potassium iodide is not precipitated except at very high concentrations, owing to its high solubility.

(b) The mass-action functions are of the same order of magnitude, but the solubility product of the constituent MB_m is low.¹²⁰ In this case metathesis takes place with the precipitation of the salt MB_m , while the solution contains an equivalent amount of the metal Ae_a . The completeness of the precipitation

¹²⁰Kraus, C.A., and Kurtz, H.F., J. Am. Chem. Soc., 47, 43 (1925).

depends upon the solubility of the salt MB_m . An example of a reaction of this type is found in a solution of potassium amide to which metallic sodium has been added. Sodium amide is much less soluble than potassium amide and accordingly precipitates, leaving behind metallic potassium. In this case, however, precipitation is incomplete because of the measurable solubility of sodium amide. A more striking example is found in the case of solutions of potassium halides to which metallic calcium has been added. The calcium halides are rather difficultly soluble in liquid ammonia and practically complete precipitation of calcium takes place, while the potassium thus reduced remains behind in the solution.

(c) The solubility product of the reducing metal Me_m is low, while the solubility product of the salt MB_m is likewise low.¹²⁰ Even though the solubility product of the metal Me_m is relatively low, which corresponds in general to the case of a weakly electropositive metal, reduction may nevertheless be effected if the solubility product of the salt MB_m is sufficiently low. An example of a reaction of this type is found in the reduction of sodium salts by means of magnesium. Magnesium is only slightly soluble in liquid ammonia, giving a transparent blue solution. When sodium bromide is treated with metallic magnesium, reduction takes place because of the low solubility of magnesium bromide, metallic sodium remaining in solution. An equilibrium must finally exist in the solution among the various constituents, the concentrations being dependent upon the solubility of the magnesium and of magnesium bromide.

(d) The reduced metal Ae_a , has a low valued solubility product and is not capable of existing as an anion.¹²⁰ In this case reaction between the salt AB_a and the reducing metal Me_m is one of simple metathesis according to the equation, $A^a + ae \longrightarrow Ae_a$ and we have the corresponding equilibrium with free metal. The completeness of the precipitation depends upon the value of the solubility of the metal Ae_a . For the less electropositive metals this value is extremely low and such metals, therefore, are completely precipitated from solution by means of more electropositive metals, whose solubility is relatively high. The reduction of silver salts by means of sodium in liquid ammonia is a typical example of a reaction of this type, since silver is only weakly electropositive and does not form a compound with sodium. Other metals, which are similarly incapable of forming compounds with the reducing metal, are precipitated in the free metallic state.

3. Reduction of Oxides

Many metal oxides are reduced by solutions of alkali metals in liquid ammonia. The primary action involved is undoubtedly the removal of oxygen, and the primary product appears to be the free element. However, in many cases the element enters into subsequent reactions which yield soluble or insoluble intermetallic compounds. During the initial step the alkali monoxide is also formed, but in most cases it is immediately ammonolyzed to the alkali amide and alkali hydroxide. The alkali hydroxide, which is insoluble, usually prevents the isolation of a single insoluble reduction product. Also the metal oxide may act as a catalyst for the reaction between the alkali metal and the liquid ammonia to form the alkali amide. Thus, in the presence of a limited quantity of alkali metal, an oxide having a marked catalytic activity toward the foregoing reaction might not be reduced to any appreciable extent because of the rapid conversion of the alkali metal to the amide; or more properly because of the elimination of electrons by virtue of the accompanying formation

of molecular hydrogen.^{121, 122}

Geo. W. Watt and W.C. Fernelius¹²² found that when 1/2 g. of Bi_2O_3 in 15 ml. of liquid ammonia was reduced with 6 equivalents of potassium, the characteristic blue color of the potassium solution was discharged immediately and the yellow trioxide was reduced to a grey metallic solid. During the process a white flocculent precipitate of KOH also appeared. The precipitate was washed several times with liquid ammonia and then with water to remove the KOH. After these washings the remaining insoluble product analyzed 98.4% free bismuth. The amount of bismuth recovered corresponded to 97.7% of the bismuth used as Bi_2O_3 .¹²²

Oxides of the transitional elements when reduced in liquid ammonia usually yield either a lower oxide or the free metal.¹²¹ However, these reactions are often incomplete due to the catalytic activity of the free metal. In Watt's experiments it was found that a few minutes after Cu_2O was treated with 2 equivalents of potassium, a non-adherent copper mirror was formed on the walls of the reaction vessel. It took approximately 1/2 hr. for the characteristic blue color of the solution to be discharged and the ammonia to assume a pale yellow color due to dissolved potassium amide. The insoluble reaction product was washed several times with ammonia but not with water because of the reactivity of the free metal. Analysis showed that 89.2 percent of the Cu_2O had been reduced to the free metal. The same type of procedure was performed on CuO , and the analysis revealed that 86.2 percent of the oxide was converted.¹²³

When Ag_2O was treated with two equivalents of potassium the black oxide was immediately converted to metallic silver; 99.7% conversion was obtained.¹²³

When MoO_2 is treated with three equivalents of an alkali metal in liquid ammonia it is reduced quantitatively to Mo_2O_3 . However, if a larger excess of the metal is used a mixture of Mo_2O_3 and the free metal is formed.¹²⁴

When Co_2O_3 is reduced by potassium in liquid ammonia, the first product is CoO . This oxide is in turn reduced to metallic cobalt to an extent dependent upon the $\text{Co}_2\text{O}_3/\text{K}$ ratio.^{124, 125} When six equivalents of potassium are used in the reduction of the Co_2O_3 , the insoluble products obtained dissolve in HCl without appreciable liberation of hydrogen. However, hydrogen is evolved extensively when the products are obtained by reduction with twelve or twenty-four equivalents. This fact serves as good evidence for the fact that the reaction proceeds in two steps. When twenty-four equivalents of the alkali metal are used, Co_2O_3 is reduced almost completely to the free metal.

¹²¹ Watt, Geo. W., Chem. Revs., 46, 289 (1950).

¹²² Watt, Geo. W. and Fernelius, W.C., J. Am. Chem. Soc., 61, 2502 (1939).

¹²³ Watt, Geo. W. and Fernelius, W.C., J. Am. Chem. Soc., 61, 1692 (1939).

¹²⁴ Watt, Geo. W., Chem. Revs., 46, 304 (1950).

¹²⁵ Moore, T.E., and Watt, Geo. W., J. Am. Chem. Soc., 64, 2775 (1942).

Nickel (II) oxide is similarly reduced to elemental nickel to an extent dependent upon the concentration of potassium employed. Holt and Watt^{124,126} found that with 2, 4, 8, and 12 equivalents of potassium, reduction occurred to the extent of 0.3, 0.5, 1.4, and 4.3%, respectively. The catalytic activity of the nickel oxide, or that of very small quantities of the reduction product, toward the conversion of the alkali metal to the amide was so pronounced that appreciable reduction of these oxides could not be accomplished.

Iron(II) oxide, like nickel, has a pronounced catalytic effect upon the amide formation. Because of this, it is reduced incompletely to elemental iron by ammonia solutions of the alkali metals. The fact that the extent of reduction of FeO does not increase appreciably with increase in the quantity of potassium used, provides good evidence that FeO, or its reduction products, are a much better catalyst for amide formation than the corresponding cobalt compounds.¹²⁵ The order of decreasing catalytic activity for amide formation is $\text{Fe}_2\text{O}_3 > \text{Ni}_2\text{O}_3 > \text{NiO} > \text{Co}_2\text{O}_3$ (The position of FeO was not given).

4. Reduction of Sulfides

At present very little work has been done on the reduction of sulfides in liquid ammonia. A big difficulty connected with the reduction of sulfides is their limited solubility in liquid ammonia. Johnson and Wheatley¹²⁷ worked with GeS and GeS₂ and they found that neither of them are ammonolyzed to any great extent. They also found that these sulfides are reduced by sodium in accordance with the following equations: (a) $\text{GeS} + 2\text{Na} \longrightarrow \text{Na}_2\text{S} + \text{Ge}$, (b) $\text{GeS}_2 + 4\text{Na} \longrightarrow 2\text{Na}_2\text{S} + \text{Ge}$, (c) $x\text{Ge} + 4\text{Na} \longrightarrow \text{Na}_4\text{Ge}_x$.

5. Reduction of Metallic Halides

The products formed when halides are reduced by alkali metals in liquid ammonia are in most cases the free metals in a highly reactive state. In many ways the reduction process is the same as that for oxides, however, one important difference must be noted. Because of the comparatively greater tendency for halides to react at an appreciable rate with alkali amides in liquid ammonia, competitive reactions often become a major factor. This is particularly true whenever a halide of a transitional element is involved, because the free elements are usually excellent catalysts for amide formation. An example of this is illustrated in the reduction of nickel halides. The primary reaction between nickel bromide and potassium in liquid ammonia results in the production of free metal. However, as soon as the metal is formed it catalyzes the formation of potassium amide, which in turn reacts with the bromide to produce nickel amide diammoniate.¹²¹ The reactions are: (a) $\text{NiBr}_2 + 2\text{K} \longrightarrow \text{Ni} + 2\text{KBr}$, (b) $2\text{K} + 2\text{NH}_3 \longrightarrow 2\text{KNH}_2 + \text{H}_2$, (c) $\text{NiBr}_2 + 2\text{KNH}_2 + 2\text{NH}_3 \longrightarrow 2\text{KBr} + \text{Ni}(\text{NH}_2)_2 \cdot 2\text{NH}_3$. The extent of nickel amide diammoniate formation increases as the scale of operation is increased and although this competitive reaction cannot be eliminated entirely, it can be reduced considerably by short over-all time of reaction, rapid addition of the alkali metal, and the use of alkali metal in excess.¹²¹

¹²⁶Holt, R. B., and Watt, Geo. W., *J. Am. Chem. Soc.*, **65**, 988 (1943).

¹²⁷Johnson, W.C., and Wheatley, A.C., *Z. anorg. allgem. Chem.*, **216**, 273 (1934).

When BiOI is treated with a solution of an alkali metal in liquid ammonia, the light red color of the oxyiodide is discharged immediately. The solid phase assumes a grayish black color, and a small amount of fluocculent alkali hydroxide is formed. The blue color of the solution, indicative of an excess of the alkali metal, persists for a short time and then gives way to a pale yellow color caused by the presence of the amide. In some cases a small amount of gas (H_2) may be discharged.¹²³ Watt and Fernelius analyzed reaction products produced in the above manner and found that the following reactions are probably involved: (a) $BiOI + 3M \longrightarrow Bi + MI + M_2O$, (b) $2NH_3 + 2M \longrightarrow 2MNH_2 + H_2$, (c) $M_2O + NH_3 \longrightarrow MOH + MNH_2$, (d) $3M + Bi \longrightarrow M_3Bi(\text{insol})$, (e) $M_3Bi + xBi \longrightarrow M_3Bi \cdot Bi_x(\text{soluble})$. The nature of the reaction products produced in reductions of this type depends upon the nature and the quantity of the alkali metal used. When three equivalents of the metal are used, the reaction medium assumes a pale yellow color which indicates that no insoluble bismuthide is formed. When five equivalents are used, colored solutions result. These colors indicate the presence of bismuthides (reactions d and e) which are sufficiently soluble to impart intense colors to the ammonia. When 6 equivalents are used the solution is strongly colored and considerable alkali metal is present in the insoluble reaction product.¹²³

The reduction of silver salts by sodium in liquid ammonia best illustrates the type of reaction in which the salt is reduced to the free metal. Sodium reacts very readily and smoothly with AgCl or AgI, forming a black precipitate of metallic silver. The results with silver salts have been checked in two ways; by the ratio of the reacting substances and by analysis of the precipitate. The ratio of gram-atoms of sodium to moles of silver halide taking part in the reaction can be determined very accurately, the blue color of the dissolved sodium serving as an excellent end-point. The reaction ratio was determined very accurately by Burgess and Holden^{128,129} and found to be 1.00. Using the same experimental procedure they found that with potassium as the reducing agent, higher values for the reaction ratio were obtained and a slight gas formation was observed. However, when a correction, determined by the amount of gas formed, was applied, the ratio was very nearly 1.00. The elemental silver obtained was found to be unreactive toward air.

Sodium in liquid ammonia reacts very rapidly with MnI_2 to produce a shiny black precipitate.¹³⁰ The reaction is accompanied by a considerable evolution of hydrogen. Contrary to the reaction with AgCl, no quantitative relations between the reacting substances exists, all of the sodium being used up irrespective of the amount of MnI_2 employed. Neither is the reaction complete after the free sodium has disappeared, as indicated by the steady production of gas over a period of several days. Actually two reactions occur; the first takes place immediately and involves the reduction of the MnI_2 to free manganese, and the elemental metal thus formed catalyzes the reaction between sodium and ammonia, liberating hydrogen; in the second or slower reaction, the reduced manganese reacts with the sodium amide formed in the previous steps, and the solvent ammonia.¹³⁰

¹²⁸Burgess, W. M. and Holden, F. R., *J. Am. Chem. Soc.*, 59, 495 (1937).

¹²⁹Burgess, W. M. and Smoker, E. H., *J. Am. Chem. Soc.*, 52, 3573 (1930).

¹³⁰Kraus, C. A., *Chem. Revs.*, 8, 269 (1931).

The simple reduction of MnI_2 requires two gram-atoms of sodium to one mole of MnI_2 . But even with a reaction ratio of thirty, all the sodium will react and the blue color will disappear within a period of 1/2 hr.¹³⁰ The reactions which explain this phenomena are: (a) $2\text{Na} + \text{MnI}_2 \rightarrow 2\text{NaI} + \text{Mn}$, (b) $2\text{Na} + 2\text{NH}_3 \rightarrow 2\text{NaNH}_2 + \text{H}_2$. The reaction between sodium and ammonia is normally very slow, even in the presence of a catalyst, therefore it may be concluded that manganese produced by this reduction is an excellent catalyst for alkali amide production.

Burgess and Eastes¹³¹ reduced nickel bromide by means of potassium in liquid ammonia. They determined the amount of potassium used in the reaction by analysis of the gaseous product formed. Theoretically the reaction ratio should be two; however, experimentally the values ranged between 2.2 and 2.5.

Watts and Davies¹³² found that when NiI_2 was reduced with 2, 4, or 6 equivalents of potassium there was a considerable variation in the volumes of hydrogen evolved. In all cases a considerable quantity of nickel(II) amide diammoniate was formed, and the total nickel content of the gross insoluble product ranged from 55 to 83 percent. When the potassium was added very rapidly, a marked increase in nickel content occurred, and a decrease in the quantity of amide and hydrogen. Watt also reported that there is a progressive decrease in purity of the nickel with increase in the K/NiI_2 ratio, and an accompanying increase in amide formation. The nickel produced was non-pyrophoric. Nickel bromide was used instead of the iodide in an attempt to produce pyrophoric nickel.¹³ It was found that the optimum conditions for its production correspond to a reaction ratio somewhat in excess of 2. The conditions must be such that the potassium in excess is sufficient to generate the H_2 that must be available for adsorption on the nickel. When nickel prepared in this manner was heated to 365° it was rendered almost entirely inactive. Since the nickel from the reduction of the iodide was non-pyrophoric, while that from the bromide was active, Watt concluded that this property was attributed to a selective adsorption of iodide ion which inhibited adsorption of hydrogen. When NiBr_2 was reduced in the presence of a quantity of potassium iodide sufficient to provide an iodide ion concentration equivalent to that prevailing in corresponding reductions of nickel (II) iodide, the product was not pyrophoric.¹³²

Watt and Jenkins¹³³ reacted iron(II) bromide hexammoniate with a potassium solution of liquid ammonia. They used a reaction ratio of $\text{K/FeBr}_2 = 3.35$. The potassium was added all in one portion; it all reacted within ten seconds; H_2 evolution was continuous throughout the total reaction time, and the bromide was converted to a black, finely divided solid. The pale yellow supernatant liquid was removed, and the solid then washed with ammonia. The solid was resuspended in ammonia and treated with an additional 1/2 g. of potassium. Again, hydrogen evolution was continuous, but there was no visible change in the solid phase. The solid was washed until the washings were free of the bromide ion. The resulting black solid was highly pyrophoric, and besides consisting principally of free iron, it contained some Fe_3N .

¹³¹Burgess, W. M. and Eastes, J. W., *J. Am. Chem. Soc.*, **63**, 2674 (1941).

¹³²Watt, Geo. W. and Davies, D.D., *J. Am. Chem. Soc.*, **70**, 3753 (1948).

¹³³Watt, Geo. W. and Jenkins, W.A., *J. Am. Chem. Soc.*, **73**, 3275 (1951).

6. Reduction of Cyanides, Cyanates, and Thiocyanates.

The reduction of cyanide compounds is very similar to that of halides in many respects. However, in the reduction of silver cyanide more sodium is needed than that which would be required for simple reduction. Burgess and Holden¹²⁸ found that the reaction ratio needed was in the range 1:1. This indicated that the silver might catalyze the reaction between sodium and ammonia. When silver cyanide is reduced with potassium, the elemental silver produced is found to be a much more efficient catalyst for the formation of the amide than silver prepared similarly from iodide or chloride. The silver is very finely divided and distinctly more reactive. This was especially marked by the fact that the precipitate from several experiments performed by Burgess and Holden burst into flame when exposed to air. It is possible that the reduced silver owes its pyrophoric property to adsorbed hydrogen. Burgess and Holden¹²⁸ observed that in all cases in which the reduced metal was pyrophoric, the formation of hydrogen also occurred.

Potassium cyanocadmiumate, $K_2Cd(CN)_4$, is reduced by potassium in liquid ammonia. The reaction proceeds slowly and in such a way that each piece of potassium added is replaced by a clump of metallic cadmium which is not reactive with water, but it is highly pyrophoric.¹³⁴

Potassium, when added to a solution of potassium cyanocopperate $K_3Cu(CN)_4$ in liquid ammonia, reacts to give a finely divided, black precipitate of pyrophoric copper. At the instant the solution turns blue, due to reaction of all of the complex cyanide and solution of the excess potassium, a mirror forms on the surface of the reaction tube.¹³⁴

When pieces of potassium are added to a liquid ammonia solution of potassium cyanosilverate, each piece reacts slowly to be replaced by a clump of black pyrophoric silver. Only a trace of hydrogen is given off. Therefore, the silver is a very poor catalyst for the formation of the potassium amide. The silver so produced is not reactive with water.¹³⁴

Sodium reacts rapidly with a liquid ammonia solution of potassium cyanozincate, $K_2Zn(CN)_4$ to give a finely divided precipitate of metallic zinc. This precipitate is not reactive with water nor is it pyrophoric. No hydrogen is given off during its formation and thus the precipitate is not a catalyst for amide formation. A mirror, which is not reactive with water, is formed on the walls of the reaction tube.^{134, 131}

In the reduction of nickel thiocyanate and nickel nitrate the anions are also reduced. The reduction of the thiocyanate with sodium or potassium occurs without the formation of hydrogen and the precipitate is very, very finely divided, however, it is not pyrophoric and is very inefficient as a catalyst. The cause of this decreased activity may be due to the presence of sulfides formed in the reduction of the thiocyanate anion.¹³¹

Burgess and Holden¹²⁸ reduced silver thiocyanate and cyanate with alkali metals in liquid ammonia. The average ratio for the reduction of silver thiocyanate is 1.08. This definitely points to another reaction, the most

¹³⁴ Eastes, J. W. and Burgess, W. M., J. Am. Chem. Soc., 64, 1188 (1942)

probable being the reduction of the thiocyanate anion. Evidently, the reduction is far from complete. The ratio for the reduction of the silver cyanate approaches 1.00, thereby proving that silver cyanate is reduced to silver and alkali cyanate, the cyanate radical not being attacked.

7. Reduction of Nitrates

Burgess and Holden¹²⁸ performed experiments on the reduction of silver nitrate in which they showed that the nitrate radical was readily reduced by both sodium and potassium in liquid ammonia. Silver nitrate diammoniate was readily reduced by sodium and the reaction product was black and pyrophoric, and a good catalyst for the reaction between sodium and ammonia.

Watt and Keenan¹³⁵ performed numerous experiments dealing with the reduction of nickel, iron, and cobalt(II) nitrate hexammoniate. In a typical experiment, the cobalt salt was titrated with a potassium solution of liquid ammonia until a mole ratio $K/Co(NO_3)_2 = 2.02$ existed. Throughout the course of the reaction a bulky blue precipitate formed; there was no liberation of hydrogen, and the supernatant solution was colorless. The insoluble product was found to contain principally cobalt (II) amide. They found that the amide could also be reduced to yield a black solid which contained about 90% elemental cobalt. The products of the reduction of cobalt(II) nitrate with two equivalents of potassium were shown to consist of insoluble cobalt(II) amide and a mixture of soluble nitrite and nitrate ions. When seven equivalents of the alkali metal were used, all of the nitrate was reduced to nitrite, and the ammonia-insoluble product consisted principally of potassium hydroxide and elemental cobalt together with small quantities of impurities.

8. Reductions which Yield Intermetallic Compounds

Many reductions in liquid ammonia which involve the transitional elements fail to yield the free metal as the final product, but instead yield an intermetallic compound. However, many of these compounds have properties which are quite similar to those of the pure elements produced in the same manner.

Mathewson¹³⁶ obtained the compounds $NaCd_2$ and $NaCd_5$ by reduction of cadmium compounds in liquid ammonia with sodium. However, with both cadmium iodide and cadmium cyanide difficulty was experienced in obtaining a satisfactory end-point, chiefly because of the low solubility of these salts. The ratio Na/Cd found for the precipitate varied from 0.2 to 1.0, many of the values lying in the neighborhood of 0.5. In many instances unchanged salt was found with the precipitated metal at the end of the reaction. It is probable that the higher values of the ratio Na/Cd are more correct and it is not improbable that a compound $NaCd$ is formed. The precipitate is very reactive toward air and water.

Sodium reacts very readily with zinc cyanide in liquid ammonia solution, forming a finely divided metallic precipitate, extremely reactive with respect to water and air.¹²⁰

¹³⁵Watt, Geo. W. and Kennan, C. W., *J. Am. Chem. Soc.*, 74, 2048 (1954).

¹³⁶Mathewson, *Z. anorg. Chem.*, 50, 182 (1906).

When a mercurous salt is added to a sodium solution, immediate reaction occurs with the precipitation of finely divided metal. The ratio of sodium to mercury atoms in the precipitate initially formed is very nearly unity. On standing, however, the supernatant liquid, which is originally colorless, gradually turns blue. On again adding a suitable amount of salt, the color is discharged but returns again on standing. Kraus¹²⁰ repeated this process a number of times. Apparently the compound initially precipitated has a composition corresponding to the formula NaHg . This compound, however, is unstable in the presence of ammonia, breaking down to a compound richer in mercury, which is insoluble, and free sodium.

On treating a tin salt, such as SnI_2 with metallic sodium a series of color changes from blue to red takes place. Kraus and Kurtz¹³⁷ found that it was impossible to determine the point at which free sodium disappears; however, on adding pellets of SnI_2 until a change from green to red occurred, a Na/Sn ratio of 3.8, which corresponds approximately with that of Na_4Sn , was obtained. On adding an excess of SnI_2 the red color is at first intensified, after which the precipitation of metallic tin occurs until the solution becomes colorless. A definite color change from blue to red does not occur and it may be inferred that the compound Na_4Sn is not stable in solution but breaks down into free sodium and a compound richer in tin.

On adding lead iodide¹³⁷ to a solution of sodium in liquid ammonia, the blue color gradually disappears and a green color takes its place. It appears probable that on the addition of the salt a reaction occurs with the initial formation of the normal plumbide Na_4Pb . This compound, however, is unstable, decomposing to free sodium and a compound richer in lead. All the sodium in solution, therefore, should not disappear until the relative amount of lead is much greater than corresponding to the ratio $\text{Na/Pb} = 4$.

When thallose iodide¹³⁷ is combined with a sodium-liquid ammonia solution, reaction takes place immediately with the formation of a metallic precipitate. The precipitated material was shown to have the composition Na_3Tl_2 . It was highly reactive toward both air and water.

D. The catalytic Activity and General Characteristics of Alkali Metal-Liquid Ammonia Reduction Products.

Particularly noteworthy are some of the properties of metals produced by the reduction of their salts in liquid ammonia. The products are nearly always very finely divided and are usually pyrophoric. Nickel, for example, exhibits pronounced catalytic activity toward amide formation and in the hydrogenation of certain organic substances. This catalytic activity is attributable to the presence of adsorbed hydrogen that may be removed either by treatment with a liquid ammonia solution of an ammonium salt or by heating to the Curie point (357°C .).¹²⁷

From the concept of the alkali metal solutions presented in this literature review, one would expect the reducing action of potassium to parallel that of sodium. However, this is not entirely true and therefore, in order

¹³⁷Kraus, C.A. and Kurtz, H. F., op. cit., p. 48.

to compare directly the reducing action of potassium and sodium Burgess¹²⁸ reduced several silver salts by each of these metals. The reactions were found to be similar in that the silver salt is reduced to free silver; but with potassium there is always a concurrent reaction with ammonia, catalyzed by the freshly reduced silver. The effectiveness of the reduced silver as a catalyst is greater when potassium is the reducing agent, and also varies with different salts, silver cyanide in particular furnishing an active catalyst.¹²⁸

In view of the presently accepted interpretation of the physical nature of solutions of metals in liquid ammonia, it seems unlikely that differences in the properties of these reduction products are attributed to any inherent differences in the nature of the metal solutions. Rather, it is more likely that both the chemical and catalytic activities of the reduction products are determined by rate factors and solubility relationships. Although the rates of solution of the alkali metals and of the ensuing reactions with NiBr_2 are too rapid for accurate measurements, Watt and Mayfield¹³⁸ were able to show qualitatively that both of these rates increase from lithium to cesium. Furthermore, the solubilities of the by-products (alkali bromides and amides) increase in the same direction. Thus one obtains from the corresponding reactions, elemental nickel that is different in only one important respect, namely surface area. This is shown by the fact that for the products obtained using lithium, sodium, potassium, rubidium, and cesium as the reducing metals, catalytic activity per unit surface area is essentially constant.¹³⁸ Burgess and Eastes¹³¹ have attributed the pyrophoric character of the elemental nickel so-produced to the presence of adsorbed hydrogen; however, in Watt's ¹³⁸ experiments, while all of the products prepared were pyrophoric in a degree that increased from lithium to cesium, the corresponding quantities of adsorbed hydrogen per unit weight of metal showed no consistent trend. Watt used these same nickel reduction products in the hydrogenation of allyl alcohol. His results indicated that the catalytic activity of the material increased in the same order as the pyrophoric nature (see Table 2).

Table 2

Ammonia-insoluble Product Surface Area¹³⁸

Alkali metal	Ni %	Hydrogen ml./g.	Area m. ² /g.	Reaction ^a rate	rate/unit area
Li	82.3	17.6	30	1.6	0.05
Na	93.6	7.5	27	3.1	0.11
K	92.0	18.7	54	3.8	0.07
Rb	90.4	10.4	105	8.8	0.08
Cs	83.9	2.1	127	9.1	0.07

a. The reaction rate is expressed as the rate (in millimoles hydrogen consumed/min/g. of catalyst) of the catalyzed hydrogenation reaction.

¹³⁸Watt, Geo. W. and Mayfield, P. I., J. Am. Chem. Soc., 75, 1760 (1953).

The reduction of salts of transitional metals by means of solutions of alkali metals in liquid ammonia typically results in rapid reduction to the elemental metals. The principle ammonia-insoluble product is usually a black finely divided solid that is pyrophoric and an excellent catalyst for the conversion of alkali metals to the corresponding amides and for the hydrogenation of olefins. Watt,¹³⁹ in order to compare the catalytic activity of nickel, prepared free nickel by two means. One sample he prepared by reducing NiO with hydrogen at 300°, the other was prepared by reduction of NiBr₂ in liquid ammonia. W-6 Raney nickel was also used in the comparison. The nickel content of the product prepared with hydrogen ranged from 96 to 97.5%, while that prepared in ammonia had a wide range of composition (Ni, 47 - 90%; N, 2-3%; and K, 10 - 28%). Surface areas for the ammonia prepared nickel ranged from 5m²/g. for a product containing 67% Ni to 8m²/g. for one containing 84% Ni. Figure 3 shows the relative reducing power of these nickel products. The catalytic activity was evaluated in terms of the rate of hydrogenation of allyl alcohol at 30° and 1500 mm. hydrogen.

Watt and Davies¹³² did similar work on the catalytic activity of NiBr₂ reduced in liquid ammonia, in which the effect of heating to the Curie point (357°C.), and the addition of KI to the reduction mixture was evaluated. Both of these processes produce the same effect, i.e., the expulsion of hydrogen from the reduction product. The effect on the catalytic activity was demonstrated in the reduction of allyl alcohol. The results are illustrated in Figure 4.

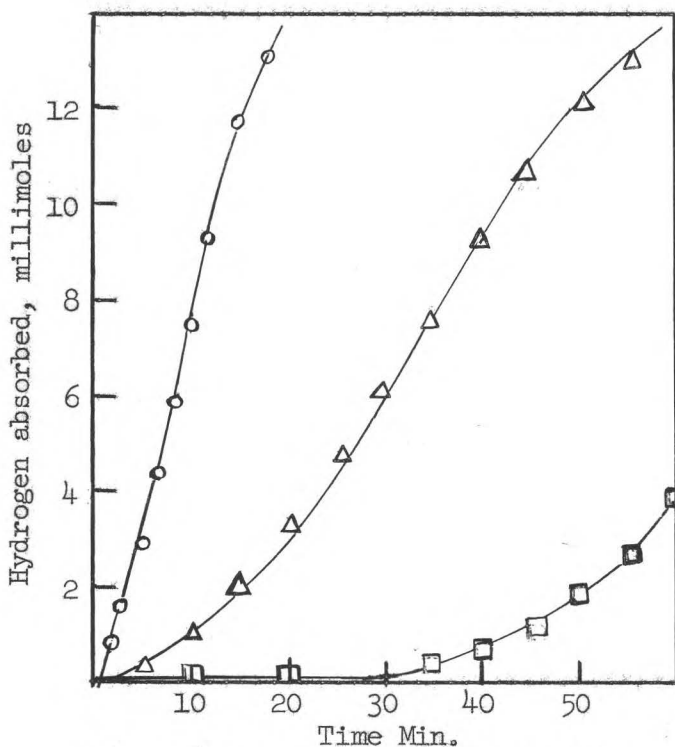


Fig. 3- Comparative activity of Ni catalysts for the hydrogenation of allyl alcohol: □, Ni from NiO; Δ, Ni from NiBr₂, O, W-6 Raney Ni.

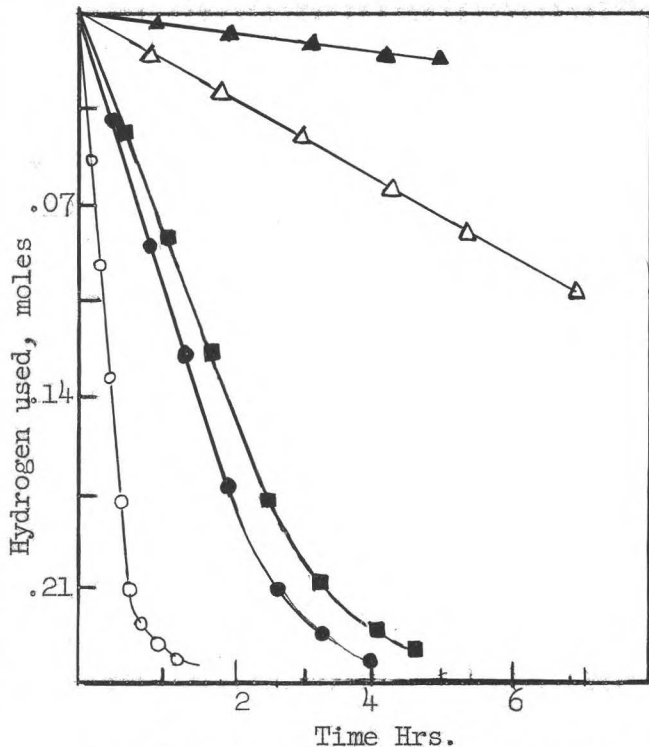


Fig. 4- Hydrogenation of allyl alcohol, O, Raney nickel, ●, Ni from NiBr₂, ■ Ni from NiBr₂ heated to 130°, Δ Ni from NiBr₂ + KI, ▲, Ni from NiBr₂ heated to 365°.

Burgess¹³¹ found that the hydrogen adsorbed by nickel prepared in liquid ammonia was held very tenaciously. Only a small fraction of the adsorbed gas was given off from a sample kept in a closed system under a pressure of 1×10^{-4} mm. at room temperature for a period of two weeks. A sample kept at 320° for a period of 135 hours did not give up all its hydrogen; however, all the adsorbed hydrogen was evolved quickly when the sample was heated above 360° under reduced pressure.

One of the requisites for an effective catalyst is that it must be finely divided. Watt and Keenan¹³⁵ showed that the surface area of cobalt from CoBr_3 was approximately $24 \text{ m.}^2/\text{g.}$ on the basis of electron photomicrographs the average particle diameters for the cobalt were estimated to be 0.01 micron. If spherical particles are assumed, the corresponding calculated area is $8.4 \text{ m.}^2/\text{g.}$ This marked divergence between the measured and estimated values suggests that the samples were quite porous. This same cobalt reduction product was used in the hydrogenation of allyl alcohol. W-6 Raney nickel was also used as a means of comparison. Before one of the hydrogenations, the catalyst was first treated with NH_4Br in liquid ammonia. This treatment causes the liberation of the adsorbed hydrogen. Its effect on the catalytic activity of the material is readily seen in Figure 5.

Watt and coworkers¹⁴⁰ have reduced tetrammineplatinum(II)bromide by means of potassium liquid ammonia. The reaction proceeds relatively slowly without evolution of gases and results in the precipitation of a yellowish-white voluminous solid that does not catalyze appreciable the formation of potassium amide. Although this primary reduction product ultimately decomposes to yield finely divided elemental platinum which is an excellent catalyst for amide formation and for olefin hydrogenation it appears that the initial reduction reaction is best interpreted as involving the formation of tetrammineplatinum (0). The thermal decomposition of the initial reduction product, which occurs at or below 25°C. , produces only gaseous ammonia and elemental platinum. The elemental platinum from the decomposition of the reduction product was used in the catalytic reduction of allyl alcohol. Its activity was compared with that of Adams catalyst (see Fig. 6).

In nearly all of the reactions presented, the reduction products have one characteristic property in common: they are particularly reactive toward air and water. Only in the case of silver salts was the product non-reactive. Reduced copper prepared in this way becomes incandescent on exposure to air. Manganese sparks vigorously and becomes white hot. The product of the reduction of nickel salts behaves similarly. Sodium-zinc reacts with explosive violence with either air or water. The excellent ability of the manganese to catalyze the reaction between sodium and ammonia further illustrates the active condition of these reduced metals. This reactivity is probably due to the finely divided state of the substance. On this basis metals formed by reduction in liquid ammonia, are probably obtained as very minute particles. This method of reduction may therefore be well utilized in the preparation of metal catalysts, where an activated state or very large surface area is essential.¹³⁰

¹⁴⁰Watt, Geo. W., Walling, Jr., T. M., and Mayfield, P. I., J. Am. Chem. Soc., 75, 6175 (1953).

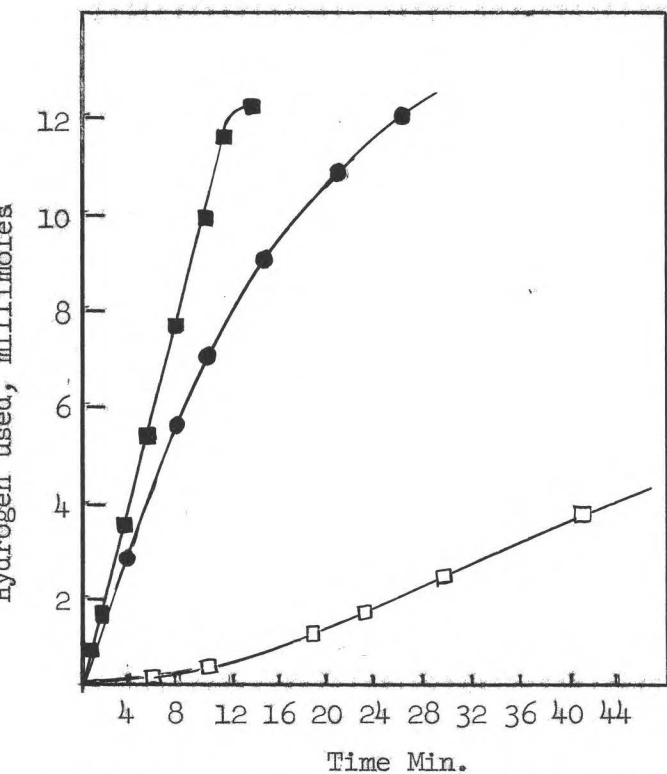


Fig. 5 - Hydrogenation of allyl alcohol over cobalt catalysts, ●, Co; ■ Raney Ni; □, Co treated with NH₄Br

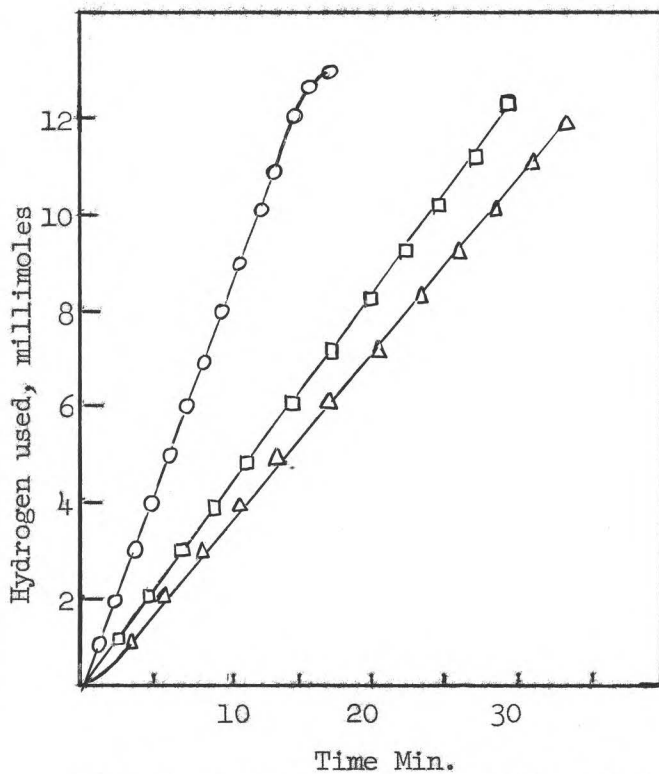


Fig. 6 - Hydrogenation of allyl alcohol, ○, 0.092 g. Adams Catalyst; □, 0.164 g. Pt from Pt(NH₃)₄Br₂; △, 0.0732 g. Pt from Pt(NH₃)₃Br₂.

III. EXPERIMENTAL

A. Liquid Ammonia Apparatus, and The Determination of the Solubility of Rhenium Salts in Liquid Ammonia.

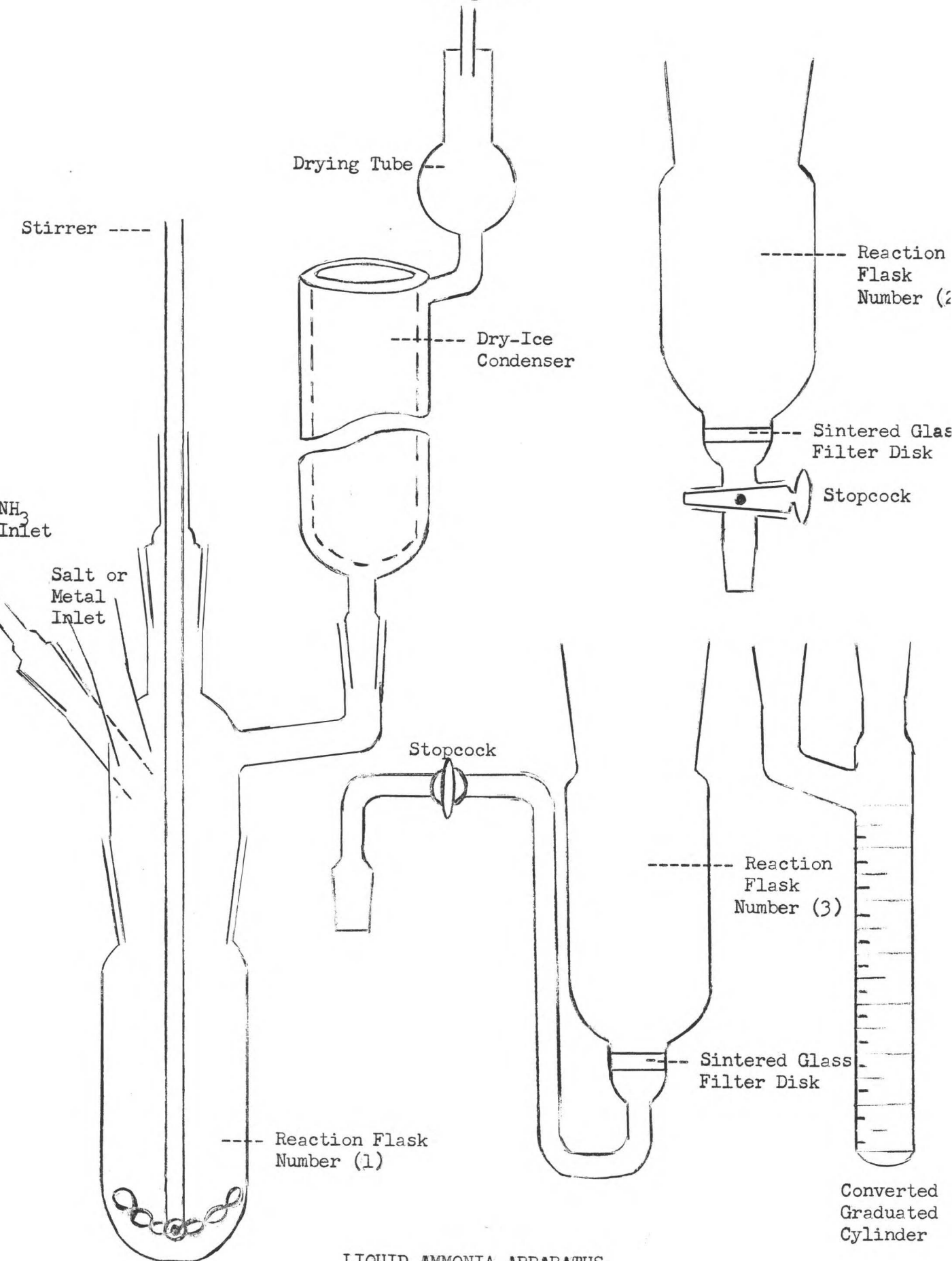
The nature of the alkali metal-liquid ammonia system necessitates the use of apparatus which is somewhat more complicated than that necessary for aqueous solutions. Such factors as prevention of air and water contact, condensation and retention of ammonia, and filtration without removal from the apparatus must be considered. In all aspects of this work an apparatus which was simple as possible was employed. Condensation of ammonia was performed by means of Dry Ice-acetone condensers. Dry Nitrogen atmospheres and soda lime drying tubes were used for protection against the atmosphere and water vapor, and sintered glass disks were built into the apparatus for filtration purposes. The components of the apparatus are shown in figure 7. Several modifications were employed throughout the work, and will be explained where their use is discussed.

If a salt is to be successfully reduced, it must exhibit an appreciable solubility in the medium in which the reduction is to be performed. For this reason it was necessary to determine at least qualitatively the solubility of various rhenium salts in liquid ammonia. The solubility determinations were made in the apparatus illustrated in Figure 7. Reaction flask No. (1) was replaced by flask (2) and the modified graduated cylinder was then connected to the pot by means of the ground glass joint immediately below the stopcock. On the side arm of the graduated cylinder was fixed a second Dry Ice-acetone condenser. Through this condenser, vacuum could be applied in order to facilitate filtration.

The solubility determinations were made in the following manner: Twenty-five to forty ml. of ammonia was condensed into the reaction flask. Fifteen ml. of this ammonia was then drawn into the graduated cylinder which was cooled in a Dry Ice-acetone bath. This step was necessary in order to establish an equilibrium between the ammonia in the condenser and that in the cylinder, so that the ammonia-salt solution could then be accurately measured. After the pure ammonia had been drawn into the graduated cylinder, the rhenium salt was added to the remaining ammonia with stirring until saturation had been reached. The saturated solution was stirred for a short while and then up to ten ml. of it was drawn through the filter into the graduated cylinder. The volume was noted accurately. The graduated cylinder was then removed and the ammonia was allowed to evaporate. The cylinder and salt were next dried at 100° for a short time and then weighed. From the original weight of the cylinder, the weight while containing the salt, and the volume of solution taken, the solubility could easily be calculated. Occasionally low results would occur, principally because it was difficult to keep the ammonia solution from decrepitating during evaporation.

The above procedure worked well with potassium perrhenate, however, when it was used on ammonium perrhenate it was unsuccessful. When ammonium perrhenate is added to liquid ammonia, apparently no saturation occurs. The solution becomes syrupy when a large amount of salt is added and filtration is very difficult, but no salt separates out. As much as 10 grams of salt was added to five or six ml. of ammonia with no apparent saturation occurring. The highest value for the solubility of NH_4ReO_4 in liquid ammonia obtained by

Figure 7



LIQUID AMMONIA APPARATUS

the above method was 83.0 g./100 ml. solution, however as indicated, it is doubtful whether or not saturation was attained, and the salt may be completely miscible.

Due to the very hygroscopic nature of rhenium heptoxide no attempt was made to determine its solubility other than to visually observe that several grams of the material easily dissolves in about 25 ml. of ammonia.

The solubility of NH_4ReO_4 in ethylamine, although not determined quantitatively is apparently very high. It was observed that a sample of the salt, when held in the vapor above ethylamine absorbed, the amine until it actually liquified forming a globule of solution. When the solution was allowed to evaporate, a solid was obtained which did not appear to be the same as the original salt, and gave up ethylamine slowly upon standing.

Table 3

Solubility of Rhenium Salts in Liquid Ammonia

<u>Salt</u>	<u>Solubility in g./100 ml. sol.</u>
KReO_4	7.4
NH_4ReO_4	83.0 ^a
Re_2O_7	very soluble

a. It is very unlikely that saturation was attained and the solubility may be much higher.

B. Catalysts, General

1. Catalyst Code

Because of the large number of catalyst preparations it was necessary to designate each by a code number. This code consists of four divisions separated by hyphens. The first part names the particular rhenium salt used in the preparation, such as NH_4ReO_4 or KReO_4 . The second designates the type of system in which the reduction was performed. It names both the amine, or ammonia, and the particular alkali metal used. As an example, Na, NH_3 would indicate that the reducing medium was sodium in ammonia. The third part of the code consists of a digit which indicates a particular preparation method. For example, several different preparation methods were used, all in which the reducing medium was sodium-ammonia. The digit is used to differentiate between them. The final part of the code also consists of a single digit. This digit merely indicates the number of times the particular preparation has been performed. An example of a complete catalyst code would be $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-2-4-}$. This code would indicate the following: The catalyst was prepared by the reduction of NH_4ReO_4 by sodium, in liquid ammonia. It was the second preparation modification for the Na- NH_3 system, and the fourth run of the particular method.

2. Catalyst Preparation

Although many catalysts were prepared, the method of preparation was essentially the same. One variation which resulted in a distinct difference in catalytic activity will be discussed here. The other variations which are minor will be discussed under the individual preparations.

The apparatus illustrated in Figure 7 was used for the catalyst preparation. Reaction flask (1) was replaced by flask (3) which contains a sintered glass filtering disk. Fifty to seventy-five ml. ammonia was liquified by passing in gaseous ammonia through the inlet indicated and allowing it to condense on the Dry Ice condenser. The rhenium salt was then added to the ammonia with stirring. During this addition the nitrogen flow, which came in through the condenser, was increased. After the salt had completely dissolved the alkali metal was added as quickly as possible. In some cases the order of addition was reversed. Assuming reduction of the perrhenate ion to free rhenium, a reaction requires a ratio of seven moles of alkali metal for each mole of perrhenate. Reaction ratios of from two to eight were employed. After addition of the alkali metal, the stirring was continued, and the solution which originally was colorless assumed a black-blue appearance. The color was due both to the precipitated rhenium material and the characteristic blue color of alkali metals in liquid ammonia. The solution was stirred from 15 minutes to 2 hours. During this period the blue color of the solution usually dissipated, indicating that any excess metal had been converted to the amide. After this reduction period, the stopcock was opened and vacuum was applied. The ammonia was drawn off into a trap, it was usually colorless. Twenty-five to fifty ml. more ammonia was liquified and this was also drawn through the filter in an attempt to wash the catalyst material. In all cases the filtration was very difficult, and in some cases it could not be completed. Skelly Solve B or ethanol was then added and the catalyst was removed and stored under it. In several preparations in which the catalyst was removed under ethanol the solvent was removed by centrifuging and the catalyst was then washed with water by centrifuging and decantation until the washings were no longer basic to litmus.

The second method of preparation was identical with the first with the exception that flask (1) was used and no attempt was made at filtering off the ammonia or washing the catalyst with it. After the reduction mixture had been stirred for one to two hours, the stoppers were removed and the ammonia was allowed to partially boil away. Before the ammonia was completely gone, so that no air contact could occur, about 50 ml. of 95% ethanol was added. The resulting mixture was stirred for some time and then the catalyst was separated from the ethanol by centrifuging, and placed in a large Soxhlet type extractor. Glass thimbles were used. The catalyst was extracted with dilute HCl for twenty-four or more hours, and then with 95% ethanol or water for an additional twenty-four hours. During the acid extraction, the solution which collected in the pot assumed a brown color. This solution would decolorize permanganate indicating that lower oxidation states of rhenium were present. It was found that when this solution was made basic with NH_4OH , a black rhenium precipitate immediately formed and the solution became colorless. The colorless solution would no longer discolorize permanganate. The precipitate, which sometimes accounted for nearly $1/3$ the total volume, was added to the catalyst remaining in the thimble and further extracted with dilute HCl. The second extraction did not appear to dissolve any further material. The catalyst after a final extraction with ethanol or water was placed in a bottle and stored under the same solvent.

The preparation of amine catalysts was performed in the same manner as the above preparation. The only exception being that there was no need for liquification of the amine. The Dry Ice-acetone condensers, however, were still employed to prevent its loss during the course of the reaction.

Most of the catalysts obtained were black in color and very finely divided. When they were stored under ethanol, the suspension formed by shaking would settle out fairly readily. Usually the solution would be clear within an hour. On the other hand, when the catalyst was stored under water, the suspension was difficult to even centrifuge down, and on just standing the solution would stay black for 24 hours or longer. Aliquots of the material were removed by shaking the bottle to resuspend the material and then withdrawn with a dropper.

3. Analysis

Two methods of analysis were extensively used. In each, aliquot amounts of the catalyst, which were usually under ethanol, were placed in tared, screw-capped vials. The vials were next placed in large polyethylene tubes and centrifuged at slow speed. The ethanol was decanted off and the vials were then placed in a vacuum drying oven or an Abderhalden drying pistol. Phosphorous pentoxide was used as a dessicant. The pistol or oven was evacuated and the pumping was continued until the solvent had been completely removed. The oven was then heated to about 75°, and the pistols were heated with various boiling solvents, but usually water. After a drying period of at least 12 hours, the vacuum was replaced with a nitrogen atmosphere and the bottles were immediately capped and weighed. In a few cases a higher drying temperature was employed.

Two different methods were used for the oxidation of the catalyst. In the first, the bottle containing the catalyst was placed in a 125 ml. beaker and then a mixture of 30% hydrogen peroxide and ammonium hydroxide was added. The solution was boiled gently on a hot plate, and the catalyst usually dissolved readily. In the second method the catalyst was left in the vial and about five drops water and two drops conc. nitric acid were added. The cap was screwed on tightly and the solution was heated to the boiling point on a hot plate. If the solution turned clear the oxidation was considered complete. If not, another drop of nitric acid was added and the process repeated.

In the first method of analysis¹⁴¹ the solution obtained by either of the oxidation methods was placed in a 100 ml. beaker and made 0.5 molar in NaCl. The solution was heated to boiling and then 1% tetraphenylarsonium chloride (8 ml./25 mg. sample) was added. The resulting precipitate was allowed to set overnight and was then collected in a tared filter crucible. The precipitate was dried at 110° before weighing. The $\text{Re}/\phi_4\text{AsReO}_4$ factor is 0.02941.

¹⁴¹Hillebrand, Lundell, Bright, and Hoffman, "Applied Inorganic Analysis", 2nd ed., John Wiley and Sons, New York, 1953, p. 321.

The second method of analysis was a colorimetric method¹⁴² and depended upon the strong absorption of the hexachlororhenate ion at 28.1 μ . Only the nitric acid oxidation procedure was followed when this method was used. The solution resulting from the oxidation was diluted to 250 ml. in a volumetric flask, and aliquots of from two to five ml. were used in each analysis. In most cases two identical aliquots were taken from each flask. The aliquots were placed in 50 ml. volumetric flasks and then 25 ml. conc. HCl was added. Nitrogen was flushed through the flask while one or two ml. of 0.1 N chromous chloride was added. The flasks were corked immediately and allowed to set five to ten minutes with intermittent shaking. Oxygen was then bubbled through the solutions for about five minutes to oxidize any excess chromous chloride. The solutions which were green in color were then diluted up to the mark with distilled water and allowed to set several hours before readings were taken. The amount of rhenium was calculated from either a working graph or from the molar absorptancy index which is 12,750. A Beckman DU quartz prism spectrophotometer and quartz cells were used in making the readings.

C. Catalysts: Preparations and Analyses

Qualitative tests performed on the supernatant reaction solutions with tetraphenylarsonium chloride indicated that in most cases the reduction of the perrhenate ion was complete. However, on the basis of the aliquot weights obtained in the analyses of the catalysts, it is estimated that recovery of the rhenium used in the reduction was only 75 to 85 percent. Therefore, some rhenium was lost either by the presence of soluble lower valent forms or during the extraction process.

The analyses were performed according to one of the two methods previously discussed. In each of the analyses below it is stated whether the analysis was gravimetric (tetraphenylarsonium chloride method), or spectrophotometric (hexachlororhenate ion method). The method of oxidizing the sample is also given.

1. Sodium-Ammonia Catalysts

(a) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-1-1-}$

Quantities: Na, 0.86 g. (0.0374 atom), in 75 ml. ammonia

NH_4ReO_4 , 0.72 g. (0.0027 mole)

The apparatus with filtering disk was used. After addition of the sodium and salt to the liquid ammonia, the solution was stirred for 15 minutes before filtration was attempted. The catalyst was washed with 15 ml. ammonia and 25 ml. Skelly Solve B and stored under the latter. The washings were tested with tetraphenylarsonium chloride but gave only a weak perrhenate test, indicating that reduction was essentially complete.

¹⁴²Meloche and Martin, Anal. Chem., 28, 1671 (1956)

(b) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-2-1-}$

Quantities: Na, 0.86 g. (0.037 atom) in 50 ml. ammonia
 NH_4ReO_4 , 0.72 g. (0.0027 mole)

The apparatus with filtering disk was employed. The reduction mixture was stirred for 15 minutes and then suction was applied. The catalyst material plugged the filter and the filtration was impossible. Twenty ml. of Skelly Solve was added while some ammonia remained. The resulting mixture was treated with ethanol to decompose any excess metal which remained.

(c) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-3-1-}$

Quantities: Na, 0.9 g. (0.039 atom) in 75 ml. ammonia
 NH_4ReO_4 , 0.72 g. (0.0027 mole)
 Super-cel, 0.75 g.

The apparatus with filtering disk was used. The sodium was added first, and then the salt which had been mixed with Super-cel to aid filtration was added. After addition of the salt, the solution was stirred for about 15 minutes and then suction was applied. The material was washed with 15 ml. ammonia and 50 ml. Skelly Solve. The catalyst was stored under Skelly Solve B.

(d) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-3-2-}$

Quantities: Na, 0.93 g. (0.040 atom) in 50 ml. ammonia
 NH_4ReO_4 , 0.77g. (0.0029 mole)
 Super-cel, 1.0 g.

The procedure was the same as (c) except that when filtration was attempted the filter immediately plugged. The ammonia was allowed to boil away and then ethanol was added. The catalyst was washed with and stored under ethanol.

(e) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-4-1-}$

Quantities: Na, 0.93 g. (0.040 atom) in 50 ml. ammonia
 NH_4ReO_4 , 0.77 g. (0.0029 mole)

The apparatus with filtering disk was used. The reduction mixture was stirred for about 10 minutes and then filtration was begun. The filter plugged immediately, and the ammonia was then allowed to boil away. The catalyst was removed as a suspension in ethanol. The catalyst was washed with ethanol until the washings were no longer basic to litmus and then stored under the same solvent.

(f) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-4-2-}$

Quantities: Na, 0.93 g. (0.040 atom) in 50 ml. ammonia

NH_4ReO_4 , 0.78 g. (0.0029 mole)

The preparation was identical with (e) with the exception that the filtering disk was covered with a filter paper mat. Filtration, however, was still impossible and ethanol had to be added as before. The catalyst was extracted in a Soxhlet extractor with ethanol until the washings were not basic, and then stored under the same solvent.

(g) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-4-3-}$

Quantities: Na, 0.93 g. (0.040 atom) in 50 ml. ammonia

NH_4ReO_4 , 0.77 g. (0.0029 mole)

The plain reaction flask was used. The salt was added to the ammonia first. Following the addition of the sodium, the reaction mixture was stirred for 10 to 15 minutes and then the ammonia was allowed to boil away. Ethanol was added to decompose any sodium. The catalyst was washed by centrifuging until the washings were no longer basic and then stored under ethanol.

(h) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-5-1-}$

Quantities: Na, 0.93 g. (0.040 atom) in 50 ml. ammonia

NH_4ReO_4 , 0.77 g. (0.0029 mole)

The plain reaction flask was used. The reduction mixture was stirred for 10 to 15 minutes, the ammonia was allowed to boil away, and then ethanol was added. The catalyst was extracted using water in the Soxhlet extractor, and then stored under the same solvent.

(i) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-5-2-}$

Quantities: Na, 0.93 g. (0.040 atom) in 50 ml. ammonia

NH_4ReO_4 , 0.77 g. (0.0029 mole)

The procedure was identical with (h).

(j) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-5-3-}$

Quantities: Na, 1.55 g. (0.067 atom) in 50 ml. ammonia

NH_4ReO_4 , 1.3 g. (0.0049 mole)

The procedure was identical with (h) with the exception that a small amount of sulfuric acid was added to the water used in the extraction process.

Anal. Found: Re, 80.4, 75.4 ($\phi_4\text{AsCl}$, H_2O_2 oxidation)

(k) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-6-2-}$

Quantities: Na, 1.86 g. (0.081 atom) in 50 ml. ammonia

NH_4ReO_4 , 0.77 g. (0.0029 mole)

The procedure was identical with (h).

(l) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-7-1-}$

Quantities: Na, 0.93 g. (0.040 atom) in 50 ml. ammonia

NH_4ReO_4 , 0.78 g. (0.0029 mole)

After addition of the sodium and salt to the ammonia, the solution was stirred for 15 minutes. The ammonia was allowed to boil away and ethanol was added. The catalyst was washed free of sodium ions by centrifuging and decantation, and then stored under ethanol.

(m) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-8-1-}$

Quantities: Na, 0.51 g. (0.022 atom) in 40 ml. ammonia

NH_4ReO_4 , 0.78 g. (0.0029 mole)

The sodium was added to the ammonia first. After the salt was added the solution was stirred for 15 minutes and then the ammonia was allowed to boil away. The catalyst was removed under ethanol. It was washed with water by centrifugation and decantation, and then stored under water.

(n) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-1-}$

Quantities: Na, 1.55 g. (0.067 atom) in 50 ml. ammonia

NH_4ReO_4 , 1.3 g. (0.0049 mole)

The usual apparatus with plain flask was used. The sodium was added to the ammonia first, and after addition of the salt the solution was stirred for 15 minutes, and then the ammonia was allowed to boil away. The catalyst was extracted in the Soxhlet extractor with dilute HCl and then stored under water.

(o) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-2-}$

Quantities: Na, 1.04 g. (0.045 atom) in 50 ml. ammonia

NH_4ReO_4 , 0.87 g. (0.0032 mole)

The procedure was identical with (n).

(p) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-3-}$

Quantities: Na, 6.0 g. (0.261 atom) in 70 ml. ammonia

NH_4ReO_4 , 2.0 g. (0.0075 mole)

The salt was added to the ammonia first and after addition of the sodium, the solution was stirred for about an hour. The ammonia was allowed to partially boil away and then ethanol was added. The catalyst was extracted in the Soxhlet extractor with water, dilute HCl, and then ethanol. The catalyst was stored under ethanol.

Anal. Found: Re, 76.7, 77.4, 75.4 (spectrophotometric, HNO_3 oxidation)

(q) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-4-}$

Quantities: Na, 6.0 g. (0.261 atom) in 75 ml. ammonia

NH_4ReO_4 , 2.0 g. (0.0075 mole)

The procedure was identical with (p) with the exception that when the catalyst was extracted with HCl the solution in the flask became dark brown. The brown material could not be centrifuged out, but when the solution was made basic with NH_4OH a black solid immediately precipitated out and the solution became clear. The precipitated material, which accounted for nearly $1/3$ of the total volume, was extracted with HCl again. The second extraction did not seem to dissolve it. The two portions of catalyst were combined, then extracted with and stored under ethanol.

(r) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-5-}$

Quantities: Na, 4.95 g. (0.215 atom) in 75 ml. ammonia

NH_4ReO_4 , 1.44 g. (0.0054 mole)

The procedure was identical with (p) with the exception that the extraction with water was not performed.

(s) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-6-}$

Quantities: Na, 7.4 g. (0.322 atom) in 75 ml. ammonia

NH_4ReO_4 , 2.16 g. (0.0081 mole)

The sodium was added to the ammonia first. Aside from this, the preparation was identical with (r).

(t) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-7-}$

Quantities: Na, 4.95 g. (0.215 atom) in 75 ml. ammonia

NH_4ReO_4 , 1.5 g. (0.0056 mole)

The preparation was identical with (q).

Anal. Found: Re; 79.4, 80.4, 80.4, 80.0, 79.0, ($\phi_4\text{AsC}$; HNO_3 oxidation)

(u) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-8-}$

Quantities: Na, 7.4 g. (0.322 atom) in 75 ml. ammonia
 NH_4ReO_4 , 2.25 g. (0.0084 mole)

The preparation was identical with (r).

Anal. Found: Re, 77.9, 75.6 ($\phi_4\text{AsCl}$, HNO_3 oxidation)

(v) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-9-}$

Quantities: Na, 5 g. (0.218 atom) in 60 ml. ammonia
 NH_4ReO_4 , 1.5 g. (0.0056 mole)

The preparation was identical with (q). The solution obtained after centrifuging down the catalyst was tested for perrhenate. The test was negative.

(w) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-10-}$

Quantities: Na, 5.07 g. (0.220 atom) in 60 ml. ammonia
 NH_4ReO_4 , 1.44 g. (0.0054 mole)

The procedure and results were identical with (v).

(x) $\text{KReO}_4\text{-Na, NH}_3\text{-1-1-}$

Quantities: Na, 0.89 g. (0.0380 atom) in 75 ml. ammonia
 K ReO_4 , 0.78 g. (0.0027 mole)

The apparatus with filter disk was employed. After addition of the sodium and salt the resulting mixture was stirred for about 5 minutes and then suction was applied. The catalyst material was washed with two 25 ml. portions of ammonia and 50 ml. Skelly Solve. The catalyst, which was brown in color, was stored under Skelly Solve.

(y) $\text{KReO}_4\text{-Na, NH}_3\text{-2-1-}$

Quantities: Na, 0.87 g. (0.0380 atom) in 75 ml. ammonia
 KReO_4 , 0.78 g. (0.0027 mole)

The preparation was identical with (x) with the exception that the order of addition was reversed, the sodium being added first.

Anal. Found: Re, 31.5, 31.4 ($\phi_4\text{AsCl}$, H_2O_2 oxidation). The low percent rhenium indicates that considerable sodium₂amide was probably present. The light brown color of the material also seemed to indicate this.

(z) $\text{KReO}_4\text{-Na, NH}_3\text{-2-2-}$

Quantities: Na, 0.9 g. (0.0390 atom) in 80 ml. ammonia

KReO_4 , 0.78 g. (0.0027 mole)

The procedure was identical with (y) with the exception that the catalyst plugged the filter and the filtration could not be completed. Skelly Solve was added after the ammonia had been allowed to boil away. The catalyst was stored under Skelly Solve.

(aa) $\text{Re}_2\text{O}_7\text{-Na, NH}_3\text{-1-1-}$

Quantities: Na, 1.86 g. (0.081 atom) in 40 ml. ammonia

Re_2O_7 , 1.56 g. (0.0032 mole)

The reaction mixture was stirred for 15 minutes and then the ammonia was allowed to partially boil away. Ethanol was added while about half the ammonia remained. The catalyst was washed with and stored under water.

(bb) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3, \text{EtOH-1-1-}$

Quantities: Na, 2.08 g. (0.0905 atom) in 50 ml. NH_3 and 25 ml. EtOH

NH_4ReO_4 , 0.87 g. (0.0032 mole)

About 25 ml. absolute ethanol was placed in the reaction flask and then the ammonia was condensed into it. The sodium was added to the solution first. After addition of the salt, the solution was stirred 10 minutes. Another equal amount of sodium was added and the solution stirred an additional 20 minutes. The catalyst was washed with 0.05 N HCl by centrifuging and then stored under water. Of note is the fact that when the dilute HCl was added to the catalyst, a rapid evolution of an odorless gas occurred.

(cc) $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3, \text{EtOH-1-2-}$

Quantities: Na, 3.12 g. (0.136 atom) in 25 ml. NH_3 and 25 ml. EtOH

NH_4ReO_4 , 0.87 g. (0.0032 mole)

The preparation was the same as (bb). The catalyst was extracted with EtOH in a Soxhlet extractor.

2. Lithium-Ammonia Catalysts

(a) $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-1-}$

Quantities: Li, 0.63 g. (0.090 atoms) in 50 ml. ammonia

NH_4ReO_4 , 0.87 (0.0032 moles)

The plain apparatus, Fig. 7(1), was used. The reduction mixture was stirred for about 45 minutes and then ethanol was added without allowing the ammonia to first boil away. The catalyst was extracted in a Soxhlet extractor with dilute HCl and then stored under water.

(b) $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-2-}$

Quantities: Li, 0.7 g. (0.10 atom) in 50 ml. ammonia
 NH_4ReO_4 , 1.0 g. (0.0037 mole)

The preparation was the same as (a) except that the order of addition was reversed, the salt being added first. The catalyst was extracted with both dilute HCl and ethanol, and then stored under ethanol.

(c) $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-3-}$

Quantities: Li, 0.7 g. (0.10 atom) in 50 ml. ammonia
 NH_4ReO_4 , 0.9 g. (0.0034 mole)

The preparation was the same as (b). The catalyst was extracted with both acidified ethanol and dilute HCl.

(d) $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-4-}$

Quantities: Li, 2.25 g. (0.321 atom) in 75 ml. ammonia
 NH_4ReO_4 , 2.16 g. (0.0081 mole)

The reduction mixture was stirred for about an hour and then the ammonia was allowed to partially boil away. The catalyst was extracted with water and then dilute HCl. During the acid extraction a considerable amount of the material dissolved, and the extracting solution in the flask became a dark-brown color. This solution, when made basic with NH_4OH , became clear and a dark colored precipitate dropped out. The precipitated material was added back to the extraction thimble and further extracted. The material was finally extracted with and stored under ethanol.

(e) $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-5-}$

Quantities: Li, 1.50 g. (0.214 atom) in 50 ml. ammonia
 NH_4ReO_4 , 1.44 g. (0.0054 mole)

The prime objective of this preparation was to obtain a material balance. The preparation was carried out as usual, the salt being added first. The reduction solution was stirred about an hour and then the ammonia was allowed to completely boil away. The material obtained was grey in color and after drying under vacuum weighed 8.8 grams. This high weight indicates that a considerable amount of the amide was present. The material was placed in the Soxhlet extractor and extracted with ethanol. Most of the material dissolved during the extraction.

Anal. Found: Li, 0.00, 0.00, 0.00 (flame photometry); N, 0.00, 0.00, 0.00 (Kjeldahl method)

The analysis clearly indicates that no nitrogen or lithium were present in the extracted product.

(f) $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-6-}$

Quantities: Li, 1.5 g. (0.214 atom) in 60 ml. ammonia

NH_4ReO_4 , 1.5 g. (0.0056 mole)

The preparation was the same as (b).

Anal. Found: Re, 77.9, 79.3, 79.6, 80.4, 81.1, 86.1, 80.4, 83.4, 84.3 (spectrophotometric, NHO oxidation); 83.8, 80.0, 81.5, 74.9, 81.2 ($\phi_4\text{AsCl}$, HNO_3 oxidation), 89.4, 88.5, ($\phi_4\text{AsCl}$, HNO_3 oxidation); Li, 0.0, 0.0, 0.0 (flame photometry), N, 0.0, 0.4, ≤ 1.0 (Kjeldahl method)

In the final rhenium determinations, above, in which the results were somewhat higher the samples were dried at 250° for several days. In the Kjeldahl determination of nitrogen the endpoint was very vague and it was impossible to titrate accurately. It is very possible that the small percent nitrogen found in the last two samples is due to titration error rather than to the actual presence of any nitrogen.

(g) $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-7-}$

Quantities: Li, 1.5 g. (0.0214 atom) in 50 ml. ammonia

NH_4ReO_4 , 1.0 g. (0.0037 mole)

The preparation was identical with (f).

(h) $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-8-}$

Quantities: Li, 1.5 (0.0214 atom) in 75 ml. ammonia

The preparation was identical with (d).

(i) $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-9-}$

Quantities: Li, 1.58 g. (0.226 atom) in 50 ml. ammonia

NH_4ReO_4 , 1.44 g. (0.0054 mole)

The preparation was identical with (d). The supernatant liquid obtained when the catalyst was centrifuged down was tested for perrhenate and the results were negative.

3. Lithium-Ethylamine Catalysts

(a) $\text{NH}_4\text{ReO}_4\text{-Li, EtNH}_2\text{-1-1-}$

Quantities: Li, 1 g. (0.142 atom) in 30 ml. ethylamine

NH_4ReO_4 , 0.87 g. (0.0032 mole)

The salt was added to the ethylamine first. After addition of the lithium the resulting solution was stirred for 1-1/2 hours and then ethanol was added. The product was extracted with acidified ethanol and dilute HCl. The catalyst was stored under water.

(b) $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-2-}$

Quantities: Li, 0.7 g. (0.10 atom) in 30 ml. ethylamine

NH_4ReO_4 , 0.9 g. (0.0034 mole)

The preparation was the same as (a).

(c) $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-3-}$

Quantities: Li, 1 g. (0.143 atom) in 40 ml. ethylamine

NH_4ReO_4 , 1 g. (0.0037 mole)

The procedure was the same as (a) with the exception that acidified ethanol was not used in the extraction process. The catalyst was extracted first with dilute HCl and then ethanol.

(d) $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-4-}$

Quantities: Li, 0.9 g. (0.129 atom) in 40 ml. ethylamine

NH_4ReO_4 , 0.7 g. (0.0026 mole)

The preparation was the same as (a).

(e) $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-5-}$

Quantities: Li, 2.34 g. (0.335 atom) in 50 ml. ethylamine

NH_4ReO_4 , 1.82 g. (0.0068 mole)

The procedure was identical with (a) with the exception that acidified cellosolve was used for the first extraction. The second extraction was with dilute HCl and the final with ethanol. The catalyst was stored under ethanol.

(f) $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-6-}$

Quantities: Li, 2.8 g. (0.40 atom) in 40 ml. ethylamine

NH_4ReO_4 , 2.0 g. (0.0075 mole)

The preparation was identical with (c)

(g) $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-7-}$

Quantities: Li, 1.5 g. (0.214 atom) in 40 ml. ethylamine

NH_4ReO_4 , 1.5 g. (0.0056 mole)

The preparation was identical with (c).

Anal. Found: Re, 78.9, 78.8, 80.3, 78.2, 78.4, 77.7, 79.7, 81.2, 79.8, 80.0, 79.5, 82.4 (spectrophotometric, HNO_3 oxidation), 83.0, 82.9 (AsCl_3 , HNO_3 oxidation); Li, 0.0, 0.0, 0.0 (flame photometry); N, 1, < 1, < 1 (Kjeldahl method)

(h) $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-8-}$

Quantities: Li, 0.9 g. (0.128 atom) in 40 ml. ethylamine
 NH_4ReO_4 , 0.9 g. (0.0034 mole)

The original purpose of the preparation was to prepare a catalyst using potassium. Therefore, to the ethylamine a very small piece of potassium was added with stirring. When it failed to dissolve after a half hour, the salt and lithium were added. The potassium was not removed. The preparation was completed in the usual manner. It was stored under ethanol.

Anal. Found: Re, 78.0, 76.0, 78.2 (spectrophotometric, HNO_3 oxidation)

(i) $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-9-}$

Quantities: Li, 1.5 g. (0.214 atom) in 35 ml. ethylamine
 NH_4ReO_4 , 1.5 g. (0.0056 mole)

The procedure was the same as (c). However, during the HCl extraction the solution in the flask turned dark brown. The rhenium material was precipitated by addition of NH_4OH , and added back to the extraction thimble. The catalyst was then extracted with and stored under ethanol.

(j) $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$

Quantities: Li, 2.25 g. (0.321 atom) in 50 ml. ethylamine
 NH_4ReO_4 , 2.25 g. (0.0084 mole)

The procedure was identical with (i).

Anal. Found: 77.8, 77.0 ($\phi_4\text{AsCl}$, HNO_3 oxidation)

(k) $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-11-}$

Quantities: Li, 0.88 g. (0.0125 atom) in 30 ml. ethylamine
 NH_4ReO_4 , 1.2 g. (0.0045 mole)

The procedure was identical with (i). The decantate obtained when the catalyst was centrifuged down was tested for perrhenate and the results were negative.

4. Miscellaneous Catalysts

(a) $\text{NH}_4\text{ReO}_4\text{-K,NH}_3\text{-1-1-}$

Quantities: K, 2.94 g. (0.0752 atom) in 50 ml. ammonia
 NH_4ReO_4 , 1.44 g. (0.0054 mole)

The plain apparatus, Fig 7(1), was used. The potassium was added to the ammonia first, and after addition of the salt the resulting solution was stirred about 15 minutes. The ammonia was then allowed to boil away and ethanol was added. The reduction product gave a strong perrhenate test, was light grey in color, and was soluble in water. It was concluded that the potassium was rapidly converted into the amide and very little actual reduction took place. No catalyst was obtained.

(b) $\text{NH}_4\text{ReO}_4\text{-K, NH}_3\text{-1-2-}$

Quantities: K, 1.1 g. (0.0281 atom) in 60 ml. ammonia
 NH_4ReO_4 , 1.0 g. (0.0034 mole)

The preparation was the same as (a) with the exception that the order of addition was reversed. The material obtained was extracted with Skelly Solve B, but all dissolved, and no catalyst was obtained.

(c) $\text{KReO}_4\text{-K, NH}_3\text{-1-1-}$

Quantities: K, 1.76 g. (0.0451 atom) in 50 ml. ammonia
 KReO_4 , 0.93 g. (0.0035 mole)

The salt was added first. It was immediately followed by the potassium and the resulting solution was stirred about an hour. The catalyst was removed under and extracted with ethanol.

(d) $\text{Re}_2\text{O}_7\text{-K, NH}_3\text{-1-1-}$

Quantities: K, 3.6 g. (0.0922 atom) in 50 ml. ammonia
 Re_2O_7 , 0.83 g. (0.00172 mole)

The potassium was added first to the ammonia, followed by the oxide. The mixture was stirred about 1/2 hour and ethanol was added. The catalyst was extracted in the Soxhlet extractor with dilute HCl and then stored under water.

(e) $\text{NH}_4\text{ReO}_4\text{-Ca, NH}_3\text{-1-1-}$

Quantities: Ca, 1.0 g. (0.0250 atom) in 50 ml. ammonia
 NH_4ReO_4 , 1.0 g. (0.0037 mole)

The salt was added to the ammonia first. After addition of the calcium the solution was stirred for about 2 hours and then ethanol was added. The product obtained was brown in color and the supernatant liquid gave a strong perrhenate test, indicating incomplete reduction. The material was extracted with dilute HCl for 36 hours. The material after extraction was black in color. It was estimated that about 15 per cent conversion was obtained.

(f) $\text{NH}_4\text{ReO}_4\text{-Na,EtNH}_2\text{-1-1-}$

Quantities: Na, 5.0 g. (0.218 atom) in 30 ml. ethylamine

NH_4ReO_4 , 1.0 g. (0.0037 mole)

The salt was added to the ethylamine first. The sodium was then added and the solution stirred for about 15 minutes. The sodium did not dissolve and the solution remained colorless. Thirty to forty ml. of ammonia was then condensed into the system. The solution still remained colorless, but material began to precipitate out indicating that reduction was taking place. The mixture was stirred for some time and then ethanol was added. The catalyst was extracted with dilute HCl.

(g) $\text{NH}_4\text{ReO}_4\text{-Na,EtNH}_2\text{-1-2-}$

Quantities: Na, 4.93 g. (0.0214 atom) in 40 ml. ethylamine

NH_4ReO_4 , 1.44 g. (0.0054 mole)

The procedure was the same as (f) with the exception that three extractions were performed. The first with dilute H_2SO_4 , the second with water and the third with ethanol. It was concluded after this experiment that sodium is too insoluble in ethylamine to be used conveniently for this type of preparation.

Anal. Found: Re, 79.1, 78.4, 80.4 ($\phi_4\text{AsCl}$, HNO_3 oxidation)

D. Hydrogenations: General

1. Procedure

Four different hydrogenation apparatuses were used for the reductions. They were as follows: (a) An American Instrument Company hydrogenation vessel, model number 406-10H1. This instrument has a fixed agitation rate of 36 cycles per minute. (b) An Autoclave Engineers Corporation "Magne-Dash" instrument. This unit has a variable agitation cycle but was normally operated below 50 cycles per minute. (c) A Parr Instrument Company high pressure bomb, model number 4011-H. This bomb has a fixed agitation rate of 36 cycles per minute. (d) A Pressure Products Industries, Inc. "Pendaclave" high pressure, hydrogenation apparatus. This bomb has four possible agitation rates. It was normally operated at 80 cycles per minute. Used in conjunction with the "Aminco" and "Pendaclave" bombs was an automatic temperature controller and a Leeds-Northrup $X_1 - X_2$ recorder for simultaneous recording of temperature and pressure. In all the instruments except the "Magne-Dash" a glass liner was used. So far as could be distinguished, the bomb used made little or no difference in the conditions necessary for the reduction of a specific substrate.

The hydrogenation procedure, in general, was as follows: The glass liner containing the substrate, catalyst and solvent, if used, was weighed and then placed in the bomb. The bomb was flushed twice with 500 psi of hydrogen and then charged by means of a booster pump up to about 3050 psi. About 50 psi of the hydrogen was usually physically adsorbed by the substrate and solvent; leaving the initial pressure at about 3000 psi. The bomb was

then agitated at room temperature for several minutes to be sure that no leaks were present and then heating was commenced. In order to obtain minimal conditions the bomb was always heated first to a temperature 25 to 50° below where the reduction was likely to take place. If no reduction occurred, then the temperature was raised in increments of 25 to 50° until a pressure drop occurred. The bombs were never heated higher than 250°C.

The theoretical pressure drop was calculated for each reduction, assuming ideal behavior of the hydrogen. When a pressure drop equal to or more than the theoretical value was attained, the bomb was cooled to room temperature and then the hydrogen vented. The percent recovery was calculated from the weight of the liner and its contents before and after the reduction.

2. Analysis of products

The analyses of simple substrates such as butanone, hexene-1, and benzene, where the reduction yields only one product, were performed by means of refractive indices. Working plots were experimentally determined for all the common substrates. All readings were made at 20°C.

When the reduction yielded complex or numerous products, or where a solvent was used, the analyses were performed by means of gas chromatography. The instrument used was a Wilkens Instrument and Research, Inc. "Aerograph", master model A100. Both hydrogen and helium were used as carrier gases, and a variety of columns were available. The recorded curves obtained were Gaussian and the area under the curve was taken proportional to the molar percentages of components in the product. When reduction resulted in a large change in molecular weight, as is the case in the reduction of the nitro or carboxyl group, and when both reduced and unreduced material were present in the product, the molar percentages were converted to weight percentages. In reductions in which both components had approximately the same molecular weight, the molar and weight percentages were assumed the same.

The percent reduction calculated for all reactions was based upon 100% recovery, assuming that any material lost had the same composition as that recovered. When chromatography was used, all the components could be observed and their percentages calculated. However, when refractive index was the method of analysis, it was assumed that other than the reduction product, only the original substrate was present.

Table 4 contains a compilation of some common functional groups and the chromatography columns which seemed best suited for their analysis, plus the temperature at which analysis was most easily performed. Table 5 contains some actual representative reduction substrates and the columns and conditions used for the analysis of the reduction product.

Table 4

Selected Functional Groups and the Columns and Temperatures
Which Were Found Best for Their Identification and
the Identification of Their Reduction Products
By Gas Chromatography

Column Fixed Phase	Functional Group	Column Operating* Temperature
Silicone	carboxyl	boiling point
	nitro	25° below b.p.
	amino	25° below b.p.
	nitriole	boiling point
Carbowax	carbonyl	25° below b.p.
	alcohol	25° below b.p.
	multiple bonds	25-50° below b.p.
Dinonylphthalate	alcohol	boiling point
	carbonyl	boiling point
	olefins	25-50° below b.p.
Diglycerol	alkanes	25-50° below b.p.
	olefins	25-50° below b.p.
	alcohol	boiling point
	carbonyl	boiling point
	triple bond	25° below b.p.
Polypropylene Glycol	alcohol	boiling point
	carbonyl	boiling point
	olefins	25° below b.p.
	aromatics	25° below b.p.

* This column gives the column operating temperature for the resolution of the mixture obtained on hydrogenation of a given substrate in terms of the boiling point of that substrate.

Table 5

Selected Substrates and the Columns and Temperatures
Used for the Analysis of Their Reduction Products

Column Fixed Phase	Representative Substrates	Column Operating Temperature, °C
Silicone	nitrobenzene	180
	acetic acid	110
	crotonic acid	135
	capronitrile	130
	pyridine	70

Table 5 (continued)

Selected Substrates and the Columns and Temperatures
Used for the Analysis of Their Reduction Products

Column Fixed Phase	Representative Substrates	Column Operating Temperature, °C
Carbowax	allylacetone	110
	cyclohexene	50
	benzene	50
Dinonylphthalate	ethyl acetate-ethanol	150
	styrene	145
	cyclohexanone	160
Diglycerol	allylacetone	115
	2-allylcyclohexanone	145
	crotonaldehyde	135
Polypropylene Glycol	hexene-1	35
	acetone	80
	2-hexanone	125
	2-nonanone	180

E. Hydrogenations: Summary of Individual Experiments

The conditions given for each reduction are the average conditions. They were obtained by calculating the average temperatures and pressures which occurred during the course of the reduction.

In most experiments the percent recovery lay between eighty and one hundred percent. For those cases in which it was determined the values are given.

Several experiments were performed to determine how closely the values obtained by refractive index and gas chromatography for the percent reduction of a substrate checked. Generally the values obtained by each method were very nearly the same. Only in the cases where a small amount of an unexpected product was present were the results divergent.

1. Sodium-Ammonia Catalysts

(a) Acetone

(1) Acetone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-3-}$ (0.1 g.)

Conditions: 78°C./3270 psi./10 hrs.

Product: 100% isopropyl alcohol (gas chromatography)

(b) Butanone

(1) Butanone: 0.3 g.

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-4-1-}$ (0.3 g.)

Conditions: 222°C./3910 psi./6 hrs.

Product: 89% recovery; 96% 2-butanol (ref. index)

(2) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-4-1-}$ (0.2 g.)

Conditions: 100°C./3790 psi./3.5 hrs.

Product: 82% recovery; 100% 2-butanol (ref. index)

(3) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-5-1-}$ (0.2 g.)

Conditions: 72°C./3100 psi./4 hrs.

Product 86% recover; 100% butanone, no red'n (ref. index)

(4) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-5-2-}$ (0.2 g.)

Conditions: 128°C./3650 psi./3 hrs.

Product: 97% recovery; 100% 2-butanol (ref. index)

(5) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-6-1-}$ (0.2 g.)

Conditions: 155°C./3855 psi./4 hrs.

Product: 91% recovery; 100% 2-butanol (ref. index)

(6) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-5-3-}$ (0.2 g.)

Conditions: 120°C./3600 psi./2 hrs.

Product: 86% recovery; 17% 2-butanol (ref. index)

(7) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-8-1-}$ (0.2 g.)

Conditions: 140°C./3760 psi./2 hrs.

Product: 92% recovery; 100% 2-butanol (ref. index)

(8) Butanone: 0.3 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-1-}$ (0.2 mole)

Conditions: $120^\circ\text{C.}/3550\text{ psi.}/$ unknown hours

Product: 79% recovery; 56% 2-butanol (ref. index)

(9) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-3-}$ (0.1 g.)

Conditions: $115^\circ\text{C.}/3590\text{ psi.}/8\text{-}10\text{ hrs.}$

Product: 54% 2-butanol, 46% unknown product (gas chromatography)

(10) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-2-}$ (0.2 g.)

Conditions: $116^\circ\text{C.}/3590\text{ psi.}/6\text{ hrs.}$

Product: 70% recovery; 100% 2-butanol (ref. index)

(11) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-6-}$ (0.1 g.)

Conditions: $120^\circ\text{C.}/3610\text{ psi.}/12\text{ hrs.}$

Product: 95% recovery; 100% 2-butanol (gas chromatography)

(12) Butanone: 0.2 mole

Catalyst: $\text{KReO}_4\text{-Na, NH}_3\text{-2-1-}$ (0.2 g.)

Conditions: $130^\circ\text{C.}/3750\text{ psi.}/18\text{ hrs.}$

Product: 91% recovery; 16% 2-butanol (ref. index)

(13) Butanone: 0.2 mole

Catalyst: $\text{Re}_2\text{O}_7\text{Na, NH}_3\text{-1-1-}$ (0.2 g.)

Conditions: $103^\circ\text{C.}/3550\text{ psi.}/12\text{ hrs.}$

Product: 83% recovery; 100% 2-butanol (ref. index)

(14) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{EtOH-1-1-}$ (0.2 g.)

Conditions: $111^\circ\text{C.}/3570\text{ psi.}/14\text{ hrs.}$

Product: 95% recovery; 100% 2-butanol (ref. index)

(c) 3-methyl-2-butanone

(1) 3-methyl-2-butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-6-}$ (0.1 g.)

Conditions: 130-160°C./3850 psi./12 hrs.

Product: 82% recovery; 100% 3-methyl-2-butanone (gas chromatography)

(2) 3-methyl-2-butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-6-}$ (0.1 g.)

Conditions: 198°C./4335 psi./7 hrs.

Product: 100% recovery; 90% 3-methyl-2-butanol, 10% 3-methyl-2-butanone (gas chromatography)

(d) 2,3-butanedione

(1) 2,3-butanedione: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-3-}$ (0.1 g.)

Conditions: 93°C./3590 psi./7.5 hrs.

Product: 96% recovery; about 50% 2,3-butanediol, four other products were present but were not identified (gas chromatography)

The material removed from the bomb was a very viscous, fluorescent green liquid. It is perhaps significant that only 50% of the theoretical pressure drop was obtained. A chromatograph of the material indicated the presence of two principal and three minor constituents. A fractionation of the material was attempted but no distinct boiling ranges could be obtained, and chromatographs of the different fractions showed that little separation had been obtained. One of the largest blips was believed to be due to the diol. The others were not identified.

(e) 2-pentanone

(1) 2-Pentanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-6-}$ (0.1 g.)

Conditions: 136°C./3790 psi./11 hrs.

Product: 100% 2-pentanol (gas chromatography)

(f) 3-Pentanone

(1) 3-Pentanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-7-1-}$ (0.2 g.)

Conditions: 175°C./3950 psi./5 hrs.

(2) 3-Pentanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-3-}$ (0.1 g.)

Conditions: $160^\circ\text{C./3820 psi./6 hrs.}$

Product: 100% 3-pentanol (gas chromatography)

(g) 4-methyl-2-pentanone

(1) 4-methyl-2-pentanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-3-}$ (0.1 g.)

Conditions: $180^\circ\text{C./3850 psi./5 hrs.}$

Product: 88% recovery; 100% 4-methyl-2-pentanol (gas chromatography)

(h) 2,4-Pentanedione

(1) 2,4-Pentanedione: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-3-}$ (0.1 g.)

Conditions: $132^\circ\text{C./3500 psi./12 hrs.}$

Product: Seven products were present, one of them constituting approximately 50% of the total was identified as the diol (gas chromatography)

A pressure drop of less than the theoretical value was obtained at about 135° . The temperature was then raised. By mistake the temperature was raised up to about 180° . This heating took place over a period of about an hour and as soon as it was discovered the agitation was stopped until the bomb cooled down. The bomb was then operated for some time more at 135° , but no further pressure drop occurred. A considerable drop occurred during the hour of overheating.

The reduction product contained seven components. The product was fractionated into three components with boiling ranges of $80\text{-}82^\circ$, $110\text{-}112^\circ$ and $188\text{-}194^\circ$, respectively. One of the major components upon fractionation, was converted to one of the other major components. Only one of the components was identified. It constituted approximately 50% of the total and was concluded to be 2,4-pentanediol.

(i) Cyclopentanone

(1) Cyclopentanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-6-}$ (0.1 g.)

Conditions: $167^\circ\text{C./3925 psi./6 hrs.}$

Product: 60% recovery; 100% cyclopentanol (gas chromatography)

(j) 2-Hexanone

(1) 2-Hexanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-3-}$ (0.1 g.)Conditions: $135^\circ\text{C.}/3100\text{ psi.}/11.5\text{ hrs.}$

Product: 98% recovery; 100% 2-hexanol (gas chromatography)

(k) 2,5-Hexanedione

(1) 2,5-Hexanedione: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-3-}$ (0.1 g.)Conditions: $121^\circ\text{C.}/3300\text{ psi.}/10.5\text{ hrs.}$

Product: 100% recovery; 95% 2,5-hexanediol, also two unidentified minor products (gas chromatography)

(1) Cyclohexanone

(1) Cyclohexanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-1-1-}$ (0.2 g.)Conditions: $205^\circ\text{C.}/4200\text{ psi.}/20\text{ hrs.}$

Product: 100% cyclohexanol (ref. index)

(2) Cyclohexanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-3-1-}$ (0.2 g.)Conditions: $172^\circ\text{C.}/3860\text{ psi.}/10\text{ hrs.}$

Product: 99% recovery; 100% cyclohexanol (ref. index)

(3) Cyclohexanone: 0.2 mole

Catalyst: $\text{KReO}_4\text{-Na, NH}_3\text{-1-1-}$ (0.17 g.)Conditions: $205^\circ\text{C.}/4150\text{ psi.}/7\text{ hrs.}$

Product: 100% recovery; 79% cyclohexanol (ref. index)

(4) Cyclohexanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-4-1-}$ (0.2 g.)Conditions: $165^\circ\text{C.}/3820\text{ psi.}/2\text{ hrs.}$

Product: 100% recovery; 75% cyclohexanol (ref. index)

(5) Cyclohexanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-4-1-}$ (0.2 g.)

Conditions: 160-175°C./3525 psi./4 hrs.

Product: 95% recovery; 100% cyclohexanol (ref. index)

(6) Cyclohexanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-4-2-}$ (0.2 g.)

Conditions: 130°C./3735 psi./3 hrs.

Product: 91% recovery; 70% cyclohexanol (ref. index)

(m) 2-Heptanone

(1) 2-Heptanone: (0.2 mole)

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-9-3-}$ (0.1 g.)

Conditions: 172°C./3945 psi./3.5 hrs.

Product 98% recovery; 96% 2-heptanol, 4% 2-heptanone (gas chromatography)

(n) 3-Heptanone

(1) 3-Heptanone: (0.2 mole)

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-9-6-}$ (0.1 g.)

Conditions: 152°C./3735 psi./5 hrs.

Product: 80% recovery; 100% 3-heptanol (gas chromatography)

(o) 4-Heptanone

(1) 4-Heptanone: (0.2 mole)

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-9-3-}$ (0.1 g.)

Conditions: 186°C./3925 psi./2 hrs.

Products: 98% 4-heptanol, 2% 4-heptanone (gas chromatography)

(p) Cycloheptanone:

(1) Cycloheptanone: (0.2 mole)

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-9-7-}$ (0.1 g.)

Conditions: 175°C./3980 psi./8.5 hrs.

Product: 100% cycloheptanol (gas Chromatography)

(q) 2-Octanone

(1) 2-Octanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-3-}$ (0.1 g.)

Conditions: 130°C./3615 psi./6 hrs.

Product: 100% recovery, 86% 2-octanol, 14% 2-octanone (gas chromatography)

(r) 2-Nonanone

(1) 2-Nonanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-6-}$ (0.1 g.)

Conditions: 178°C./3960 psi./6 hrs.

Product: 100% 2-nonanol (gas chromatography)

(s) Phenyl-2-propanone

(1) Phenyl-2-propanone

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-3-}$

Conditions: 184°C./3970 psi./1.25 hrs.

Product: 100% recovery; 100% phenyl-2-propanone (gas chromatography)

(t) Acetophenone

(1) Acetophenone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-4-2-}$ (0.2 g.)

Conditions: 125°C./3600 psi./9 hrs.

Product: 97% recovery; 67% methylphenylcarbinol (ref. index)

The refractive index was determined on the substrate without considering the possible presence of ethylbenzene. The analysis is therefore probably in error to some extent.

(2) Acetophenone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-6-1-}$ (0.2 g.)

Conditions: 160°C./3760 psi./6 hrs.

Product: 95% recovery; 74% methylphenylcarbinol (ref. index)

The analysis was performed in the same manner as (1) above and the results likewise are probably in error to a small degree.

(u) Hexene-1

(1) Hexene-1: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-7-1-}$ (0.2 g.)

Conditions: 135°C./3850 psi./16 hrs.

Product: 100% hexene-1 (ref. index)

(2) Hexene-1: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-9-2-}$ (0.1 g.)

Conditions: 122°C./3515 psi./4 hrs.

Product: 94% recovery; 100% hexane (ref. index)

(3) Hexene-1: 0.2 mole

Catalyst: $\text{Re}_2\text{O}_7\text{-Na,NH}_3\text{-1-1-}$ (0.2 g.)

Conditions: 100-300°C./3925 psi./0.5 hrs.

Product: 89% recovery; 85% hexane (ref. index)

During the heating, the bomb was erroneously overheated to about 300°C. As soon as the heating was discovered the mantle was immediately dropped and the bomb cooled as soon as possible. Reduction occurred during the overheating.

(4) Hexene-1: 0.2 mole

Catalyst: $\text{Re}_2\text{O}_7\text{-Na,NH}_3\text{-1-1-}$ (0.2 g.)

Conditions: 124°C./3625 psi./12 hrs.

Product: 97% recovery; 90% hexane (ref. index)

(5) Hexene-1: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-EtOH-1-1-}$ (0.2 g.)

Conditions: 127°C./3665 psi./6 hrs.

Product: 93% recovery 100% hexane (ref. index)

(v) Hexene-2

(1) Hexene-2: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-5-2-}$ (0.2 g.)

Conditions: 151°C./3600 psi./3 hrs.

Product: 85% recovery; 100% hexane (ref. index)

(w) Cyclohexene

(1) Cyclohexene: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-3-1-}$ (0.2 g.)Conditions: $125^\circ\text{C./3400 psi./10 hrs.}$

Product: 91% recovery; 100% cyclohexene, no reduction (ref. index)

(2) Cyclohexene: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-1-1-}$ (0.16 g.)Conditions: $250^\circ\text{C./4250 psi./4 hrs.}$

Product: 90% recovery; 37% cyclohexane (ref. index)

(3) Cyclohexene: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-4-1-}$ (0.2 g.)Conditions: $212^\circ\text{C./4152 psi./11 hrs.}$

Product: 72% recovery; 100% cyclohexane (ref. index)

(4) Cyclohexene: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-9-8-}$ (0.1 g.)Conditions: $120^\circ\text{C./3730 psi./3 hrs.}$

Product: 100% cyclohexane (gas chromatography)

(x) Styrene

(1) Styrene: 0.2 mole in 50 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-5-1-}$ (0.2 g.)Conditions: $108^\circ\text{C./3465 psi./3 hrs.}$

Product: 99% recovery; 15% polymer, 85% ethylbenzene (ref. index)

The analysis was carried out as follows: The product was distilled to remove the ethanol. The ethylbenzene which codistilled was separated by means of a separatory funnel after the addition of water. The recovered ethylbenzene was added back to that in the distilling flask. The remaining ethanol and water were distilled off and then the styrene and ethylbenzene were distilled over. The refractive index was determined on the ethylbenzene-styrene mixture.

(2) Styrene: 0.2 mole in 50 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-6-1-}$ (0.2 g.)

Conditions: $105^\circ\text{C.}/3485\text{ psi.}/6\text{ hrs.}$

Product: 74% recovery; polymer, 37% ethylbenzene, 30% styrene (ref. in

The analysis was performed in the same manner as (1) above.

(3) Styrene: 0.1 mole in 25 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-9-7-}$ (0.1 g.)

Conditions: $110^\circ\text{C.}/3565\text{ psi.}/0.75\text{ hrs.}$

Product: 93% recovery; 100% ethylbenzene (gas chromatography)

(y) Benzene

(1) Benzene: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-5-2-}$ (0.2 g.)

Conditions: $170^\circ\text{C.}/3740\text{ psi.}/4\text{ hrs.}$

Product: 55% recovery; 44% cyclohexane (ref. index)

(2) Benzene: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-4-2-}$ (0.2 g.)

Conditions: $239^\circ\text{C.}/4780\text{ psi.}/\text{unknown time}$

Product: 86% recovery; 12% cyclohexane (ref. index)

The temperature was first raised to 150° , and eventually up to 250°C. No pressure drop could be observed, and it was thought that no reduction occurred. An analysis of the product indicated that a slight reduction had occurred.

(3) Benzene: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-8-1-}$ (0.2 g.)

Conditions: $222^\circ\text{C.}/4450\text{ psi.}/12\text{ hrs.}$

Product: 73% recovery; 36% cyclohexane (ref. index)

(4) Benzene: 0.2 mole

Catalyst: $\text{Re}_2\text{O}_7\text{-Na,NH}_3\text{-1-1-}$ (0.2 g.)

Conditions: 202°C./4245 psi./10 hrs.

Product: 85% recovery; 67% cyclohexane (ref. index)

(5) Benzene: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{,EtOH -2-1-}$ (0.2 g.)

Conditions: 160°C./3000 psi./36 hrs.

Product: 37% recovery; 100% benzene (ref. index)

A bad leak developed in the bomb and it was impossible to determine if reduction was occurring. The maximum temperature attained was 160°C.

(6) Benzene: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-9-7-}$ (0.1 g.)

Conditions: 240°C./4875 psi./8 hrs.

Product: 56% recovery; 5% cyclohexane, 95% benzene (gas chromatography)

(z) Nitrobenzene

(1) Nitrobenzene: 0.2 mole in 40 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-3-1-}$ (0.16 g.)

Conditions: 202°C./3500 psi./18 hrs.

Product: 87% recovery; 67% aniline (ref. index)

The analysis was performed as follows: The catalyst was removed and the ethanol stripped off. After the ethanol was completely removed, the remaining material was likewise distilled over. It passed over at about 180°C. A refractive index was then taken to determine the percent aniline in the product.

(2) Nitrobenzene: 0.2 mole in 40 ml. EtOH

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-7-1-}$ (0.2 g.)

Conditions: 160°C./3250 psi./6 hrs.

Product: 96% recovery; 88% aniline (ref. index)

The method of analysis was identical with that in (1) above.

(3) Nitrobenzene: 0.2 mole in 75 ml. EtOH

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-9-1-}$ (0.2 g.)

Conditions: 175°C./3650 psi./12 hrs.

Product: 94% recovery; 75% aniline (ref. index)

The method of analysis was identical with (1).

(4) Nitrobenzene: 0.2 mole in 40 ml. EtOH

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{,EtOH-1-1-}$ (0.2 g.)

Conditions: 127°C./3225 psi./2.5 hrs.

Product: 100% recovery; 94% aniline (ref. index)

The analysis was the same as in (1).

(5) Nitrobenzene: 0.2 mole in 40 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{,EtOH-2-1-}$ (0.2 g.)

Conditions: 130-140°C./3900 psi./ unknown

Product: 94% recovery; 67% aniline (ref. index)

The analysis method was the same as in (1).

(6) Nitrobenzene: 0.1 mole in 25 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-5-3-}$ (0.1 g.)

Conditions: 130°C./3770 psi./6 hrs.

Product: 48% recovery; 11% aniline, 89% nitrobenzene (gas chromatograph)

(7) Nitrobenzene: 0.2 mole in 20 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-9-6-}$ (0.1 g.)

Conditions: 195°C./4260 psi./18 hrs.

Product: 71% recovery; 60% aniline, 40% nitrobenzene (gas chromatograph)

(aa) Acetic Acid

(1) Acetic Acid: 0.1 mole in 10 ml. water

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,NH}_3\text{-9-8-}$ (0.1 g.)

Conditions: 178°C./4060 psi./7 hrs.

Product: 100% recovery; 100% ethanol (gas chromatography)

(bb) Allylacetone

(1) Allylacetone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, NH}_3\text{-9-7-}$ (0.1 g.)Conditions: $119^\circ\text{C.}/3520\text{ psi.}/6\text{ hrs.}$

Product: 90% recovery; 71% 2-hexanone, 29% 2-hexanol (gas chromatography)

This reduction points out the possible selectivity of the catalyst to reduce the double bond in preference to the carbonyl group.

2. Lithium-Ammonia Catalysts

(a) Acetone

(1) Acetone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-7-}$ (0.1 g.)Conditions: $125^\circ\text{C.}/3770\text{ psi.}/0.5\text{ hrs.}$

Product: 83% recovery; 100% isopropyl alcohol (gas chromatography)

(b) Butanone

(1) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-1-}$ (0.2 g.)Conditions: $111^\circ\text{C.}/3475\text{ psi.}/4\text{ hrs.}$

Product: 100% recovery; 100% 2-butanol (ref. index)

(2) Butanone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-1-}$ (0.1 g.)Conditions: $100^\circ\text{C.}/3620\text{ psi.}/15\text{ hrs.}$

Product: 98% 2-butanol (ref. index)

The bomb was operated 36 hours at room temperature to see if any reduction could be accomplished under such mild conditions. No pressure drop occurred; therefore, the bomb was heated up to 100°C. where the reduction occurred rather slowly.

(3) Butanone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-2-}$ (0.1 g.)Conditions: $120^\circ\text{C.}/3870\text{ psi.}/<12\text{ hrs.}$

Product: 81% recovery; 94% 2-butanol (ref. index)

(c) Cyclohexanone

(1) Cyclohexanone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-4-}$ (0.1 g.)

Conditions: 120°C./3800 psi./15 hrs.

Product: 100% recovery; 100% cyclohexanone (gas chromatography)

(d) Acetophenone

(1) Acetophenone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-4-}$ (0.1 g.)

Conditions: 158°C./3880 psi./5 hrs.

Product: 100% recovery; 64% methylphenylcarbinol, 36% ethylbenzene (gas chromatography)

(e) Hexene-1

(1) Hexene-1: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-4-}$ (0.1 g.)

Conditions: 96°C./3600 psi./10 hrs.

Product: 54% recovery; 100% hexane (gas chromatography)

The bomb was operated at about 100° for some time, and it appeared that a pressure drop occurred. The bomb was therefore cooled and the cool pressure observed. A pressure drop of only about 40 psi had been obtained. The bomb was therefore reheated and operated at about 110°. No further drop occurred. Chromatographic analysis, however, revealed that reduction was complete. It is unknown why a pressure drop of only 32% of theoretical was obtained.

(2) Hexene-1: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-7-}$ (0.1 g.)

Conditions: 104°C./3540 psi./0.5 hrs.

Product: 65% recovery; 100% hexane (ref. index)

The reduction apparently occurred during the heating up process from room temperature to 105°C.

(f) 2,2,4-trimethylpentene-1

(1) 2,2,4-trimethylpentene-1: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-7-}$ (0.1 g.)

Conditions: 178-224°C./4300 psi./0.5 hrs.

Product: 78% recovery; 100% isooctane (gas chromatography)

(g) Styrene

(1) Styrene: 0.1 mole in 40 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-4-}$ (0.1 g.)

Conditions: 70°C./3275 psi./12 hrs.

Product: 91% recovery; 56% ethylbenzene, 44% styrene (gas chromatography)

(h) p-Chlorostyrene

(1) p-Chlorostyrene: 0.1 mole in 25 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-4-}$ (0.1 g.)

Conditions: 82-108°C./3475 psi./13 hrs.

Product: 53% polymer, 47% p-chloroethylbenzene (gas chromatography)

(i) Cyclohexene

(1) Cyclohexene: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-3-}$ (0.2 g.)

Conditions: 99°C./3610 psi./22 hrs.

Product: 100% recovery; 100% cyclohexane (gas chromatography)

(j) Benzene

(1) Benzene: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-1-}$ (0.2 g.)

Conditions: 206°C./4400 psi./12 hrs.

Product: 83% recovery; 34% cyclohexane (ref. index)

(k) Nitrobenzene

(1) Nitrobenzene: 0.2 mole in 40 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-1-}$ (0.2 g.)

Conditions: 113°C./3380 psi./18 hrs.

Product: good recovery; 75% aniline (ref. index)

The analysis was performed as follows. The reduced substrate was placed in a distilling apparatus and the ethanol was stripped off. After the ethanol was completely removed the higher boiling fraction (ca. 180°C.) was distilled over. This fraction containing both aniline and nitrobenzene was analyzed refractometrically.

(2) Nitrobenzene: 0.2 mole in 40 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-1-}$ (0.2 g.)

Conditions: 125°C./2845 psi./25 hrs.

Product: 83% recovery; 51% aniline (ref. index)

The method of analysis was the same as (1) above.

(3) Nitrobenzene: 0.1 g. in 25 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-1-}$ (0.1 g.)

Conditions: 90-110°C./3400 psi./8 hrs.

Product: 97% recovery; 100% aniline (gas chromatography)

(1) 1-Nitropropane

(1) 1-Nitropropane: 0.1 mole in 25 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-2-}$ (0.1 g.)

Conditions: 135°C./3700 psi./14 hrs.

Product: 98% recovery; numerous unidentified products (gas chromatography)

The chromatograph of the reduction substrate indicated the presence of seven or eight products. They were not identified. It is perhaps significant that no 1-nitropropane was present.

(m) Capronitrile

(1) Capronitrile: 0.1 mole in 50 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-3-}$ (0.1 g.)

Conditions: 185°C./4300 psi./8 hrs.

Product: 9 products were present; some of these products are undoubtedly the amines. Their relative amounts, however, were not determined. (gas chromatography)

(n) Acetic Acid

(1) Acetic Acid: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-4-}$ (0.1 g.)

Conditions: 180°C./4060 psi./18 hrs.

Product: 92% recovery; 54% ethanol, 45% ethylacetate (gas chromatography)

(o) Allylacetone

(1) Allylacetone: 0.1 mole in 20 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-2-}$ (0.1 g.)

Conditions: 81°C./3350 psi./6 hrs.

Product: 98% recovery; 72% 2-hexanone, 28% 2-hexanol (gas chromatography)

The reduction indicates the possible selectivity of the catalyst toward the reduction of the double bond over the reduction of the carbonyl group.

(p) 2-Allylcyclohexanone

(1) 2-Allylcyclohexanone: 0.1 mole in 25 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-6-}$ (0.1 g.)

Conditions: 115-124°C./3650 psi./≤ 16 hrs.

Product: 96% recovery; 32% 2-propylcyclohexanone, 18% 2-allylcyclohexanone (gas chromatography)

(2) 2-Allylcyclohexanone: 0.1 mole in 15 ml ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-2-}$ (0.1 g.)

Conditions: 123°C./3800 psi./14 hrs.

Product: 88% 2-propylcyclohexanone, 8% 2-allylcyclohexanone, 4% 2-propylcyclohexanol (gas chromatography)

(q) o-Phenylenediamine

(1) o-Phenylenediamine: 0.1 mole in 40 ml. Skelly Solve B

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_3\text{-1-4-}$ (0.2 g.)

Conditions: 250°C./4950 psi./13 hrs.

Product: 100% o-phenylenediamine, no reduction (melting point)

3. Lithium-Ethylamine Catalysts

(a) Acetone

(1) Acetone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-6-}$ (0.1 g.)

Conditions: 55°C./3000 psi./15 hrs.

Product: 88% recovery; 30% isopropyl alcohol (ref. index)

(b) Butanone

(1) Butanone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-1-}$ (0.1 g.)

Conditions: 85°C./3570 psi./ 12 hrs.

Product: 88% recovery; 86% 2-butanol (ref. index)

(2) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-1-}$ (0.1 g.)

Conditions: 90°C./3500 psi./24 hrs.

Product: 35% 2-butanol (ref. index)

The purpose of the run was to establish the minimal conditions for the reduction. The Magne-Dash bomb was set to run during the night at room temp. However, the next morning it was observed that the dasher had stuck. The bomb was dismantled and reassembled, and another tenth mole of substrate was added. The bomb was then heated to 90° where it was operated for 24 hrs. No pressure drop appeared to occur; however, analysis of the product indicated that approximately 35% reduction had occurred.

(3) Butanone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-2-}$ (0.1 g.)

Conditions: $90^\circ\text{C.}/3500\text{ psi.}/15\text{ hrs.}$

Product: 100% recovery; 97% 2-butanol (ref. index)

(4) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-5-}$ (0.2 g.)

Conditions: $70\text{-}100^\circ\text{C.}/3550\text{ psi.}/1.5\text{-}2\text{ hrs.}$

Product: 100% recovery; 74% 2-butanol (ref. index)

(5) Butanone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-6-}$ (0.1 g.)

Conditions: $95^\circ\text{C.}/3525\text{ psi.}/8\text{ hrs.}$

Product: 100% recovery; 100% 2-butanol (ref. index)

(6) Butanone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-6- Dried}$ (0.1 g.)

Conditions: $115^\circ\text{C.}/3000\text{ psi.}/3\text{ hrs.}$

Product: 8% 2-butanol, 92% butanone (gas chromatography)

The object of the reduction was to determine if drying altered the activity of the catalyst. The catalyst, therefore, before use was dried in air at 110°C. in the drying oven. Although the reduction was poor it is felt that the results are inconclusive because of a bad leak present.

(7) Butanone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-9-}$ (0.1 g.)

Conditions: $100^\circ\text{C.}/2925\text{ psi.}/2.5\text{ hrs.}$

Product: 100% 2-butanol (gas chromatography)

(c) Cyclohexanone

(1) Cyclohexanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-4-}$ (0.2 g.)

Conditions: $119^\circ\text{C.}/3655\text{ psi.}/2.5\text{ hrs.}$

Product: 96% recovery; 100% cyclohexanol (ref. index)

(d) Hexene-1

(1) Hexene-1: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-4-}$ (0.2 g.)

Conditions: 119°C./3655 psi./2.5 hrs.

Product: 98% recovery; 100% hexane (ref. index)

(e) 2,2,4-Trimethylpentene-1

(1) 2,2,4-Trimethylpentene-1: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-2-}$ (0.2 g.)

Conditions: 120°C./3875 psi./12 hrs.

Product: 100% recovery; 8% 2,2,4-trimethylpentane, 92% 2,2,4-trimethylpentene-1 (gas chromatography)

(f) Cyclohexene

(1) Cyclohexene: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-1-}$ (0.1 g.)

Conditions: 105°C./3600 psi./16 hrs.

Product: 89% recovery; 100% cyclohexane (gas chromatography)

(2) Cyclohexene: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-5-}$ (0.1 g.)

Conditions: 146°C./4000 psi./2.5 hrs.

Product: 89% recovery; 100% cyclohexane (gas chromatography)

(3) Cyclohexene: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$ (0.1 g.)

Conditions: 149°C./3930 psi./2 hrs.

Product: 69% recovery; 100% cyclohexane (gas chromatography)

(g) Styrene

(1) Styrene: 0.2 mole in 25 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-5-}$ (0.1 g.)

Conditions: 30°C./2850 psi./11 hrs.

Product: 98% recovery; 64% ethylbenzene (ref. index)

(h) 1-Phenylbutene-2

(1) 1-Phenylbutene-2: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-8-}$ (0.1 g.)

Conditions: 171°C./3950 psi./2.5 hrs.

Product: 93% recovery; 100% n-butylbenzene (gas chromatography)

(i) Benzene

(1) Benzene: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-1-}$ (0.1 g.)

Conditions: 200-250°C./4700 psi./3 hrs.

Product: 81% recovery; 50% cyclohexane (ref. index)

(2) Benzene: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-2-}$ (0.2 g.)

Conditions: 208°C./4560 psi./1.5 hrs.

Product: 68% recovery; 22% cyclohexane (ref. index)

(3) Benzene: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-4-}$ (0.2 g.)

Conditions: 179°C./4050 psi./29 hrs.

Product: 75% recovery; 51% cyclohexane (ref. index)

(4) Benzene: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-2-}$ (0.1 g.)

Conditions: 250°C./4800 psi./6 hrs.

Product: 100% benzene, no reduction (gas chromatography)

The catalyst when used was old. It had been stored several months. This may have contributed to its inactivity.

(j) Toluene

(1) Toluene: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-3-}$ (0.2 g.)

Conditions: 222°C./4455 psi./35 hrs.

Product: 87% recovery; 35% methylcyclohexane (ref. index)

(k) Allyl bromide

(1) Allyl bromide: 0.2 mole in 25 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-5-}$ (0.2 g.)Conditions: $135^\circ\text{C.}/3700\text{ psi.}/7\text{ hrs.}$

Product: 85% recovery The products were unidentified, a total of eight were present (gas chromatography)

The allyl bromide apparently reacted with the ethanol to give a variety of products. They were not identified.

(l) Nitrobenzene

(1) Nitrobenzene: 0.1 mole in 50 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-1-}$ (0.1 g.)Conditions: $106^\circ\text{C.}/3209\text{ psi.}/7\text{ hrs.}$

Product: 63% recovery; 91% aniline (ref. index)

The analysis was performed as follows: The ethanol and water were stripped off at atmospheric pressure and then vacuum was applied and the higher boiling components distilled over. A refractive index was taken to determine the percent reduction.

(2) Nitrobenzene: 0.1 mole in 15 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$ (0.1 g.)Conditions: $126^\circ\text{C.}/3400\text{ psi.}/3\text{ hrs.}$

Product: 100% recovery; 100% aniline (gas chromatography)

(m) 1-Nitropropane

(1) 1-Nitropropane: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-6-}$ (0.1 g.)Conditions: $114^\circ\text{C.}/2600\text{ psi.}/\leq 16\text{ hrs.}$

Product: Numerous products were present, none were identified. (gas chromatography)

(n) Pyridine

(1) Pyridine: 0.1 mole in 10 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-9-}$ (0.1 g.)Conditions: $215^\circ\text{C.}/4335\text{ psi.}/7\text{ hrs.}$

Product: 80% recovery; 100% piperidine (gas chromatography)

(o) Acetic Acid

(1) Acetic Acid: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-2-}$ (0.2 g.)

Conditions: 124°C./3755 psi./29 hrs.

Product: 100% recovery; 72% ethyl acetate, 3% ethanol, 25% acetic acid (titiation and fractional distillation)

(2) Acetic Acid: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-6-}$ (0.1 g.)

Conditions: < 230°C./unknown/unknown

Product: 82% recovery; 79% ethanol, 21% ethyl acetate (gas chromatography)

Due to the large volume of the bomb, and the corresponding small pressure drop, it was impossible to observe when the pressure drop occurred.

(3) Acetic Acid: 0.1 mole in 15 ml. water

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-9-}$ (0.1 g.)

Conditions: 140-150°C./3950 psi./4.5 hrs.

Product: 100% recovery; 100% ethanol (gas chromatography)

(p) Propionic Acid

(1) Propionic Acid: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-3-}$ (0.2 g.)

Conditions: 145-175°C./4150 psi./< 1 hr.

Product: 25% n-propyl alcohol, 25% n-propyl propionate, 50% propionic Acid (fractional distillation)

The reduction appeared to occur during the temperature rise from 144°C. to 178°C. The product was analyzed by fractional distillation.

(2) Propionic Acid: 0.1 mole in 15 ml. water

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-9-}$ (0.1 g.)

Conditions: 162°C./3885 psi./6 hrs.

Product: 100% recovery; 100% n-propyl alcohol (gas chromatography)

(q) Isobutyric Acid

(1) Isobutyric Acid: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-6-}$ (0.1 g.)Conditions: $\ll 240^\circ\text{C.}/\text{unknown}/\text{unknown}$

Product: 60% recovery; 1% isobutyric acid; 40% isobutyl alcohol; 50% isobutyrisobutyrate; 9% unknown (gas chromatography)

Due to the large volume of the bomb it was impossible to tell where a pressure drop occurred. The pressure drop obtained was actually much less than theoretical.

(2) Isobutyric Acid: 0.1 mole in 10 ml. water

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$ (0.1 g.)Conditions: $172^\circ\text{C.}/4025\text{ psi.}/5\text{ hrs.}$

Product: 100% recovery; 95% isobutylalcohol, 5% isobutyl isobutyrate (gas chromatography)

The bomb was heated directly to 172°C. The reduction evidently would have occurred at a lower temperature.

(r) Valeric Acid)

(1) Valeric Acid: 0.1 mole in 10 ml. water

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$ (0.1 g.)Conditions: $168^\circ\text{C.}/3890\text{ psi.}/7\text{ hrs.}$

Product: 87% 1-pentanol, 13% amyl valerate (gas chromatography)

No attempt was made to obtain reduction at minimal conditions. The reduction possibly would have occurred at a somewhat lower temperature.

(s) Caproic Acid

(1) Caproic Acid: 0.1 mole in 10 ml. water

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$ (0.1 g.)Conditions: $177^\circ\text{C.}/4070\text{ psi.}/3\text{ hrs.}$ Product: 91% recovery; 73% 1-hexanol, 27% n-hexyl caproate (gas chromatography)

No attempt was made to obtain reduction at minimal conditions. The reaction evidently would have gone at a somewhat lower temperature.

(t) Caprylic Acid

(1) Caprylic Acid: 0.1 mole in 10 ml. water

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$ (0.1 g.)Conditions: $173^\circ\text{C.}/4080\text{ psi.}/5\text{ hrs.}$

Product: 93% recovery; 100% 1-octanol (gas chromatography)

No attempt was made to obtain reduction at minimal conditions.
The reaction evidently would have occurred at a lower temperature.

(u) Capric Acid

(1) Capric Acid: 0.1 mole in 10 ml. water

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$ (0.1 g.)Conditions: $173^\circ\text{C.}/3725\text{ psi.}/6\text{ hrs.}$

Product: 100% recovery; 100% 1-decanol (gas chromatography)

No attempt was made to obtain reduction at minimal conditions.

(v) Lauric Acid

(1) Lauric Acid: 0.05 mole in 10 ml. water

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$ (0.1 g.)Conditions: $170\text{-}184^\circ\text{C.}/4100\text{ psi.}/7\text{ hrs.}$

Product: 100% recovery; 100% 1-dodecanol (gas chromatography)

(w) Benzoic Acid

(1) Benzoic Acid: 0.1 mole in 15 ml. water

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$ (0.1 g.)Conditions: $198^\circ\text{C.}/4090\text{ psi.}/10\text{ hrs.}$

Product: 75% recovery; 100% toluene (gas chromatography)

(x) Nitrocyclohexane

(1) Nitrocyclohexane: 0.1 mole in 15 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$ (0.1 g.)Conditions: $120^\circ\text{C.}/3475\text{ psi.}/7\text{ hrs.}$

Product: 100% recovery; 100% cyclohexylamine (gas chromatography)

The reduction was occurring rather slowly at 108°C. When the temperature was raised to 125°C. the reduction became very rapid.

(y) Capronitrile

(1) Capronitrile: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-6-}$ (0.1 g.)

Conditions: 135-150°C./3900 psi./6 hrs.

Product: almost 100% capronitrile (gas chromatography)

The pressure drop which occurred must have been due to a leak. The chromatograph indicated that the product was almost entirely the unreduced substrate.

(z) Allylacetone (5-Hexene-2-one)

(1) Allylacetone: 0.2 mole in 40 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-5-}$ (0.1 g.)

Conditions: 65-70°C./3070 psi./13 hrs.

Product: 91% 2-hexanone, 9% allylacetone (gas chromatography)

(2) Allylacetone: 0.2 mole in 40 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-5-}$ (0.1 g.)

Conditions: 100°C./3475 psi./12 hrs.

Product: 98% recovery; 74% 2-hexanone; 26% 2-hexanol (gas chromatography)

The temperature was raised directly up to about 100°C. The reduction undoubtedly would have occurred at a somewhat lower temperature. Possibly none of the completely reduced product would have been obtained at a lower temperature.

(3) Allylacetone: 0.1 mole in 15 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$ (0.1 g.)

Conditions: 155°C./4200 psi./2.5 hrs.

Product: 97% recovery; 60% allylacetone, 14% 2-hexanone, 26% 5-hexene-2-ol (gas chromatography)

The drastic conditions necessary for this reduction are the result of partial poisoning of the bomb caused by a previous pyridine reduction. It is significant that this poisoning resulted in the production of 5-hexene-2-ol as well as 2-hexanone. This product has been absent from all previous reductions. It is also perhaps significant that none of the completely reduced product was present.

(aa) 2-Allylcyclohexanone

(1) 2-Allylcyclohexanone: 0.1 mole in 25 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-5-}$ (0.1 g.)Conditions: $125^\circ\text{C./3700 psi./6 hrs.}$

Product: 93% recovery; 73% 2-propyl-cyclohexanone, 5% 2-allylcyclohexanone, 22% 2-propylcyclohexanol (gas chromatography)

(bb) Crotonaldehyde

(1) Crotonaldehyde: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-6-}$ (0.1 g.)Conditions: $88^\circ\text{C./3400 psi./8 hrs.}$

Product: 91% crotonaldehyde, 9% crotyl alcohol (gas chromatography)

(2) Crotonaldehyde: 0.1 mole in 50 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-6-}$ (0.1 g.)Conditions: $140^\circ\text{C./3950 psi./20 hrs.}$

Product: 100% n-butyl alcohol (gas chromatography)

The conditions employed were undoubtedly somewhat too drastic. It actually appeared that two separate pressure drops occurred. The first during the temperature rise from 78°C. to 130°C. and the second at about 140°C. From a previous reduction it may be assumed that the first drop was due to reduction of the carbonyl group and the second due to the double bond.

(3) Crotonaldehyde: 0.1 mole in 15 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$ (0.1 g.)Conditions: $92^\circ\text{C./3475 psi./12 hrs.}$

Product: 100% crotonaldehyde (gas chromatography)

The conditions employed were undoubtedly too mild. The temperature was not raised, even though the pressure drop was slight, because it was desired to obtain selective reduction if possible.

(4) Crotonaldehyde: 0.1 mole in 10 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-10-}$ (.1 g.)

Conditions: 100°C./3650 psi./10 hrs.

Product: 50% n-butyraldehyde, 50% crotonaldehyde (gas chromatography)

(cc) m-Nitroacetophenone

(1) m-Nitroacetophenone: 0.1 mole in 40 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-7-}$ (0.1 g.)

Conditions: 107-117°C./3870 psi./24 hrs.

Product: 94% recovery; 100% m-aminoacetophenone (melting point)

The analysis was performed as follows: The material was removed from the bomb and more ethanol was added. The solution was heated to boiling and all the material dissolved. It was then filtered to remove the catalyst. As much of the ethanol as possible was stripped off and the resulting material was added to water. Colored crystals immediately formed. Hydrochloric acid was then added and the material dissolved. The solution was decolorized with carbon and then made basic with sodium hydroxide. The crystals obtained were colorless, and when recrystallized melted at 97°C. The literature value for the melting point of m-aminoacetophenone is 99.5°C.

(dd) p-Nitrophenylacetic acid

(1) p-Nitrophenylacetic acid: 0.1 mole in 50 ml. water

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-8-}$ (0.1 g.)

Conditions: 157°C./3750 psi./2.5 hrs.

Product: 39% polymer, 61% p-aminophenylacetic acid (melting point)

The conditions were apparently more drastic than necessary for the reduction. When the bomb was opened it was observed that a considerable amount of condensation product had formed. It probably was an amide type polymer which resulted when the nitro group was reduced. The analysis of the remaining product was conducted as follows: The water solution was filtered to remove the polymer and catalyst and then taken to dryness. The resulting material was taken up and recrystallized from ethanol. The material obtained decomposed or melted at 198°C. The literature value for the decomposition point of p-aminophenylacetic acid is 199-200°C. The product was, therefore, concluded as being the same.

(ee) Nitrophenylmethane

(1) Nitrophenylmethane: 0.1 mole in 20 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-8-}$ (0.1 g.)Conditions: $136^\circ\text{C./3750 psi./15 hrs.}$ Product: 20% benzylamine, 16% nitrophenylmethane, 64% unknown, possibly reaction product of amine and nitro compound.
(gas chromatography)

The analysis was performed as follows: The material when removed from the bomb was still dissolved in the ethanol. The catalyst was removed by centrifuging and then the ethanol was partially stripped off. As the ethanol was removed a solid deposited. The solid was distilled at about 250° under vacuum. It was then observed that a similar solid results when benzylamine and nitrophenylmethane are mixed. The distilled product in as little ethanol as possible was chromatographed. The chromatograph showed two small blips corresponding to the nitro and amine compounds, and another much larger, higher boiling blip which probably corresponded to the reaction product of the two. It is possible that reduction was 50% complete, the nitrophenylmethane reacting with the benzylamine as soon as it was formed.

(ff) m-Nitrostyrene

(1) m-Nitrostyrene: 0.03 mole in 10 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-9-}$ (0.1 g.)Conditions: $118^\circ\text{C./3690 psi./1 hr.}$

Product: 100% recovery; 100% m-aminostyrene (acid solubility)

The conditions were undoubtedly more drastic than necessary. The analysis was performed as follows: The material when removed from the bomb was in the form of a white solid, insoluble in ethanol but soluble in dilute HCl. The material was amorphous and did not seem to melt, but rather softened as the temperature was raised. When conc. HCl was added to the dilute HCl solution of the substance, a white precipitate resulted. All attempts to isolate the original material from a basic solution resulted in polymerization. From its tendency to polymerize and its acid solubility the product was concluded to be m-aminostyrene.

(gg) m-Nitrobenzaldehyde

(1) m-Nitrobenzaldehyde: 0.1 mole in 25 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-9-}$ (0.1 g.)Conditions: 84° and 124°C./3220 and 3720 psi./16 and 10 hrs.

Product: 100% recovery; 100% m-aminobenzaldehyde (acid solubility)

A pressure drop occurred at 85°C. However, the theoretical was not attained and it was unknown whether the drop was due to a leak or a reduction. The bomb was therefore recharged and heated to about 125° where a second pressure drop occurred. The product obtained was soluble in dilute acids but could not be isolated when made basic in any form but the polymer. It was concluded from its solubility in acids and from its tendency to polymerize that the product was m-aminobenzaldehyde.

(hh) Propargyl alcohol

(1) Propargyl alcohol (2-propyn-1-ol): 0.1 mole in 20 ml. ethanol

Catalyst: $\text{NH}_4\text{ReC}_4\text{-Li,EtNH}_2\text{-1-8-}$ (0.1 g.)

Conditions: 135-150°C./3930 psi./2.5 hrs.

Product: 84% recovery; 23% allyl alcohol, 77% n-propyl alcohol (gas chromatography)

It actually appeared that a pressure drop occurred at 135°C and then a second drop at about 150°C. It is possible if the reduction had been stopped at 135° allyl alcohol would have been the only product.

4. Miscellaneous Catalysts

(a) Butanone

(1) Butanone: 0.2 mole

Catalyst: $\text{KReO}_4\text{-K,NH}_3\text{-1-1-}$ (0.2 g.)

Conditions: 129°C./3710 psi./4 hrs.

Product: 82% recovery; 100% 2-butanol (ref. index)

(2) Butanone: 0.2 mole

Catalyst: $\text{Re}_2\text{O}_7\text{-K,NH}_3\text{-1-1-}$ (0.2 g.)

Conditions: 117°C./3800 psi./15 hrs.

Product: 83% recovery; 56% 2-butanol (ref. index)

(3) Butanone: 0.2 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Ca,NH}_3\text{-1-1-}$ (0.1 g.)

Conditions: 147°C./4100 psi./4 hrs.

Product: 100% recovery; 100% butanone, no reduction (ref. index)

The catalyst was difficult to prepare and shows no activity.

(4) Butanone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,EtNH}_2\text{-1-1-}$ (0.1 g.)

Conditions: $96^\circ\text{C.}/3537\text{ psi.}/12\text{ hrs.}$

Product: 83% recovery; 2% 2-butanol, 98% butanone (gas chromatography)

(5) Butanone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,EtNH}_2\text{-1-2-}$ (0.1 g.)

Conditions: $110^\circ\text{C.}/3720\text{ psi.}/2\text{ hrs.}$

Product: 96% 2-butanol; 4% butanone (gas chromatography)

(6) Butanone: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_2(\text{CH}_2)_2\text{NH}_2\text{-1-2-}$

Conditions: $120^\circ\text{C.}/3775\text{ psi.}/10\text{ hrs.}$

Product: 95% recovery; 20% 2-butanol (ref. index)

(b) Hexene-1

(1) Hexene-1: 0.2 mole

Catalyst: $\text{KReO}_4\text{-K,NH}_3\text{-1-1-}$ (0.2 g.)

Conditions: $100\text{-}190^\circ\text{C.}/3400\text{ psi.}/5\text{-}10\text{ minutes}$

Product: 86% recovery; 100% n-hexane (ref. index)

(2) Hexene-1: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na,EtNH}_2\text{-1-2-}$ (0.1 g.)

Conditions: $90^\circ\text{C.}/2600\text{ psi.}/8\text{ hrs.}$

Product: 78% recovery; 12% n-hexane, 49% hexene-1, 15% hexene-2, 24% hexene-3 (gas chromatography)

The pressure drop was evidently due to a bad leak, however, the catalyst apparently catalyzed the isomerization of the substrate.

(3) Hexene-1: 0.1 mole

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Li,NH}_2(\text{CH}_2)_2\text{NH}_2\text{-}$ (0.1 g.)

Conditions: $170^\circ\text{C.}/4000\text{ psi.}/4\text{ hrs.}$

Product: 80% recovery; 100% hexene-1, no reduction (ref. index)

(c) Benzene

(1) Benzene: 0.2 mole

Catalyst: $\text{Re}_2\text{O}_7\text{-K, NH}_3\text{-1-1-}$ (0.2 g.)

Conditions: 200°C., pressure and time data not known

Product: 81% recovery; 18% cyclohexane; 82% benzene (ref. index)

(d) Nitrobenzene

(1) Nitrobenzene: 0.2 mole in 40 ml. ethanol

Catalyst: $\text{Re}_2\text{O}_7\text{-K, NH}_3\text{-1-1-}$ (0.2 g.)

Conditions: 137°C./3275 psi./50 hrs.

Product: 100% recovery; 100% aniline (ref. index)

The method of analysis was as follows: The ethanol was stripped of then vacuum was applied and the higher boiling constituents distilled over. The percent aniline in the distillate was determined by a refractive index.

(2) Nitrobenzene: 0.1 mole in 25 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, EtNH}_2\text{-1-1-}$ (0.1 g.)

Conditions: 120°C./3825 psi./4 hrs.

Product: 100% recovery; 18% aniline; 82% nitrobenzene (gas chromatography)

(3) Nitrobenzene: 0.1 mole in 25 ml. ethanol

Catalyst: $\text{NH}_4\text{ReO}_4\text{-Na, EtNH}_2\text{-1-2-}$ (0.1 g.)

Conditions: 95°C./3380 psi./10 hrs.

Product: 100% aniline (gas chromatography)

5. Standard Catalysts

(a) Butanone

(1) Butanone: 0.1 mole

Catalyst: W-2 Raney nickel (0.1 g.)

Conditions: 30°C./2700 psi./18 hrs.

Product: 95% recovery; 100% butanone, no red'n (ref. index)

(2) Butanone: 0.1 mole

Catalyst: W-2 Raney nickel (0.1 g.)

Conditions: 90°C./2900 psi./2 hrs.

Product: 100% recovery; 95% 2-butanol (ref. index)

(b) Hexene-1

(1) Hexene-1: 0.1 mole

Catalyst: W-2 Raney nickel (0.1 g.)

Conditions: 30°C./3000 psi./10 minutes

Product: 100% n-hexane (ref. index)

(c) Cyclohexene

(1) Cyclohexene: 0.2 mole

Catalyst: W-6 Raney nickel (0.2 g.)

Conditions: 30°C./2950 psi./1 hr.

Product: 100% cyclohexane (ref. index)

(2) Cyclohexene: 0.2 mole

Catalyst: W-6 Raney nickel (0.2 g.)

Conditions: 30°C./50 psi./5 hrs.

Product: 64% cyclohexane (ref. index)

(3) Cyclohexene: 0.2 mole

Catalyst: Adam's catalyst (0.2 g.)

Conditions: 30°C./56 psi./2 hrs.

Product: 45% cyclohexane (ref. index)

(d) Styrene

(1) Styrene: 0.2 mole in 30 ml. ethanol

Catalyst: W-2 Raney nickel (0.2 mole)

Conditions: 35°C./2850 psi./1 hr.

Product: 100% ethylbenzene

(e) Nitrobenzene

(1) Nitrobenzene: 0.1 mole in 15 ml. ethanol

Catalyst: W-2 Raney nickel (0.1 g.)

Conditions: 30°C./2700 psi./27 hrs.

Product: 100% aniline (gas chromatography)

(f) Allylacetone

(1) Allylacetone: 0.1 mole in 10 ml. ethanol

Catalyst: W-2 Raney nickel (0.1 g.)

Conditions: 30°C./3000 psi./10 minutes

Product: 100% recovery; 100% 2-hexanone (gas chromatography)

(g) 2-Allylcyclohexanone

(1) 2-Allylcyclohexanone: 0.1 mole in 10 ml. ethanol

Catalyst: W-2 Raney nickel (0.1 g.)

Conditions: 30°C./2950 psi./2 hrs.

Product: 98% recovery; 100% 2-n-propylcyclohexanone

(h) Crotonaldehyde

(1) Crotonaldehyde: 0.1 mole in 10 ml. ethanol

Catalyst: W-2 Raney nickel (0.1 g.)

Conditions: 30°C./2900 psi./1 hr.

Product: 100% n-butyraldehyde

6. Determination of Valence State of Rhenium in Catalysts.

Due to the very high atomic weight of rhenium, very little change in rhenium composition occurs in passing from one rhenium oxide to another. Because of this fact, even though the analytical data had consistently shown that the rhenium content of the catalysts lay between 78 and 80%, it was impossible to definitely conclude what the compound was. An attempt was, therefore, made to determine the valence state of the rhenium material. The procedure used was as follows: The catalyst was first analyzed to determine if the rhenium content was consistent with previous preparations (cf. (u).p 45) After this was shown to be the case, a large sample (0.6 g.) of the catalyst was dried under vacuum at 200°C. for a period of about four hours. After cooling, the vacuum was replaced by an atmosphere of nitrogen and samples of the catalyst were then weighed out into Erlenmeyer flasks. An approximate 100% excess of potassium dichromate was also weighed out into the flasks.

A small amount of water and about one ml. of dilute sulfuric acid were added. The catalyst material dissolved readily when the resulting solution was heated. A large excess of potassium iodide was added, and then the iodine liberated was titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ using starch as an indicator. The number of equivalents of potassium dichromate required per mole of rhenium was then calculated at 4.51, 5.16, 5.17, 4.94 and 5.21 respectively. These results indicate that the rhenium in the catalyst was oxidized through a total of five valence states in reaching the perrhenate state. This would then establish the valence state of the rhenium in the catalyst material as being two, and the compound fitting both the analytical and oxidation state data would be $\text{ReO}\cdot 2\text{H}_2\text{O}$. This compound has been previously reported in the literature (cf. p.7). It is rather unusual that no water is lost under the strong heating conditions employed in the drying process.

IV. Discussion

A. Catalyst Preparation

The activity of catalysts prepared by reduction of ammonium perrhenate in liquid ammonia by sodium appeared to be essentially independent of the order of addition of the salt and alkali metal, and of the ratio of amounts of the reactants. The amount of solvent ammonia used also seemed to be of no consequence.

The primary reaction in the reduction of NH_4ReO_4 by alkali metals in liquid ammonia is undoubtedly reduction of the perrhenate ion to some lower valence state. A secondary reaction is also indicated by the fact that irrespective of the amount of alkali metal used, the ammonia solution always loses the blue color characteristic of the free metal. This second reaction most assuredly is a reaction between the excess alkali metal and the ammonia to form the alkali metal amide. The reaction is no doubt strongly catalyzed by the reduced rhenium material.

The reduction of rhenium heptoxide by sodium in liquid ammonia yields a catalyst with properties similar to that obtained from ammonium perrhenate. Due to its very hygroscopic nature and consequent difficulty in handling, few preparations using this salt were made.

The reduction of potassium perrhenate with sodium in liquid ammonia was totally unsuccessful. The sodium was completely used up and a yellow-brown material precipitated out, but very little catalyst material was produced. A possible explanation of this phenomenon is that the potassium was reduced in a metathetical reaction (cf. (c), p. 23) according to equation (1).



The free potassium thus produced would react rapidly with the ammonia according to equation (2). The potassium amide which resulted from reaction (2) would then be reduced to yield free potassium because of the markedly lower solubility of the sodium amide (cf. (b), p. 22). The net effect of this sequence of reactions would be the consumption of the sodium without a corresponding reduction of the perrhenate ion. The small amount of catalyst that was obtained showed no unusual activity.

In one method of preparation, ethanol was mixed with the liquid ammonia. The purpose of this procedure was to provide a medium which would easily liberate hydrogen for adsorption by the catalyst. The catalysts obtained exhibited good activity; however, the preparation gave rather poor yields due to the extensive reaction of the alkali metal with the ethanol.

The most important step in the preparation of an effective catalyst proved to be the complete removal of the alkali metal amide, which was always present, from the catalyst material (cf. Table 6). This was accomplished by washing the catalyst material by centrifugation and decantation until the washings were no longer basic to litmus or by extraction in a Soxhlet extractor. The most effective method found for complete removal of the amide was extraction in a Soxhlet extractor with dilute HCl.

During the HCl extraction process, the extraction solution usually became dark brown in color. It is unknown whether the catalyst material was dissolved or merely carried through the sintered glass filter disk. In all cases the bulk of the catalyst material was greatly decreased, primarily because of the removal of the amide which constituted a considerable percent of the untreated material. When the brown rhenium solution was made basic with ammonium hydroxide, the suspended or dissolved material appeared to coagulate and precipitate out, and the solution was left clear. The precipitated material evidently had the same composition as that which did not dissolve, because mixing the two caused no change in the rhenium content as determined by analysis.

A second extraction was usually performed using 95% ethanol. When this step was not performed, the catalyst would not disperse well in many substrates such as hexene-1 or benzene, but would settle out as a globule. Evidently the water could not be completely removed by simple washing.

The lithium-ammonia and lithium-ethylamine catalysts were prepared in the same manner as the sodium-ammonia catalysts. In all cases the catalysts were extracted with dilute HCl in the Soxhlet extractor, and in most cases stored under ethanol. As was the case with the sodium-ammonia catalysts, the order of addition, the reaction ratios, and the amount of solvent used apparently had little effect on the catalytic activity.

A number of preparations using potassium as the reducing agent were attempted. None were successful. The potassium reacted with the ammonia so rapidly that no reduction of the perrhenate occurred. In most cases no catalyst was obtained.

One preparation was attempted in which calcium was the reducing agent. A small amount of catalyst was obtained, but the calcium apparently was too insoluble in ammonia to serve as an effective reducing agent.

The reduction of ammonium perrhenate in ethylamine by sodium was also attempted. The sodium was too insoluble in the ethylamine and ammonia had to be liquified into the system in order for the reduction to take place. The catalyst obtained had good activity.

One catalyst was prepared in an aqueous medium. A seventy percent aqueous ethylenediamine-lithium system was used for the reduction of ammonium perrhenate. The yield was poor and the catalyst showed little activity.

Table 6

A COMPARISON OF THE CATALYTIC ACTIVITY OF SEVERAL CATALYSTS
ON DIFFERENT SUBSTRATES ILLUSTRATING THE EFFECT
OF ACID EXTRACTION OF THE CATALYST

Substrate	Catalyst	Extracted	Avg. Temp. °C.	Avg. Pres. psig.	Time Hours	Product ^a
Cyclohexanone	NH ₄ ReO ₄ -Na, NH ₃ -1-1-	no	205	3780	32	100% cyclohexanol
Cyclohexanone	NH ₄ ReO ₄ -Na, NH ₃ -3-1-	nc	172	3860	10	100% cyclohexanol
Cyclohexanone	NH ₄ ReO ₄ -Na, NH ₃ -4-1-	yes*	130	3735	3	70% cyclohexanol
Nitrobenzene	NH ₄ ReO ₄ -Na, NH ₃ -3-1-	no	202	3500	13	67% aniline
Nitrobenzene	NH ₄ ReO ₄ -Na, NH ₃ -9-1-	yes	175	3650	6	75% aniline
Cyclohexene	NH ₄ ReO ₄ -Na, NH ₃ -1-1-	no	250	4250	4	37% cyclohexane
Cyclohexene	NH ₄ ReO ₄ -Na, NH ₃ -9-8-	yes	120	3730	3	100% cyclohexane

a. The balance of the product in each case was unreduced substrate.

* The catalyst was not actually extracted but was washed free of sodium by centrifugation and decantation

Butanone was chosen as a convenient substrate against which to standardize the catalysts. In most cases good reduction could be obtained under relatively mild conditions, and the analysis of the reduction product was very easy (ref. index). It is significant that in spite of the variations employed in the preparation of the catalysts, they showed very little difference in activity. It is notable that for different catalyst preparations, by a particular method, the temperature range over which the reduction of butanone occurred was of the order of only about ten degrees. This indicates that within the limits of accuracy of the study their activities were identical (cf. 2-12, Table 7; 3-4, Table 8; 2-8, Table 9).

B. Analysis of Catalysts

Although the activity of all the catalysts was not entirely the same, analysis indicated that the chemical composition was in each case nearly identical.

In all cases the analyses indicated that the rhenium content of the catalysts was between 78 and 81%. This consistency indicates that the catalysts were a definite compound rather than an indefinite mixture.

The average value for the rhenium content of the catalysts, obtained by averaging a total of 46 analyses, was 79.5%. Valence state determinations (cf. p. 89) showed that the oxidation state of the rhenium was two, and therefore the catalyst was concluded to be the hydrated oxide, $\text{ReO} \cdot 2\text{H}_2\text{O}$. This compound has been reported previously in the literature (cf. reference 46).

Several catalysts were analyzed after being used for the reduction of a substrate. The catalysts used for the reduction of benzene and acetic acid, both of which required rather drastic conditions for reduction, were recovered as metallic rhenium. On the other hand, a catalyst used in the reduction of hexene-1, which required only mild conditions, was recovered unchanged.

Of the two methods of analysis employed, the gravimetric method seemed to give the most reliable results with the least amount of divergence. The spectrophotometric method offered some advantage in speed, but many variables apparently are inherent in the method and great care and consistency in procedure had to be exercised or poor results were obtained. One factor which continually caused difficulty in the method was the presence of excess oxidizing agent which had been used in the oxidation of the catalyst. When this was the case, the oxidizing agent interfered with the reduction of the perrhenate ion to the hexachlororhenate ion. Reducing agents such as sodium bisulfite were used in an attempt to destroy any excess oxidizing agent, but little success was obtained. It was also found that when absorbancy readings were made on the solutions immediately after dilutions, the results were erroneous. If the solutions were allowed to set several hours or over night the results were more accurate and consistent.

The errors which are inherent in spectrophotometric analysis procedures were also apparent. For instance, an error in reading of only 0.01 unit could lead to an error of one percent or more for the total rhenium content of the sample.

It was concluded that the spectrophotometric method of analysis was suitable for obtaining an approximate analysis, but where precision and accuracy were desired the gravimetric method was necessary.

C. Hydrogenations

1. Sodium-Ammonia Catalysts

The sodium-ammonia catalysts were evaluated using a variety of reducible substrates. Nitrobenzene was used in evaluating the activity of the catalyst toward the nitro group. Activity toward reduction of the olefinic bond was determined using hexene-1, cyclohexene, and styrene; and for a compound containing the carboxyl group acetic acid was used. A large number of different ketones were used in determining the catalysts activity toward the carbonyl group, and a very interesting relationship was shown to exist for these reductions. Allylacetone was used in an attempt to determine any selectivity in activity, for the reduction of the carbonyl group or olefinic bond, which the catalyst might exhibit.

The carbonyl group of ketones was reduced under varying conditions depending upon the nature of the compound. Acetone was by far the easiest of the ketones to reduce (ca. 80°C.), while 2-methyl-2-butanone (198°C.) was the most difficult. These two ketones were exceptions to a relationship which seemed to exist for all other ketones reduced. Other than the two exceptions, all the ketones containing an even number of carbon atoms in the principal chain seemed to reduce under milder conditions than those containing an odd number (cf. Figure 8 and Nos. 1-39, Table 7). Steric effects appeared to play an important role, 3-methyl-2-butanone and 4-methyl-2-pentanone, respectively, required much more drastic conditions for reduction than butanone and 2-pentanone or 3-pentanone. Furthermore cyclohexanone appeared to reduce more easily than cyclopentanone or cycloheptanone. Reduction of the carbonyl group conjugated to the benzene ring in acetophenone required somewhat more drastic conditions than the even-numbered series of ketones, but somewhat milder conditions than the odd-numbered series (cf. 40-41, Table 7).

2,3-Butanedione, 2,4-pentanedione and 2,5-hexanedione all reduced under relatively mild conditions (cf. 18, 23, 26, Table 7), but in all cases a variety of products was obtained. With 2,3-butanedione, it appeared that possibly a chelate compound may have been formed. One of the major components from the reduction of 2,4-pentanedione decomposed upon distillation.

As has been shown the case with other rhenium catalysts, the double bond most easily reduced was that conjugated with the benzenoid structure as in styrene. However, hexene-1 and cyclohexene were reduced under only slightly more drastic conditions, and the difference between their reduction temperature and that required for styrene was less than for most previously prepared rhenium catalysts. Hexene-2 required slightly more drastic conditions (cf. 42-54, Table 7).

The reduction of benzene required drastic conditions (cf. 55-60, Table 7) and in no case was the reduction complete.

Figure 8

TEMPERATURES NECESSARY FOR REDUCTION OF VARIOUS
KETONES USING SODIUM-AMMONIA CATALYSTS

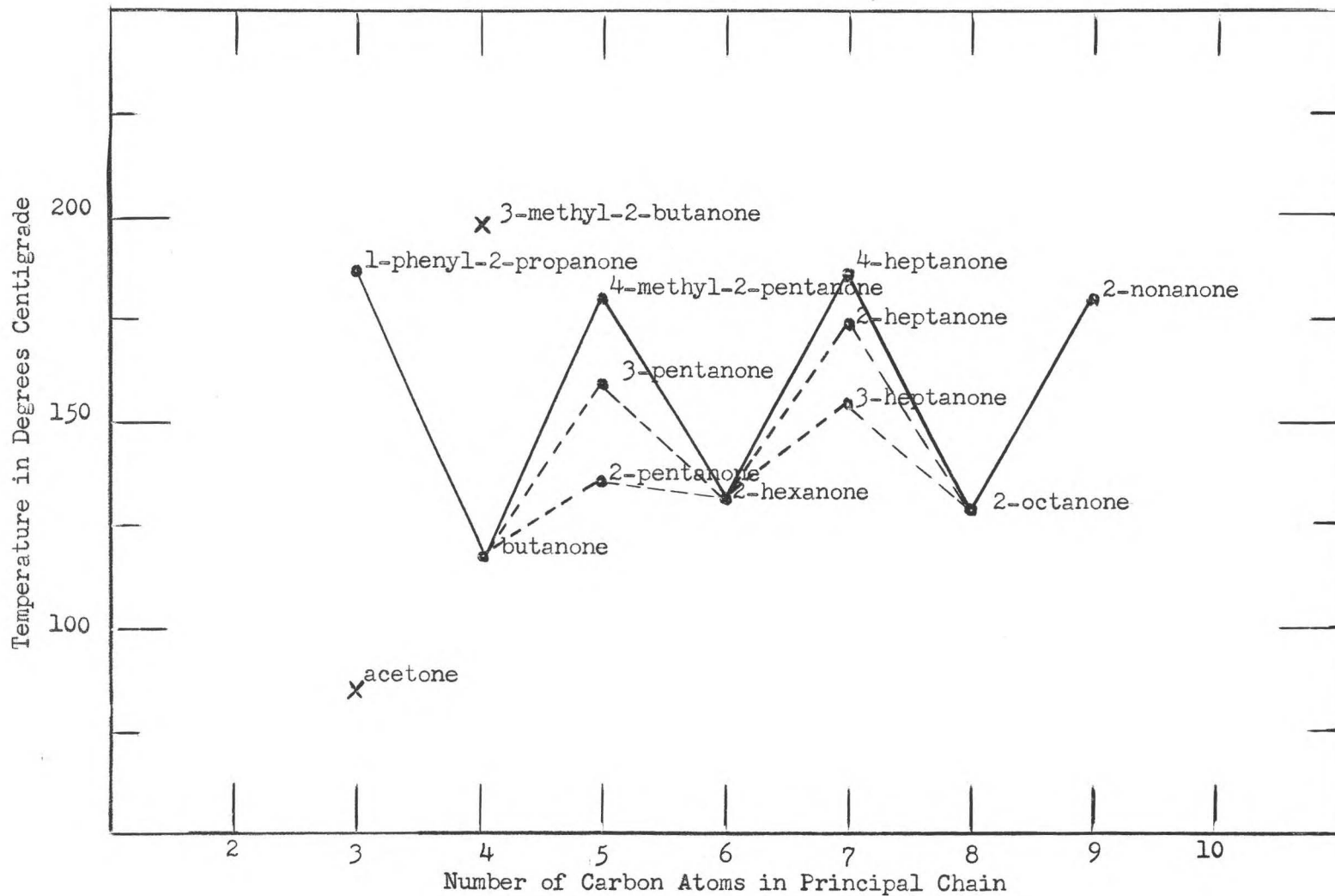


Table 7

HYDROGENATIONS PERFORMED USING SODIUM-AMMONIA CATALYSTS

No.	Substrate ^a	Catalyst	Avg. Temp. (°C.)	Avg. Pres. (psig.)	Time (hrs.)	Product ^b
1.	Acetone	NH ₄ ReO ₄ -Na, NH ₃ -9-3-	78	3270	10	100% isopropyl alcohol
2.	Butanone	NH ₄ ReO ₄ -Na, NH ₃ -4-1-	222	3910	6	96% 2-butanol
3.	Butanone	NH ₄ ReO ₄ -Na, NH ₃ -4-1-	100	3790	3.5	100% 2-butanol
4.	Butanone	NH ₄ ReO ₄ -Na, NH ₃ -5-1-	72	3100	4	100% 2-butanone
5.	Butanone	NH ₄ ReO ₄ -Na, NH ₃ -5-2-	128	3650	3	100% 2-butanol
6.	Butanone	NH ₄ ReO ₄ -Na, NH ₃ -6-1-	155	3835	4	100% 2-butanol
7.	Butanone	NH ₄ ReO ₄ -Na, NH ₃ -5-3-	120	3600	2	17% 2-butanol
8.	Butanone	NH ₄ ReO ₄ -Na, NH ₃ -8-1-	140	3760	2	100% 2-butanol
9.	Butanone	NH ₄ ReO ₄ -Na, NH ₃ -9-1-	120	3550	unknown	56% 2-butanol
10.	Butanone	NH ₄ ReO ₄ -Na, NH ₃ -9-3-	115	3590	8-10	54% 2-butanol 46% unknown
11.	Butanone	NH ₄ ReO ₄ -Na, NH ₃ -9-2-	116	3590	6	100% 2-butanol
12.	Butanone	NH ₄ ReO ₄ -Na, NH ₃ -9-6-	120	3610	12	100% 2-butanol
13.	Butanone	KReO ₄ -Na, NH ₃ -2-1-	130	3750	18	16% 2-butanol
14.	Butanone	Re ₂ O ₇ -Na, NH ₃ -1-1-	103	3550	12	100% 2-butanol
15.	Butanone	NH ₄ ReO ₄ -Na, NH ₃ , EtOH-1-1-	111	3570	14	100% 2-butanol
16.	3-methyl-2-butanone	NH ₄ ReO ₄ -Na, NH ₃ -9-6-	130-160	3850	12	100% 3-methyl-2-butanone
17.	3-methyl-2-butanone	NH ₄ ReO ₄ -Na, NH ₃ -9-6-	198	4335	7	100% 3-methyl-2-butanol
18.	2,3-Butanedione	NH ₄ ReO ₄ -Na, NH ₃ -9-3-	93	3590	7.5	50% 2,3-butanediol, four unidentified products
19.	2-Pentanone	NH ₄ ReO ₄ -Na, NH ₃ -9-6-	136	3790	11	100% 2-pentanol
20.	3-Pentanone	NH ₄ ReO ₄ -Na, NH ₃ -7-1-	175	3950	5	100% 3-pentanol
21.	3-Pentanone	NH ₄ ReO ₄ -Na, NH ₃ -9-3-	160	3820	6	100% 3-pentanol
22.	4-methyl-2-pentanone	NH ₄ ReO ₄ -Na, NH ₃ -9-3-	180	3850	5	100% 4-methyl-2-pentanol
23.	2,4-Pentanedione	NH ₄ ReO ₄ -Na, NH ₃ -9-3-	132	3500	12	50% 2,4-pentanediol, six unidentified products
24.	Cyclopentanone	NH ₄ ReO ₄ -Na, NH ₃ -9-6-	167	3925	6	100% cyclopentanol
25.	2-Hexanone	NH ₄ ReO ₄ -Na, NH ₃ -9-3-	135	3100	11.5	100% 2-hexanol
26.	2,5-Hexanedione	NH ₄ ReO ₄ -Na, NH ₃ -9-3-	121	3300	10.5	95% 2,5-hexanediol
27.	Cyclohexanone	NH ₄ ReO ₄ -Na, NH ₃ -1-1-	205	4200	20	100% cyclohexanol
28.	Cyclohexanone	NH ₄ ReO ₄ -Na, NH ₃ -3-1-	172	3860	10	100% cyclohexanol

Table 7, Continued

No.	Substrate ^a	Catalyst	Avg. Temp. (°C.)	Avg. Pres. (psig.)	Time (hrs.)	Product ^b
29.	Cyclohexanone	KReO ₄ -Na, NH ₃ -1-1-	205	4150	7	79% cyclohexanol
30.	Cyclohexanone	NH ₄ ReO ₄ -Na, NH ₃ -4-1-	165	3820	2	75% cyclohexanol
31.	Cyclohexanone	NH ₄ ReO ₄ -Na, NH ₃ -4-1-	160-175	3525	4	100% cyclohexanol
32.	Cyclohexanone	NH ₄ ReO ₄ -Na, NH ₃ -4-2-	130	3735	3	70% cyclohexanol
33.	2-Heptanone	NH ₄ ReO ₄ -Na, NH ₃ -9-3-	172	3945	3.5	96% 2-heptanol
34.	3-Heptanone	NH ₄ ReO ₄ -Na, NH ₃ -9-6-	152	3735	5	100% 3-heptanol
35.	4-Heptanone	NH ₄ ReO ₄ -Na, NH ₃ -9-3-	186	3925	2	98% 4-heptanol
36.	Cycloheptanone	NH ₄ ReO ₄ -Na, NH ₃ -9-7-	175	3980	8.5	100% cycloheptanol
37.	2-Octanone	NH ₄ ReO ₄ -Na, NH ₃ -9-3-	130	3615	6	86% 2-octanol
38.	2-Nonanone	NH ₄ ReO ₄ -Na, NH ₃ -9-6-	178	3960	6	100% 2-nonanol
39.	Phenyl-2-propanone	NH ₄ ReO ₄ -Na, NH ₃ -9-3-	184	3970	1.25	100% phenyl-2-propanone
40.	Acetophenone	NH ₄ ReO ₄ -Na, NH ₃ -4-2-	125	3600	9	67% methylphenylcarbinol
41.	Acetophenone	NH ₄ ReO ₄ -Na, NH ₃ -6-1-	160	3760	6	74% methylphenylcarbinol
42.	Hexene-1	NH ₄ ReO ₄ -Na, NH ₃ -7-1-	135	3850	16	100% hexene-1
43.	Hexene-1	NH ₄ ReO ₄ -Na, NH ₃ -9-2-	122	3515	4	100% n-hexane
44.	Hexene-1	Re ₂ O ₇ -Na, NH ₃ -1-1-	100-300	3925	0.5	85% n-hexane
45.	Hexene-1	Re ₂ O ₇ -Na, NH ₃ -1-1-	124	3625	12	90% n-hexane
46.	Hexene-1	NH ₄ ReO ₄ -Na, NH ₃ , EtOH-1-1-	127	3665	6	100% n-hexane
47.	Hexene-2	NH ₄ ReO ₄ -Na, NH ₃ -5-2-	151	3600	3	100% n-hexane
48.	Cyclohexene	NH ₄ ReO ₄ -Na, NH ₃ -3-1-	125	3400	10	100% cyclohexene
49.	Cyclohexene	NH ₄ ReO ₄ -Na, NH ₃ -1-1-	250	4250	4	37% cyclohexane
50.	Cyclohexene	NH ₄ ReO ₄ -Na, NH ₃ -4-1-	212	4152	11	100% cyclohexane
51.	Cyclohexene	NH ₄ ReO ₄ -Na, NH ₃ -9-8-	120	3730	3	100% cyclohexane
52.	Styrene (ethanol)	NH ₄ ReO ₄ -Na, NH ₃ -5-1-	108	3465	3	85% ethylbenzene 15% polymer
53.	Styrene (ethanol)	NH ₄ ReO ₄ -Na, NH ₃ -6-1-	105	3485	6	37% ethylbenzene 33% polymer
54.	Styrene (ethanol)	NH ₄ ReO ₄ -Na, NH ₃ -9-7-	110	3565	0.75	100% ethylbenzene
55.	Benzene	NH ₄ ReO ₄ -Na, NH ₃ -5-2-	170	3740	4	44% cyclohexane
56.	Benzene	NH ₄ ReO ₄ -Na, NH ₃ -4-2-	240	4780	unknown	12% cyclohexane
57.	Benzene	Re ₂ O ₇ -Na, NH ₃ -1-1-	202	4225	10	67% cyclohexane
58.	Benzene	NH ₄ ReO ₄ -Na, NH ₃ , EtOH-2-1-	160	3000	36	100% benzene
59.	Benzene	NH ₄ ReO ₄ -Na, NH ₃ -9-7-	240	4875	8	5% cyclohexane
60.	Benzene	NH ₄ ReO ₄ -Na, NH ₃ -8-1-	222	4450	12	34% cyclohexane

Table 7, Continued

No.	Substrate ^a	Catalyst	Avg. Temp. (°C.)	Avg. Pres. (psig.)	Time (hrs.)	Product ^b
61.	Nitrobenzene(ethanol)	NH ₄ ReO ₄ -Na, NH ₃ -3-1-	202	3500	18	67% aniline
62.	Nitrobenzene(ethanol)	NH ₄ ReO ₄ -Na, NH ₃ -7-1-	160	3250	6	88% aniline
63.	Nitrobenzene(ethanol)	NH ₄ ReO ₄ -Na, NH ₃ -9-1-	175	3650	12	75% aniline
64.	Nitrobenzene(ethanol)	NH ₄ ReO ₄ -Na, NH ₃ , EtOH-1-1-	127	3225	2.5	94% aniline
65.	Nitrobenzene(ethanol)	NH ₄ ReO ₄ -Na, NH ₃ , EtOH-1-2-	135	3900	unknown	67% aniline
66.	Nitrobenzene(ethanol)	NH ₄ ReO ₄ -Na, NH ₃ -5-3-	130	3770	6	12% aniline
67.	Nitrobenzene(ethanol)	NH ₄ ReO ₄ -Na, NH ₃ -9-6-	195	4260	18	60% aniline
68.	Acetic Acid(water)	NH ₄ ReO ₄ -Na, NH ₃ -9-8-	178	4060	7	100% ethanol
69.	Allylacetone	NH ₄ ReO ₄ -Na, NH ₃ -9-7-	119	3520	6	71% 2-hexanone 29% 2-hexanol

a. Except as indicated no solvent was used.

b. The balance of the product in each case was the unreduced substrate.

Nitrobenzene required relatively drastic conditions for its reduction (ca. 175°C.). The catalyst prepared in the ethanol-ammonia mixture was appreciably better for this reduction than any of the other catalysts. The reduction in all cases was less than 100%. Difficulty in reduction of nitrobenzene is apparently a characteristic of all rhenium catalysts so far prepared with the exception of rhenium heptasulfide, which reduced it under very mild conditions (cf 61-67, Table 7 and 3, Table 12).

The reduction of allylacetone indicated a selectivity of the catalyst toward reduction of the olefinic bond. The material was reduced in ethanol solution at about 120°C. to give a good yield of the saturated ketone. A minor product was the saturated alcohol which resulted from complete reduction (cf. 69, Table 7).

Possibly the most significant reduction performed was the hydrogenation of acetic acid in water. The reduction took place under good conditions (ca. 175°C.) yielding only the alcohol. No acid or ester could be detected (cf. 68, Table 7).

2. Lithium-Ammonia Catalysts

The lithium-ammonia catalysts were evaluated against the same substrates as the sodium-ammonia catalysts. 2-Allylcyclohexanone as well as allylacetone was used as a means of evaluating the selectivity of the catalyst. A reduction was also attempted on the nitrile group in capronitrile.

The carbonyl group in acetone and butanone was reduced under mild conditions (cf. 1-4, Table 8) to give good yields of the corresponding alcohol with the lithium-ammonia catalysts. Cyclohexanone was reduced under approximately the same conditions, but acetophenone required conditions somewhat more drastic (ca. 160°C.). Its reduction also produced an appreciable amount of ethylbenzene as well as methyl-phenylcarbinol.

The olefinic bond in styrene was the most easily reduced of the olefinic bonds. Its reduction was accomplished at about 70°C. Hexene-1 was reduced at about 100°C., but isooctene required very drastic conditions (cf. 7-10, Table 8). This would probably be expected in light of steric considerations. Cyclohexene was reduced under conditions similar to that required by hexene-1.

The reduction of benzene required drastic conditions (ca. 200°C.) and only a rather poor yield of cyclohexane was obtained.

Nitrobenzene on the other hand was reduced comparatively easily at about 125°C. to give good yields of aniline. Nitropropane was reduced at about the same temperature, but the products evidently reacted with the ethanol which had been used as a solvent and a total of eight or nine components resulted. The product smelled strongly of amines, but none of the components were identified.

Capronitrile was reduced under relatively mild conditions (185°C.) for the nitrile group; however, as was the case with nitropropane, numerous products were obtained, and none were identified. The product smelled strongly of amines.

Table 8

HYDROGENATIONS PERFORMED USING LITHIUM-AMMONIA CATALYSTS

No.	Substrate	Prep. Number ^a	Solvent	Avg. Temp. (°C.)	Avg. Pres. (psig.)	Time (hrs.)	Product ^b
1.	Acetone	7	none	125	3770	0.5	100% isopropyl alcohol
2.	Butanone	1	none	111	3475	4	100% 2-butanol
3.	Butanone	1	none	100	3620	15	98% 2-butanol
4.	Butanone	2	none	120	3870	<12	94% 2-butanol
5.	Cyclohexanone	4	none	120	3800	15	100% cyclohexanone
6.	Acetophenone	4	none	158	3880	5	64% methylphenylcarbinol 36% ethylbenzene
7.	Hexene-1	4	none	96	3600	10	100% n-hexane
8.	Hexene-1	7	none	104	3540	0.5	100% n-hexane
9.	Isooctene	7	none	178-224	4300	0.5	100% isooctene
10.	Styrene	4	ethanol	70	3275	12	56% ethylbenzene
11.	p-Chlorostyrene	4	ethanol	82-108	3475	13	52% p-chloroethylbenzene 48% polymer
12.	Cyclohexene	3	none	99	3610	22	100% cyclohexane
13.	Benzene	1	none	206	4400	12	34% cyclohexane
14.	Nitrobenzene	1	ethanol	113	3380	18	75% aniline
15.	Nitrobenzene	2	ethanol	125	2845	25	51% aniline
16.	Nitrobenzene	1	ethanol	90-110	3400	8	100% aniline
17.	Nitropropane	2	ethanol	135	3700	14	Unidentified
18.	Capronitrile	3	ethanol	185	4300	8	Unidentified
19.	Capronitrile	8	none	<200	4800	1	100% capronitrile
20.	Acetic Acid	4	none	180	4060	18	54% ethanol 46% ethyl acetate
21.	Allylacetone	2	ethanol	81	3350	6	72% 2-hexanone 28% 2-hexanol
22.	2-Allylcyclohexanone	6	ethanol	120	3650	<16	82% 2-propylcyclohexanone
23.	2-Allylcyclohexanone	2	ethanol	123	3800	14	88% 2-propylcyclohexanone 4% 2-propylcyclohexanol
24.	o-Phenylenediamine	4	Skelly Solve	250	4950	13	100% o-phenylenediamine

a. The catalyst code in each case was $\text{NH}_4\text{ReO}_4\text{-Li, NH}_3\text{-1-}$, therefore only the final digit which indicates the preparation number is given.

b. The balance of the product in each case was the unreduced substrate.

Acetic acid was reduced at about 180°C. to give a fair yield of the alcohol and a good yield of the ester (cf. 20, Table 8). No unreduced acid was present. After this experiment had been performed, it was discovered that when water was used as a solvent for the reduction of carboxylic acids the product obtained was usually the alcohol instead of the ester. It is therefore very possible that if water had been used in this reduction the product would have been principally the alcohol.

The reduction of allylacetone and 2-allylcyclohexanone indicated the selectivity of the catalyst toward olefinic bond hydrogenation in preference to carbonyl group reduction. This would probably be expected in light of the somewhat milder conditions required for the reduction of hexene-1 as compared to butanone. Both allylacetone and 2-allylcyclohexanone gave the saturated ketone as the major component of reduction, and either the alcohol resulting from complete reduction or the unreduced substrate as the minor component (cf. 21-23, Table 8).

One unsuccessful attempt was made to reduce *o*-phenylenediamine at 250°C.

3. Lithium-Ethylamine Catalysts

The lithium-ethylamine catalysts, as well as being evaluated against the substrates used for the Na-NH₃ and the Li-NH₃ catalysts, were used in the reduction of a series of carboxylic acids. These hydrogenations are probably some of the most important reductions performed in this investigation.

As with the previously discussed catalysts, acetone was the most easily reduced of all the ketones used. It was reduced at 55°C. to give a 30% yield of isopropyl alcohol. Butanone was reduced in all attempts at a temperature of about 90°C. Cyclohexanone was reduced easily at about 120°C. in only 2.5 hours. The short period of reduction indicates that the substrate could probably have been reduced at a somewhat lower temperature (cf. 9, Table 9).

Hexene-1 was reduced at ca. 120°C., but cyclohexene usually required a temperature of 135-150°C. One reduction of cyclohexene; however, occurred at 105°C. and gave 100% cyclohexane. Styrene, as was the case with the catalysts previously discussed, was the easiest of all substrates to reduce. In the only reduction which was attempted, styrene in ethanol was reduced at room temperature to give a 64% yield of ethylbenzene. This was the only room temperature reduction obtained throughout the course of the work (cf. 10, 12-15, Table 9).

In contrast to the easy reduction of styrene, 1-phenylbutene-2 required a temperature of 170°C. before reduction would take place. Likewise isooctene was reduced only to the extent of eight percent at 120°C. and undoubtedly somewhat more drastic conditions would be necessary in order to obtain a good reduction (cf. 11, 16, Table 9).

In one experiment, benzene was reduced at 179°C. to give a 51% yield of cyclohexane. However, the period of reduction was 29 hours. Most reductions of benzene required rather drastic conditions (220-225°C.) and 50% reduction appeared to be about the maximum attainable. Toluene yielded 35% methylcyclohexane when reduced at about 225°C. for 35 hours (cf. 17-21, Table 9).

Table 9

HYDROGENATIONS PERFORMED USING LITHIUM-ETHYLAMINE CATALYSTS

No.	Substrate	Prep. Number ^a	Solvent	Avg. Temp. (°C.)	Avg. Pres. (psig.)	Time (hrs.)	Product ^b
1.	Acetone	6	none	55	3000	15	30% isopropyl alcohol
2.	Butanone	1	none	85	3570	<12	86% 2-butanol
3.	Butanone	2	none	90	3500	15	97% 2-butanol
4.	Butanone	5	none	70-100	3550	1.5 - 2	74% 2-butanol
5.	Butanone	1	none	90	3500	24	35% 2-butanol
6.	Butanone	6	none	95	3525	8	100% 2-butanol
7.	Butanone	6(dired)	none	115	3000	3	3% 2-butanol
8.	Butanone	9	none	100	2925	2.5	100% 2-butanol
9.	Cyclohexanone	4	none	119	3655	2.5	100% cyclohexanol
10.	Hexene-1	4	none	119	3655	2.5	100% n-hexane
11.	Isooctene	2	none	120	3875	12	8% isooctane
12.	Cyclohexene	1	none	105	3600	16	100% cyclohexane
13.	Cyclohexene	5	none	146	4000	2.5	100% cyclohexane
14.	Cyclohexene	10	none	149	3930	2	100% cyclohexane
15.	Styrene	5	ethanol	30	2850	11	64% ethylbenzene
16.	1-Phenylbutene-2-	8	none	171	3950	2.5	100% n-butylbenzene
17.	Benzene	1	none	200-250	4700	3	50% cyclohexane
18.	Benzene	2	none	208	4560	1.5	22% cyclohexane
19.	Benzene	4	none	179	4050	29	51% cyclohexane
20.	Benzene	2	none	250	4800	6	100% benzene
21.	Toluene	3	none	222	4450	35	35% methylcyclohexane
22.	Allyl bromide	5	ethanol	135	3700	7	Unidentified
23.	Nitrobenzene	1	ethanol	106	3210	7	91% aniline
24.	Nitrobenzene	10	ethanol	126	3400	3	100% aniline
25.	Nitropropane	6	none	114	2600	<16	Unidentified
26.	Pyridine	9	ethanol	215	4335	7	100% piperidine
27.	Acetic Acid	2	none	124	3750	29	3% ethanol 73% ethyl acetate
28.	Acetic Acid	6	none	<230	unknown	unknown	79% ethanol 21% ethyl acetate
29.	Acetic Acid	9	water	145	3950	4.5	100% ethanol
30.	Propionic Acid	3	none	145-175	4150	1	25% n-prppyl alcohol 25% n-propyl propionate

Table 9, Continued

No.	Substrate	Prep. Number ^a	Solvent	Avg. Temp. (°C.)	Avg. Pres. (psig.)	Time (hrs.)	Product ^b
31.	Propionic Acid	9	water	162	3885	6	100% n-propyl alcohol
32.	Isobutyric Acid	6	none	<240	unknown	unknown	40% isobutyl alcohol 52% isobutyl isobutyrate
33.	Isobutyric Acid	10	water	172	4025	5	95% isobutyl alcohol 5% isobutyl isobutyrate
34.	Valeric Acid	10	water	168	3890	7	87% n-pentyl alcohol 13% n-pentyl valerate
35.	Caproic	10	water	177	4070	3	73% n-hexyl alcohol 27% n-hexyl caproate
36.	Caprylic Acid	10	water	173	4080	5	100% 1-octanol
37.	Capric Acid	10	water	173	3725	6	100% 1-decanol
38.	Lauric Acid	10	water	170-184	4100	7	100% 1-dodecanol
39.	Benzoic Acid	10	water	198	4090	10	100% toluene
40.	Nitrocyclohexane	10	ethanol	120	3475	7	100% cyclohexylamine
41.	Capronitrile	6	none	135-150	3900	6	100% capronitrile
42.	Allylacetone	5	ethanol	68	3070	<13	91% 2-hexanone
43.	Allylacetone	5	ethanol	100	3475	12	74% 2-hexanone 26% 2-hexanol
44.	Allylacetone(poisoned)	10	ethanol	155	4200	2.5	14% 2-hexanone 26% 5-hexene-2-ol
45.	2-Allylcyclohexanone	5	ethanol	125	3700	6	73% 2-propylcyclohexanone 22% 2-propylcyclohexanol
46.	Crotonaldehyde	6	none	88	3400	8	9% crotyl alcohol
47.	Crotonaldehyde	6	ethanol	140	3950	20	100% n-butyl alcohol
48.	Crotonaldehyde	10	ethanol	92	3475	12	100% crotonaldehyde
49.	Crotonaldehyde	10	ethanol	100	3650	10	50% n-butyraldehyde
50.	m-Nitroacetophenone	10	ethanol	107-117	3870	24	100% m-aminoacetophenone
51.	p-Nitrophenylacetic A.	8	water	157	3750	2.5	39% polymer 61% p-aminophenylacetic acid
52.	Nitrophenylmethane	8	ethanol	136	3750	15	16% nitrophenylmethane 20% benzylamine

Table 9, Continued

No.	Substrate	Prep. Number ^a	Solvent	Avg. Temp. (°C.)	Avg. Pres. (psig.)	Time (hrs.)	Product ^b
53.	<u>m</u> -Nitrostyrene	9	ethanol	118	3690	1	100% <u>m</u> -aminostyrene
54.	<u>m</u> -Nitrobenzaldehyde	9	ethanol	124	3720	10	100% <u>m</u> -aminobenzaldehyde
55.	Propargyl alcohol	9	ethanol	135-150	3930	2.5	23% allyl alcohol 77% <u>n</u> -propyl alcohol

a. The catalyst code in each case was $\text{NH}_4\text{ReO}_4\text{-Li,EtNH}_2\text{-1-}$, therefore only the final digit which indicates the preparation number is given.

b. The balance of the product in each case was the unreduced substrate.

Table 10

HYDROGENATIONS PERFORMED USING MISCELLANEOUS RHENIUM CATALYSTS

No.	Substrate	Catalyst Code	Avg. Temp. (°C.)	Avg. Pres (psig.)	Time (hrs.)	Product
1.	Butanone	$\text{KReO}_4\text{-K, NH}_3\text{-1-1-}$	129	3710	4	100% 2-butanol
2.	Butanone	$\text{Re}_2\text{O}_7\text{-K, NH}_3\text{-1-1-}$	117	3800	15	56% 2-butanol
3.	Butanone	$\text{NH}_4\text{ReO}_4\text{-Ca, NH}_3\text{-1-1-}$	147	4100	4	100% butanone
4.	Butanone	$\text{NH}_4\text{ReO}_4\text{-Na, EtNH}_2\text{-1-1-}$	96	3575	12	98% 2-butanol
5.	Butanone	$\text{NH}_4\text{ReO}_4\text{-Na, EtNH}_2\text{-1-2-}$	110	3720	2	96% 2-butanol
6.	Butanone	$\text{NH}_4\text{ReO}_4\text{-Li, NH}_2(\text{CH}_2)_2\text{NH}_2\text{-1-2-}$	120	3775	10	20% 2-butanol
7.	Hexene-1	$\text{KReO}_4\text{-K, NH}_3\text{-1-1-}$	100-190	3400	10 min.	100% hexane
8.	Hexene-1	$\text{NH}_4\text{ReO}_4\text{-Na, EtNH}_2\text{-1-2-}$	90	2600	8	12% hexane 49% hexene-1 15% hexene-2 24% hexene-3
9.	Hexene-1	$\text{NH}_4\text{ReO}_4\text{-Li, NH}_2(\text{CH}_2)_2\text{NH}_2\text{-1-2-}$	170	4000	4	100% hexene-1
10.	Benzene	$\text{Re}_2\text{O}_7\text{-K, NH}_3\text{-1-1-}$	200	unknown	unknown	18% cyclohexane
11.	Nitrobenzene (ethanol)	$\text{Re}_2\text{O}_7\text{-K, NH}_3\text{-1-1-}$	137	3275	50	100% aniline
12.	Nitrobenzene (ethanol)	$\text{NH}_4\text{ReO}_4\text{-Na, EtNH}_2\text{-1-1-}$	120	3825	4	18% aniline
13.	Nitrobenzene (ethanol)	$\text{NH}_4\text{ReO}_4\text{-Na, EtNH}_2\text{-1-2-}$	95	3380	10	100% aniline

One attempt was made to reduce allyl bromide; however, ethanol was used as solvent and apparently several reactions occurred. The reduction was conducted at 135°C. and a total of eight components were present in the reduction product. None were identified.

Nitrobenzene and nitrocyclohexane were reduced under conditions similar to those required for hexene-1 (cf. 23-24, 40, Table 9). One attempt was made to reduce nitropropane. The reduction took place under rather mild conditions (cf. 25, Table 9), but a variety of products which could not be identified resulted.

The reduction of pyridine was the only reduction attempted on a heterocyclic compound. It was reduced in ethanolic solution at about the same temperature as that required for benzene; however, unlike the reductions of benzene, the substrate was 100% reduced, piperidine being the only product.

Probably the most notable of all reductions performed with these catalysts is the reduction of carboxyl groups. An important observation dealing with these reductions is that when water was used as a solvent, the product obtained under essentially the same conditions as those required when no water was used, was primarily the alcohol instead of the ester. The mildest reduction obtained on a carboxylic acid was the reduction of acetic acid (no water) at 124°C. In this reduction a good yield of the ester was obtained, but almost no alcohol (cf. 27, Table 9). Possibly the best reduction performed on an acid was the reduction of acetic acid in water at 145°C. to produce ethanol exclusively (cf. 29, Table 9).

In most of the acid reductions, the bomb was heated directly to a temperature at which it was supposed the material would reduce at a good rate, and no attempt was made to obtain minimal conditions. The rate of reduction; however, in several cases indicated that the reduction would have occurred at a reasonable rate at a somewhat lower temperature.

Propionic acid in water was reduced quantitatively to the alcohol at 162°C. in six hours. Isobutyric acid under similar conditions yielded principally the alcohol and a trace of the ester. Valeric, caproic, caprylic, capric and lauric acids in water solution were all reduced to the alcohol exclusively at temperature of from 162°C. to 180°C. (cf. 28-39, Table 9).

The reduction of benzoic acid in water required a temperature of nearly 200°C. and the product obtained was toluene (cf. 39, Table 9).

Allylacetone in ethanol was reduced at about 70°C. to give a good yield of 2-hexanone and a small amount of the unreduced substrate. Another reduction performed at 100°C. gave a good yield of the ketone and the totally reduced product. One other reduction was attempted on the substrate which gave possibly very significant results. The bomb had been partially poisoned by a previous pyridine reduction when the allylacetone reduction was performed. Conditions considerably more drastic than usual (155°C.) were necessary and the product besides containing unreduced substrate contained almost twice as much 5-hexene-2-ol as 2-hexanone. This is the reverse of the normal behavior of this catalyst. It appears that the pyridine's partial poisoning of the catalyst caused this effect (cf. 42-44, Table 9).

2-Allylcyclohexanone was reduced at 125°C. to give a good yield of the saturated ketone and some completely reduced product.

Several reductions were attempted on crotonaldehyde. The first performed at about 90°C. produced about 10% crotyl alcohol. This product probably would not be expected in the light of the products obtained from allylacetone and 2-allylcyclohexanone; however, it is in line with what would be predicted on the basis of the ease of reduction of hexene-1 and butanone. Another reduction performed at 140°C. resulted in the totally reduced product. Two more reductions were attempted after the poisoning of the bomb by pyridine as mentioned above. The first was conducted at 92°C. and no reduction was obtained. The second was conducted at 100°C. and the product obtained was n-butyraldehyde. This reduction illustrates a complete reversal of the effect of poisoning as illustrated in the case of allylacetone (cf. 46-49, Table 9).

m-Nitroacetophenone in ethanol was reduced under mild conditions to m-aminoacetophenone. This reduction, as well as others that follow, is in accordance with results obtained in previous investigations in which attempts were made with rhenium catalysts to selectively reduce some group other than the nitro group. With most rhenium catalysts the nitro group has proved rather difficult to reduce. However, all attempts to selectively hydrogenate another group, which normally is reduced under milder conditions than the nitro group, have been unsuccessful. The reduction of m-nitrobenzaldehyde resulted in a polymer which was concluded to be a condensation product of m-aminobenzaldehyde.

The reduction of p-nitrophenylacetic acid in water yielded a condensation product as well as p-aminophenylacetic acid. Nitrophenylmethane in ethanol, on reduction, besides yielding benzylamine, gave a solid material which apparently was the same as that which was observed to result when benzylamine and nitrophenylmethane were mixed, presumably the salt. The reduction of m-nitrostyrene gave m-aminostyrene.

Propargyl alcohol in ethanol was reduced between 135 and 150°C. to give both allyl alcohol and n-propyl alcohol. The reduction period was short, and the reduction possibly would have occurred under somewhat milder conditions to give a better yield of the unsaturated alcohol.

4. Miscellaneous Catalysts

Butanone was reduced under relatively good conditions by $KReO_4$ -K, NH_3 -1-1-, Re_2O_7 -K, NH_3 -1-1-, and NH_4ReO_4 -Na, $EtNH_2$ -1-1- to give good yields of the alcohol (cf. 1-6, Table 10).

When NH_4ReO_4 -Na, $EtNH_2$ -1-2- was used in an attempt to reduce hexene-1, the substrate was isomerized and all three isomers as well as the completely reduced product resulted. The reduction occurred at about 90°C. This is the lowest temperature at which any of the catalysts were able to reduce hexene-1.

Nitrobenzene was reduced by several of the catalysts under fairly mild conditions. Again the activity of the catalyst NH_4ReO_4 -Na, $EtNH_2$ -1-2- was demonstrated by reducing the substance in 100% yield at 95°C.

D. A Comparison of the Catalysts Prepared in this Investigation

The catalytic activities of the sodium-ammonia, lithium-ammonia, and lithium-ethylamine catalysts were, in general, very similar. It is noticeable however, that for almost all substrates, the lithium-ethylamine catalyst was somewhat superior, and in most cases the lithium-ammonia catalyst appeared to occupy a rather intermediate position. Some peculiarities were apparent as will be mentioned below.

Acetone was reduced most easily by the Li-EtNH₂ catalyst, secondly by the Na-NH₃ catalyst and thirdly by the Li-NH₃ catalyst. The Li-NH₃ catalyst required a temperature 70° higher than that required by the Li-EtNH₂ catalyst; however, the period of reduction was only 0.5 hours as compared to 15 hours (cf. 1, Table 11).

With butanone and cyclohexanone the Li-EtNH₂ was most active while the Na-NH₃ catalyst was least active (cf. 2-3, Table 11).

For the olefinic bond in Hexene-1 and cyclohexene, the Li-NH₃ catalyst was most effective; the Li-EtNH₂ catalyst was intermediate in activity, and the Na-NH₃ catalyst was the least effective (cf. 4-5, Table 11).

For styrene, the order of increasing difficulty of reduction for the catalysts was Li-EtNH₂ < Li-NH₃ < Na-NH₃ (cf. 6, Table 11).

All the catalysts encountered great difficulty in reducing benzene and it is impossible to make a statement as to which one was the most successful (cf. 7, Table 11).

Acetic acid was reduced under essentially the same conditions by all the catalysts. Possibly the Li-EtNH₂ catalyst was somewhat more effective (cf. 8, Table 11).

The reduction of nitrobenzene was rather difficult for all the Na-NH₃ catalysts except the one which was prepared in an ethanol-ammonia solution. The activity of this catalyst toward the reduction of nitrobenzene was approximately the same as that exhibited by the Li-EtNH₂ and Li-NH₃ catalysts (cf. 9, Table 11).

Several peculiarities of the catalysts may also be noted. While the Li-NH₃ and Na-NH₃ catalysts reduced butanone with approximately the same ease as hexene-1, the Li-EtNH₂ catalyst reduced it under milder conditions. Similarly the Li-NH₃ and Li-EtNH₂ catalysts reduced cyclohexene at conditions only slightly higher than that required by for butanone, but the Na-NH₃ catalysts required conditions considerably more drastic.

Also worthy of mention is one catalyst classed under miscellaneous. This catalyst, which carries the code NH₄ReO₄-Na₂EtNH₂-1-, catalyzed the reduction of nitrobenzene at 95°C. and hexene-1 at 90°C. (cf. 8, 13, Table 10). These conditions are the mildest obtained for the reduction of these substrates in this investigation. The catalyst was not used extensively because of the difficulty of its preparation.

Table 11

A COMPARISON OF THE CATALYTIC ACITIVITY OF SODIUM-AMMONIA,
LITHIUM-AMMONIA, AND LITHIUM-ETHYLAMINE CATALYSTS
FOR THE REDUCTION OF VARIOUS SELECTED SUBSTRATES

No.	Substrate	Catalyst	Avg. Temp. (°C.)	Avg. Pres. (psig.)	Time (hrs.)	Product ^a
1.	Acetone	NH ₄ ReO ₄ -Na, NH ₃ -9-3-	78	3270	10	100% isopropyl alcohol
		NH ₄ ReO ₄ -Li, NH ₃ -1-7-	125	3770	0.5	100% isopropyl alcohol
		NH ₄ ReO ₄ -Li, EtNH ₂ -1-6-	55	3000	15	30% isopropyl alcohol
2.	Butanone	NH ₄ ReO ₄ -Na, NH ₃ -5-2-	128	3650	3	100% 2-butanol
		NH ₄ ReO ₄ -Li, NH ₃ -1-1-	111	3475	4	100% 2-butanol
		NH ₄ ReO ₄ -Li, EtNH ₂ -1-9-	100	2925	2.5	100% 2-butanol
3.	Cyclohexanone	NH ₄ ReO ₄ -Na, NH ₃ -4-1-	160-170	3525	4	100% cyclohexanol
		NH ₄ ReO ₄ -Li, NH ₃ -1-4-	120	3800	15	100% cyclohexanone
		NH ₄ ReO ₄ -Li, EtNH ₂ -1-4-	119	3655	2.5	100% cyclohexanol
4.	Hexene-1	NH ₄ ReO ₄ -Na, NH ₃ -9-2-	122	3515	4	100% <u>n</u> -hexane
		NH ₄ ReO ₄ -Li, NH ₃ -1-7-	104	3540	0.5	100% <u>n</u> -hexane
		NH ₄ ReO ₄ -Li, EtNH ₂ -1-4-	119	3655	2.5	100% <u>n</u> -hexane
5.	Cyclohexene	NH ₄ ReO ₄ -Na, NH ₃ -9-8-	120	3730	3	100% cyclohexane
		NH ₄ ReO ₄ -Li, NH ₃ -1-3-	99	3610	22	100% cyclohexane
		NH ₄ ReO ₄ -Li, EtNH ₂ -1-4-	146	4000	2.5	100% cyclohexane
6.	Styrene ^b	NH ₄ ReO ₄ -Na, NH ₃ -5-1-	108	3465	3	85% ethylbenzene 15% polymer
		NH ₄ ReO ₄ -Li, NH ₃ -1-4-	70	3275	12	56% ethylbenzene
		NH ₄ ReO ₄ -Li, EtNH ₂ -1-5-	30	2850	11	64% ethylbenzene
7.	Benzene	NH ₄ ReO ₄ -Na, NH ₃ -8-1-	222	4450	12	36% cyclohexane
		NH ₄ ReO ₄ -Li, NH ₃ -1-1-	206	4400	12	34% cyclohexane
		NH ₄ ReO ₄ -Li, EtNH ₂ -1-4-	179	4050	29	51% cyclohexane

Table 11, Continued

No.	Substrate	Catalyst	Avg. Temp. (°C.)	Avg. Pres. (psig.)	Time (hrs.)	Product ^a
8.	Acetic Acid	NH ReO -Na,NH -9-8-	178	4060	7	100% ethanol ^c
		NH ReO -Li,NH -1-4-	180	4060	18	54% ethanol 46% ethyl acetate
		NH ReO -Li,NH -1-9-	145	3950	4.5	100% ethanol ^c
9.	Nitrobenzene ^b	NH ReO -Na,NH -7-1-	160	3250	6	88% aniline
		NH ReO -Li,NH -1-1-	110	3400	8	100% aniline
		NH ReO -Li,EtNH 1-1-	106	3210	7	91% aniline

a. The balance of the product in each case was the unreduced substrate.

b. The solvent used was ethanol.

c. The solvent used was water.

E. A Comparison of Previously Studied Rhenium Catalysts with Metal-Ammonia (Amine) Types

The catalysts prepared in this investigation compare very favorably with most rhenium catalyst heretofore prepared. Table 12 gives a comparison on a variety of substrates.

The carbonyl group in cyclohexanone was reduced most easily by Re_2O_7^a and Re_2O_3 . The ammonia and ethylamine catalysts however appear to be somewhat more active than the Re_2Se_7 catalyst.

The double bond in cyclohexene was reduced under as mild conditions with the Li-NH_3 catalyst as with any other rhenium catalyst before used. The Li-EtNH_2 catalyst required more drastic conditions and compared closely with the Re_2O_7 -THP catalyst, but the Na-NH_3 catalyst was the poorest tried so far on this substrate.

The Li-EtNH_2 and Li-NH_3 catalysts while being comparable with Re_2O_3 for the reduction of nitrobenzene were considerably less active than Re_2S_7 . Rhenium heptasulfide apparently occupies a unique position among rhenium catalysts for the reduction of nitrobenzene. All other rhenium catalysts investigated require rather drastic conditions for the reduction of nitrobenzene (cf. 3, Table 12).

Rhenium apparently occupies a unique position among all catalysts for the reduction of carboxylic acids. The conditions required for the reduction of acids with rhenium catalysts are the mildest yet reported in the literature. The catalysts prepared in this investigation were probably as good for the reduction of acetic acid as any catalyst previously prepared. The acid was reduced under conditions similar to those required by Re_2O_3 and Re_2O_7 , and when the substrate was mixed with water, the reduction gave almost exclusively the alcohol.

The ethylamine and ammonia catalysts proved to be as effective in the reduction of benzene as most other rhenium catalysts. Although inferior to Re_2O_7 -THP they were definitely superior to Re_2S_7 , Re_2Se_7 and Re_2O_7 .

For the reduction of all substrates discussed, the ammonia and ethylamine catalysts were definitely superior to the Re_2Se_7 catalyst. They also appeared to be superior to Re_2S_7 except for the reduction of nitrobenzene, for which they were much less active.

Rhenium heptoxide is apparently superior to the ammonia and ethylamine catalysts in the reduction of cyclohexanone and cyclohexene, but inferior in the reduction of nitrobenzene and benzene, and about equal for the reduction of acetic acid.

The rhenium sesquioxide catalyst prepared by reduction of aqueous perrhenate with sodium borohydride exhibits parallel but somewhat superior activity to the ammonia and ethylamine catalysts for all substrates investigated except possibly acetic acid. Compared with the latter the Re_2O_7 -THP catalyst is apparently inferior for acetic acid and nitrobenzene; very comparable for cyclohexene and cyclohexanone, and definitely superior for benzene.

Table 12

A COMPARISON OF RHENIUM CATALYSTS OF DIFFERENT TYPES
IN THE REDUCTION OF SOME SELECTED SUBSTRATES

No.	Substrate	Catalyst	Reference	Avg. Temp. (°C.)	Avg. Pres. (psig.)	Time (hrs.)	Product ^a
1.	Cyclohexanone	Re ₂ O ₇ ^b	91	64	2100	5	84% cyclohexanol
		Re ₂ Se ₇	92	155	3910	9	100% cyclohexanol
		Re ₂ O ₃	94	64	3260	4.5	77% cyclohexanol
		Re ₂ O ₇ -THP ^c	94	113	3650	5.5	100% cyclohexanol
		Li-EtNH ₂	No. 9, Tab. 9	119	3655	2.5	100% cyclohexanol
		Na-NH ₃	No. 32, Tab. 7	130	3735	3	70% cyclohexanol
2.	Cyclohexene	Re ₂ O ₇ , <u>in situ</u>	91	100	2300	6	98% cyclohexane
		Re ₂ Se ₇	92	200	4500	3	40% cyclohexane
		Re ₂ O ₃	94	100	3550	3	86% cyclohexane
		Re ₂ O ₆ -THP	94	151	3880	13	100% cyclohexane
		Li-EtNH ₂	No. 14, Tab. 9	149	3930	2	100% cyclohexane
		Li-NH ₃	No. 12, Tab. 8	99	3610	22	100% cyclohexane
		Na-NH ₃	No. 50, Tab. 7	212	4152	11	100% cyclohexane
3.	Nitrobenzene	Re ₂ S ₇	d	25	1900	6	100% aniline
		Re ₂ Se ₇	92	110	3550	1.25	100% aniline
		Re ₂ O ₇	91	165	2100	3.5	100% aniline
		Re ₂ O ₃	94	75	2880	4	100% aniline
		Re ₂ O ₇ -THP	94	250	4900	4	11% aniline 46% decomposition product
		Li-EtNH ₂	No. 23, Tab. 9	106	3210	7	91% aniline
		Li-NH ₃	No. 16, Tab. 8	90-110	3400	8	100% aniline
		Na-NH ₃	No. 62, Tab. 7	175	3650	12	75% aniline
4.	Acetic Acid	Re ₂ S ₇	d	198	4250	215	23% ethyl alcohol 77% ethyl acetate
		Re ₂ Se ₇	92	210	4610	11	17% ethyl alcohol 69% ethyl acetate
		Re ₂ O ₇	91	150	2400	10	77% ethyl alcohol 23% ethyl acetate

Table 12, Continued

No.	Substrate	Catalyst	Reference	Avg. Temp. (°C.)	Avg. Pres. (psig.)	Time (hrs.)	Product ^a
4.	Acetic Acid (continued)	Re ₂ O ₃	94	150	3630	6.5	35% ethyl alcohol
		Re ₂ O ₇ -THP	94	195	4120	4	65% ethyl acetate
		Li-EtNH ₂	No. 29, Tab. 9	145	3950	4.5	23% ethyl alcohol
		Li-NH ₃	No. 20, Tab. 9	180	4060	18	40% ethyl acetate
		Na-NH ₃	No. 68, Tab. 7	178	4060	7	100% ethyl alcohol
5.	Benzene	Re ₂ S ₇	d	300	3400	4	57% cyclohexane
		Re ₂ Se ₇	92	240	4890	62	5% cyclohexane
		Re ₂ O ₇	91	330	3400	13	40% methane
		Re ₂ O ₃	94	195	4380	6	11% cyclohexane
		Re ₂ O ₇ -THP	94	160	3600	10	61% cyclohexane
		Li-EtNH ₂	No. 18, Tab. 9	208	4560	1.5	100% cyclohexane
		Li-NH ₃	No. 13, Tab. 8	206	4400	12	22% cyclohexane
		Na-NH ₃	No. 57, Tab. 7	202	4225	10	34% cyclohexane
						67% cyclohexane	

- a. The balance of the product in each case was the unreduced substrate
 b. Re₂O₇ reduced *ex situ* in HOAc
 c. THP - tetrahydropyran
 d. Broadbent, Slauch and Jarvis, *J. Am. Chem. Soc.*, 76, 1519 (1954).

F. A Comparison of the Activity of the Catalysts Prepared in this Investigation with Several "Standard" Catalysts.

The results of the Comparison are presented in tabular form in Table 13.

Platinum and nickel were undoubtedly the best catalysts for the reduction of cyclohexene, nitrobenzene and cyclohexanone. They probably were also the best catalysts for the reduction of butanone, however, in this case, the activity of the Li-EtNH₂ catalyst was very comparable.

Copper chromite was a much better catalyst for the reduction of benzene than was PtO₂, it was however, very inferior to nickel and somewhat inferior to the rhenium catalysts.

The rhenium catalysts were decidedly superior to the "Standard" catalysts for the reduction of acetic acid. The only "Standard" catalyst showing any activity for this reduction was copper chromite.

Several reductions were performed on substrates with more than one reducible group in hope of obtaining selective reduction. In the case of allylacetone the rhenium catalysts normally reduce the olefinic bond in preference to the carbonyl group. This was shown to also be the case with both platinum and nickel. One reduction was run with the Li-EtNH₂ catalyst in which a partial poisoning by pyridine occurred, and the major product obtained was 2-hexene-2-ol, the reverse of the behavior of the unpoisoned catalyst. This product was not observed in any of the reductions performed by the "Standard" catalysts. 2-Allylcyclohexanone was reduced by the "Standard" catalysts under milder conditions than those required by the ammonia and ethylamine catalysts to give the same product, *i.e.* 2-propylcyclohexanone. In the case of crotonaldehyde the "Standard" catalysts preferentially reduced the double bond to give *n*-butyraldehyde. In one hydrogenation using the Li-EtNH₂ catalyst, reduction occurred at 88°C. to give a small yield of crotyl alcohol. In a subsequent reduction in which a partial poisoning by pyridine occurred, the same catalyst gave only *n*-butyraldehyde.

Table 13

A COMPARISON OF THE CATALYTIC ACTIVITY OF CATALYSTS PREPARED
IN THIS INVESTIGATION WITH SEVERAL "STANDARD"
CATALYSTS ON SELECTED SUBSTRATES

No.	Substrate	Catalyst	Avg. Temp. (°C.)	Avg. Pres. (psig.)	Time (hrs.)	Product ^a
1.	Cyclohexanone ^b	PtO ₂	21	60	5	91% cyclohexanol
		Ni	60	60	3	92% cyclohexanol
		CuO·CuCr ₂ O ₄	115	2200	0.25	94% cyclohexanol
		Li-EtNH ₂	119	3655	2.5	100% cyclohexanol
		Li-NH ₃	130	3735	3	70% cyclohexanol
2.	Butanone	PtO ₂ ^d	30	3000	40	37% 2-butanol
		Ni	95	2700	18	95% 2-butanol
		Li-EtNH ₂	90	3500	15	97% 2-butanol
		Li-NH ₃	100	3620	15	98% 2-butanol
		Na-NH ₃	128	3650	3	100% 2-butanol
3.	Cyclohexene	PtO ₂	25	56	2	45% cyclohexane
		Ni	30	2950	1	100% cyclohexane
		Li-EtNH ₂	149	3930	2	100% cyclohexane
		Li-NH ₃	99	3610	22	100% cyclohexane
		Na-NH ₃	212	4152	11	100% cyclohexane
4.	Nitrobenzene ^b	PtO ₂	25	15	0.25	100% aniline
		Ni	25	15	0.25	100% aniline
		CuO·CuCr ₂ O ₄	205	2400	1.5	98% aniline
		Li-EtNH ₂	106	3210	7	91% aniline
		Li-NH ₃	90-110	3400	8	100% aniline
		Na-NH ₃	175	3650	12	75% aniline
5.	Acetic Acid ^d	PtO ₂	300	3800	12	7% ethyl acetate
		Ni		Catalyst Dissolved		
		CuO·CuCr ₂ O ₄	250	4500	21	20% ethyl acetate
		Li-EtNH ₂	145	3950	4.5	100% ethyl alcohol
		Li-NH ₃	180	4060	18	54% ethyl acetate 46% ethyl alcohol
		Na-NH ₃	178	4060	7	100% ethyl alcohol

Table 13, Continued

No.	Substrate	Catalyst	Avg. Temp. (°C.)	Avg. Pres. (psig.)	Time (hrs.)	Product ^a
6.	Benzene	PtO ₂	255	4650	10	7% cyclohexane
		Ni	100	3000	0.5	100% cyclohexane
		CuO·CuCr ₂ O ₄	260	4440	12	83% cyclohexane
		Li-EtNH ₂	208	4560	1.5	22% cyclohexane
		Li-NH ₃	206	4400	12	34% cyclohexane
		Na-NH ₃	202	4225	10	67% cyclohexane
7.	Allylacetone	PtO ₂ ^d	30	2900	2	87% 2-hexanone 13% 2-hexanol
		Ni	30	3000	10 min.	100% 2-hexanone
		Li-EtNH ₂	68	3070	13	91% 2-hexanone
		Li-EtNH ₂ (poisoned)	155	4200	2.5	26% 5-hexene-2-ol 14% 2-hexanone
		Li-NH ₃	81	3350	6	72% 2-hexanone 28% 2-hexanol
		Na-NH ₃	119	3520	6	71% 2-hexanone 29% 2-hexanol
8.	2-Allylcyclohexanone	PtO ₂ ^d	30	2900	2	68% 2-propylcyclohexanone 32% 2-propylcyclohexanol
		Ni	30	2950	10 min.	100% 2-propylcyclohexanone
		Li-EtNH ₂	125	3700	6	73% 2-propylcyclohexanone 27% 2-propylcyclohexanol
		Li-NH ₃	123	3800	14	88% 2-propylcyclohexanone 4% 2-propylcyclohexanol
9.	Crotonaldehyde	PtO ₂ ^d	30	2900	2	75% <u>n</u> -butyraldehyde 18% <u>n</u> -butyl alcohol
		Ni	30	2900	1	100% <u>n</u> -butyraldehyde
		Li-EtNH ₂	88	3400	8	9% <u>c</u> rotyl alcohol
		Li-EtNH ₂ (poisoned)	100	3650	10	50% <u>n</u> -butyraldehyde

a. The balance of the product in each case was the unreduced substrate.

b. Data taken from Shaw's thesis, reference 91.

c. Data taken from Johnson's thesis, reference 94.

d. Selin, Terry G., Rhenium Catalysts: I. Hydrogenation and Hydroformylation using Rhenium Carbonyl Compounds. II. Hydrogenation Using Catalysts Obtained from the Reduction of Perrhenate with Metals in Aqueous Solution, Master's Thesis, Dept. of Chemistry, Brigham Young University, 1957.

V. Summary

1. A review is given of the history and production, some chemical and physical properties, and the catalytic applications of rhenium; of the rhenide ion, on the nature of liquid ammonia-alkali metal systems in the reduction of inorganic salts, and on the catalytic activities of metals so produced.

2. Ammonium perrhenate and rhenium heptoxide were shown to be easily reduced by a solution of sodium in liquid ammonia to yield a rhenium black with a high degree of catalytic activity. Lithium was used in an analogous manner in reducing ammonium perrhenate in both liquid ammonia and ethylamine. The catalyst prepared in ethylamine was in general somewhat superior to those prepared in ammonia.

3. Several other systems such as potassium in ammonia, lithium in ethylenediamine and sodium in ethylamine were investigated in attempts to prepare catalysts. In most cases these systems were rather unsuccessful.

4. Standard procedures were developed for the preparation of the sodium-ammonia, lithium-ammonia and lithium-ethylamine catalysts. Probably the most important step in their preparation proved to be complete removal of the alkali metal amide formed during the reduction process.

5. The catalysts were analyzed both spectrophotometrically and gravimetrically and found to have the same composition. Experiments performed to determine the valence state of the rhenium plus the analytical data showed the elementary composition of the catalysts to be $\text{ReO} \cdot 2\text{H}_2\text{O}$.

6. The catalysts were evaluated in the hydrogenation of a variety of substrates. A total of 161 reductions were performed and it was shown that the activity of the catalysts closely paralleled that of the Re_2O_3 catalyst previously studied.⁹⁴ The catalysts were active on olefins and the carbonyl group under relatively mild conditions. They reduced benzene at temperatures considerably less than those required by the "Standard" catalysts except for nickel. Pyridine was reduced completely under approximately the same conditions as required by benzene, and the triple bond was selectively reduced to the double bond under relatively mild conditions.

7. A number of experiments were conducted in an attempt to selectively hydrogenate various reducible groups in preference to a nitro group contained in the same molecule. In all cases the group in question in a given molecule was more easily reduced than the nitro group in another comparable molecule, for instance, butanone was more easily reduced than nitrobenzene. However, in all cases in which reduction was attempted on a molecule containing both a nitro group and a second easily reducible function, the nitro group was reduced preferably. This phenomenon has been observed in previous investigations in which selectivity of reduction involving the nitro group has been attempted.

8. Normally the catalysts when used in the reduction of allyl-acetone or 2-allylcyclohexanone reduced the double bond in preference to the carbonyl group. This was shown to also be the case with the "Standard" catalysts. However, in one experiment in which the Li-EtNH₂ catalyst was partially poisoned with pyridine, the major product obtained was 5-hexene-2-ol.

9. Probably the greatest worth of the catalysts was shown to be for the reduction of carboxylic acids. The Li-EtNH₂ catalyst reduced acetic acid at 145^o C. Other acids were reduced under comparable conditions. It was also observed that when water was used as a solvent for the reduction, the product obtained in most cases was the alcohol exclusively.

BIBLIOGRAPHY

- Agte, C., Alterthum, H., Becker, K., Heyne, G., and Moers, K., Naturwissenschaften, 19, 108 (1931), [Sims, C. F., Wyler, E. N., Gaines, G.B., and Rosenbaum, D.M., A Survey of the Literature on Rhenium, WADC Tech. report 56-319, ASTIA Document No. AD 110596, Battelle Memorial Institute to Aeronautical Research Laboratory, Wright-Patterson Air Force Base, Ohio (June 1956) p. 22].
- Agte, C., Alterthum, H., Becker, K., Heyne, G., and Moers, K., Z. anorg. allgem. Chem., 196, 129 (1931), [Sims, op. cit., p. 22].
- Aston, F., Nature, 127, 591 (1931).
- N.-V. de Bataafsche Petroleum Maatschappij, British Pat. 358,180 July 29, 1930, [C. A., 26, P 4924 (1932).]
- N.-V. de Bataafsche Petroleum Maatschappij, German Pat. 393,707 June 20, 1940, [C. A., 35, P4941 (1941).]
- Bertolus, M., U.S. Pat. 2, 579,107 Dec. 18, 1951, [Sims, op. cit., p. 13].
- Boyd, G., Cobble, J., and Smith, W., J. Am. Chem. Soc., 75, 5783 (1953).
- Bravo, J. B., Griswold, E., and Kleinberg, J., J. Am. Chem. Soc., 58, 18 (1954).
- Briscoe, H., Robinson, P., and Rudge, A., J. Chem. Soc., 1931, 3087.
- Briscoe, H., Robinson, P., and Stoddart, E., J. Chem. Soc., 1931, 1439-43.
- Brown, H. and Goldgerg, E., Phys. Rev., 76, 1260 (1949).
- Burgess, W. M. and Eastes, J.W., J. Am. Chem. Soc., 63, 2674 (1941).
- Burgess, W. M. and Holden, F. R., J. Am. Chem. Soc., 59, 495 (1937).
- Burgess, W. M. and Smoker, E. H., J. Am. Chem. Soc., 52, 3573 (1930).
- Cappel, N. O., and Watt, G. W., J. Chem. Education, 14, 174 (1937).
- Chittum, J. R., and Hunt, H., J. Phys. Chem., 40, 581 (1936).
- Cobble, J. W., "On the Structure of the Rhenide Ion", Dept., of Chem. University of Purdue to Chemistry Division, Air Force Office of Scientific Research, T N - 56-348, July 26, 1956.
- De Benedetti, S., and McGowan, F., Phys. Rev., 71, 380 (1947).
- De Benedetti, S., and McGowan, F., Phys. Rev., 74, 728 (1948).
- Driggs, F. (To Westinghouse Elec. Co.), U.S. Pat. 1,911,943, May 30, 1933, [Sims, op. cit., p. 11].

- Druce, J., Chem. News, 131, 273 (1925), [Sims, op. cit., p. 2].
- Druce, J., "Rhenium", Univ. Press, Cambridge, 1948, pp. 12-15 [Sims, op. cit., p. 51].
- Dolejsek, V., and Heyrovsky, J., Nature, 116, 782 (1925).
- Eastes, J. W. and Burgess, W. M., J. Am. Chem. Soc., 64, 1188 (1942).
- Fernelius, W. Conrad, and Watt, G.W., Chem. Revs., 20, 195-204 (1937).
- Fernelius, W. C., and Johnson, W. C., J. Chem. Education, 664-7 (1928).
- Fernelius, W. C., Unpublished Observations, [Fernelius, Conrad W., and Watt, G.W., op. cit., p. 195].
- Fink, C. G. and Deren, P., Bull. Amer. Electrochem. Soc., 66, 381 (1934), [Sims, op. cit., p. 4].
- Frank, F. Proc. Phys. Soc. (London), 60, 211 (1948), [Sims, op. cit., p. 4].
- Franklin and Kraus, Am. Chem. J., 21, 8 (1899), [Fernelius, Conrad W., and Watt, G. W., op. cit., p. 204].
- Gibson, G. E., and Argo, W.L., J. Am. Chem. Soc., 40, 1327 (1918).
- Gibson, G. E., and Phipps, T.E., J. Am. Chem. Soc., 48, 312 (1926).
- Gonser, B., Resources for Freedom, IV, A Report to the President by the President's Materials Policy Commission, p. 109, U.S. Govt. Printing Office, Washington. (June, 1952), [Sims, op. cit., p. 7].
- Griswold, E., Kleinberg, J., and Bravo, J. B., Science, 115, 375 (1952).
- Grosse, A. V., Z. Naturforsch., 8b, 533 (1953), [C. A., 48, 4347d (1952)].
- Hahn, H., and Konrad, A., Z. anorg. allgem. Chem., 264, 174 (1952), [Sims, op. cit., p. 205].
- Heyrovsky, J., Nature, 135, 870 (1935).
- Hillebrand, Lundell, Eright and Hoffman, "Applied Inorganic Analysis", 2nd Ed., John Wiley and Sons, New York, 1953, p. 321
- Holt, R. B., and Watt, Geo. W., J. Am. Chem. Soc., 65, 988 (1943).
- Honigschmid, O., and Sachtleben, R., Z. anorg. allgem. Chem., 191, 309 (1930), [Sims, op. cit., p. 21].
- Hsu, "A Correlation of the Catalytic Activity of Various Mixtures of Rhenium and Molybdenum Sulfides in Liquid-Phase Hydrogenations of Certain Reducible Organic Groups", Master's Thesis, Dept. of Chemistry, Brigham Young University, 1956.

Hund, J. Chem. Education, 10, 605 (1933).

Investigations of Rhenium, Wright-Air Development Center Tr., 54-371, Battelle Memorial Institute to Aeronautical Research Laboratory, Wright-Patterson Air Force Base, Ohio (June, 1954), [Sims, op. cit., p. 167].

Jaeger, F., and Rosenbohm, E., Proc. Acad. Sci. Amsterdam, 36, 786 (1933), [Sims, op. cit., p. 22].

Jakob, W., and Jezowska, B., Z. anorg. allgem. Chem., 220, 16 (1934), [Sims, op. cit., p. 56].

Johnson, "The Catalytic Hydrogenation Activity of Rhenium Blacks Produced by the Action of Sodium Borohydride on Ammonium Ferrhenate and of Tetrahydrophyran on Rhenium Heptoxide", Master's Thesis, Department of Chemistry, Brigham Young University, 1956.

Johnson, W. C., and Fernelius, C., J. Chem. Education, 6, 20 (1926).

Johnson, W. C. and Meyer, A. W., Chem. Revs., 8, 272 (1931).

Johnson, W. C., and Wheatley, A. C., Z. anorg. allgem. Chem., 216, 273 (1934).

Kates, L. W., Materials and Methods, 39, No. 3., 88 (1954), [C. A., 48, 4398i(1954)]

Kraus, C. A., Chem. Revs., 8, 269 (1931).

Kraus, C. A., Chem. Revs., 26, 95 (1940).

Kraus, C. A., J. Am. Chem. Soc., 29, 1557 (1907).

Kraus, C. A. and Kurtz, H. F., J. Am. Chem. Soc., 47, 43-48 (1925).

Kraus, C. A. and Lucasse, J. Am. Chem. Soc., 43, 2529 (1921).

Kraus, C. A., and Pidderhof, J. A., J. Am. Chem. Soc. 56, 79 (1934).

Kriengl, F., Stupkol, F., and Stupkol, K., Monatsh., 63, 394 (1933), [Fernelius, Conrad, W., and Watt, G.W., op. cit., p. 199].

Lingane, J.J., J. Am. Chem. Soc., 64, 1001 (1942).

Lingane, J.J., J. Am. Chem. Soc., 64, 2182 (1942).

Loring, F., Chem. News. 132, 407 (1926), [Sims, op. cit., p. 2].

Lundell, G.E.F., and Knowles, H. B., Bur. Standards J. Research, 18629 (1937), [C. A., 31, 77796 (1937)].

Manchot, W., and Dusing, J., Z. anorg. allgem. Chem., 212, 21, [Sims, op. cit., p. 56].

- Manescu, I., Compt. rend., 226, 1010 (1948), [Sims, op. cit., p. 32].
- Mathewson, Z. anorg. Chem., 50, 182 (1906).
- Maun, E. K., and Davidson, N., J. Am. Chem. Soc., 72, 3509 (1950).
- Melaven, A., and Bacon, J. (To University of Tennessee Research Corp.)
U.S. Pat. 2,414,965, Jan. 28, 1957, [Sims, op. cit., p. 13].
- Mellor, J., The Physical Properties of Masurium and Rhenium, "A Comprehensive Treatise on Inorganic Chemistry", vol. 12, p. 469, [Sims, op. cit., p. 27].
- Meloche and Martin, Anal. Chem., 28, 1671 (1956).
- "Metals Handbook", The American Soc. for Metals, Cleveland, Ohio, 1948,
p. 20, [Sims, op. cit., p. 22].
- Minor Metals-Rhenium in "Minerals Yearbook", U.S. Gov't Printing Office, 1948,
[Sims, op. cit., p. 32].
- Moissan, H., Compt. rend., 128, 26(1899), [Fernelius, Conrad W., and Watt,
G.W., op. cit., p. 195].
- Moore, L.W., and Watt, Geo. W., J. Am. Chem. Soc., 64, 2775 (1942).
- Naldrett, S., and Libby, W., Phys. Rev., 73, 487, 929 (1948).
- Nechamkin, H., Melaven, A., et. al., "Inorganic Synthesis", McGraw-Hill
Book Co., New York (1950) vol. 40, p. 50. [Sims, op. cit., p. 60].
- Netherton, L., and Holt, M., J. Electrochem. Soc., 95, 324 (1949), [Sims,
op. cit., p. 51].
- Netherton, L., and Holt, M., J. Electrochem. Soc., 98, 106 (1951), [Sims,
op. cit., p. 51].
- Noddack, I., Z. Electrochem., 34, 629 (1929), [Sims op. cit., p. 21].
- Noddack, I. and W., Brit. Pat. 317,035, July 28, 1930, [Sims, op. cit., p. 10].
- Noddack, I. and W., Ger. Pat. 606,488, Dec. 3, 1934, [Sims, op. cit., p. 10].
- Noddack, I. and W., Metallborse, 21, 603,650 (1931), [Sims, op. cit., p. 10].
- Noddack, I. and W., Z. anorg. allgem. Chem., 183, 353 (1929), [Sims, op. cit.,
p. 13].
- Noddack, K. and W., Naturwissenschaften, 17, 93 (1929), [Sims, op. cit., p. 56].
- Noddack, K. and W., Z. anorg. allgem. Chem., 181, 1-37 (1929), [Sims, op. cit.,
p. 56].

- Noddack, W., Z. Electrochem., 34, 627 (1928), [Sims, op. cit., p. 56].
- Noddack, W. and I., (to Siemens and Halske A. G.), Brit. Pat. 346,652 (October 8, 1929), [Sims, op. cit., p. 104].
- Noddack, W., and I., Z. anorg. allgem. Chem., 181, 1-37 (1929), [Sims, op. cit., p. 56].
- Noddack, W. and I., Z. anorg. Chem., 215, 129 (1933), [Sims, op. cit., p. 57].
- Noddack, W. and Tacke, I., Oesterr. Chem. Ztg., 28, 127 (1925), [Sims, op. cit., p. 2].
- Noddack, W. Tacke, I., and Berg. O., Naturwissenschaften, 13, 567 (1925), [Sims, op. cit., p. 2].
- Pauling, L., Chem. Eng. News, 25, 2970 (1947).
- Pauling, L., Proc. Royal Soc. (London), A196, 343 (1942), [Sims, op. cit., p. 52].
- Platonov, M. S., J. Gen. Chem. (U.S.S.R.), 11, 683 (1941), [C.A., 36, 3977 (1942)].
- Platonov, M. S., and Anisimov, S. B., J. Gen. Chem. (U.S.S.R.), 7, 1360 (1937), [C.A., 31, 8503³] (1937)
- Platonov, M. S., Anisimov, S. B., and Krashenennikova, V. M., Ber, 68B, 761 (1935), [C.A., 29, 5005² (1935)].
- Platonov, M. S., and Tomilov, V.I., J. Gen. Chem. (U.S.S.R.), 7, 788 (1937), [C.A., 31, 6189⁷ (1937)].
- Platonov, M.S., and Tomilov, V.K., and Tur, E.V., J. Gen. Chem. (U.S.S.R.), 7, 1803 (1937), [C. A., 31, 8341⁷ (1937)].
- Ringade, E., Compt rend., 140, 246 (1905), [Fernelius, Conrad W., and Watt, G. W., op. cit., p. 195].
- Richardson, D., "Proc. of the 5th Summer Conference (at MIT) on Spectroscopy and Applications", 1937, pp. 64-70 (Published 1938), [Sims, op. cit., p. 22].
- Roth, W., and Becker, G., Ber., 65B, 373 (1932), [Sims, op. cit., p. 59].
- Rulfs, C., and Elving, P.J., J. Am. Chem. Soc., 73, 328⁷ (1951).
- Schacherl, F., Chem. Listy, 28, 623 (1929), [Sims, op. cit., p. 70].
- Schmidt, F.C., Studer, F. J., and Sottysiak, J., J. Am. Chem. Soc., 60, 2780 (1938)
- Searcy, A., and McNeas, R., J. Am. Chem. Soc., 75, 1578 (1953).

- Seely, Chem. News, 22, 117 (1870), [Johnson, op. cit., p. 272].
- Seely, Chem. News, 23, 169 (1871), [Johnson, op. cit., p. 272].
- Seely, J. Franklin Inst., 61, 110 (187), [Johnson, op. cit., p. 272].
- Seliger, H., and Bradt, H., Phys. Rev., 73, 1408 (1948).
- Selin Terry G. Rhenium Catalysts: I. Hydrogenation and Hydroformylation using Rhenium carbonyl Compounds. II. Hydrogenation using catalysts obtained from the reduction of perrhenate with metals in aqueous solution. Master's thesis, Dept. of Chemistry, Brigham Young University, 1957.
- Shaw, "Liquid-Phase Catalytic Hydrogenations with Rhenium Heptoxide Derived Catalysts", Master's Thesis, Department of Chem. B.Y.U., 1955.
- Siebert Geo. m. b. H., Brit. Pat. 385,859, June 8, 1932, [Sims, op. cit., p. 104].
- Siemens, A., and Halske, G. French Pat. 658,446, Sept. 30, 1929, [C.A., 24, P4362⁵(1930)].
- Siemens, A., Halske, G. Noddack, W., and Noddack, I., British Pat 346,652, Oct. 8, 1929, [C.A., 26, P569²(1932)].
- Sims, C., Craighead, C., and Jaffee, R., Journal of Metals (Transactions), 1955, 168. [Sims, op. cit., p. 169].
- Sims, C. F., Wyler, E.N., Gaines, G.B., and Rosenbaum, D.M., A Survey of the Literature on Rhenium, WADC Tech. report 56-319, ASTIA Document No. AD 110596, Battelle Memorial Institute to Aeronautical Research Laboratory, Wright-Patterson Air Force Base, Ohio (June 1956).
- Suess, H., Z. Naturforsch., 2A, 604 (1947), [Sims, op. cit., p. 4].
- Tomicek, O. and F., Coll. Chech. Commun, 11, 626 (1939), [Griswold, E., op. cit., p. 375].
- Triblat, S., Compt. rend., 222, 1388 (1946), [Sims, op. cit., p. 56].
- Tropsch, H., and Kassler, R., Ber., 63B, 2149 (1930), [C.A., 25, 22²(1931)].
- Tur, E.V., Anisimov, S.B., and Platonov, M.S., J. Gen. Chem. (U.S.S.R.), 7, 2895 (1937), [C.A., 32, 5383⁴(1938)].
- Turkiewicz, E., Roczniki Chem., 12, 589 (1932), [Sims, op. cit., p. 56].
- Watt, Geo. W., Chem Revs., 46, 289-304 (1950).
- Watt, Geo. W., and Davies, D. D., J. Am. Chem. Soc., 70, 3753 (1948).
- Watt, Geo. W., and Fernelius, W. D., J. Am. Chem. Soc., 61, 1692 (1939).
- Watt, Geo. W., and Fernelius, W. C., J. Am. Chem. Soc., 61, 2502 (1939).

- Watt, Geo. W., and Jenkins, W.Z., J. Am. Chem. Soc., 73, 3275 (1951).
- Watt, Geo. W., and Kennan, C.W., J. Am. Chem. Soc., 75, 2048 (1954).
- Watt, Geo. W., and Mayfield, J., J. Am. Chem. Soc., 75, 1760 (1953).
- Watt, Geo. W., Roper, W.F., and Parker, S.G., J. Am. Chem. Soc., 73, 5791 (1953).
- Watt, Geo. W., Walling, Jr., T.M., and Mayfield, P. I., J. Am. Chem. Soc., 75, 6175 (1953).
- Weeks, E., J. Chem. Education, 22, 519 (1935).
- Welsch, T.W.G., J. Am. Chem. Soc., 37, 501 (1915), [Fernelius, Conrad W., and Watt, G.W., op. cit., p. 195].
- Weyl, Ann. Physik, 121, 601 (1864), [Johnson, op. cit., p. 272].
- Whittle, "Rhenium Heptaselenide as a Hydrogenation Catalyst," Master's Thesis, Dept. of Chemistry, B.Y.U.
- Young, R., and Irvine, J., J. Am. Chem. Soc., 57, 2648 (1937).
- Zenghelis, C., and Stathis, K., Atti X^o Congr. intern. chim., 2, 821 (1938), [C.A., 33, 8081² (1939)].
- Zenghelis, C.,⁴ and Stathis, K., Osterr. Chem. Ztg., 40, 88 (1937, [C.A., 34, 5383 (1940)]).

THE PREPARATION AND CATALYTIC PROPERTIES OF RHENIUM BLACKS
OBTAINED BY REDUCTION OF RE(VII) IN ANHYDROUS
AMMONIA AND AMINES WITH ALKALI METALS

An Abstract

of a Thesis Submitted to the Department of Chemistry

Brigham Young University

Provo, Utah

In Partial Fulfillment
of the Requirements for the Degree of
Master of Science

by

David W. Seegmiller

September, 1957

ABSTRACT

The purpose of the investigation was to determine the catalytic activity of rhenium blacks obtained by reduction of rhenium salts in alkali metal-ammonia or amine systems.

A review is presented on the chemical, physical and catalytic properties of rhenium, and on the rhenide ion, on the nature of the alkali metal-liquid ammonia system, and the reduction of metallic salts therein.

The first reduction system studied was that obtained by dissolving sodium in liquid ammonia. The salts reduced in this system were $KReO_4$, Re_2O_7 and NH_4ReO_4 . The reduction of $KReO_4$ was unsuccessful, and the heptoxide was difficult to handle. The product obtained by the reduction of NH_4ReO_4 was the best characterized. The lithium-ammonia system was also used to reduce NH_4ReO_4 . One amine-alkali metal system was studied extensively. Lithium was used as the reducing agent and ethylamine as the solvent on NH_4ReO_4 .

A standard method of preparation was developed for each catalyst. It was found that the order of addition of the salt and alkali metal, the reaction ratio employed and the amount of solvent used apparently had no effect on the activity of the catalyst. It was found, however, that unless the alkali metal amide formed during the reduction process was removed completely, the catalysts were almost entirely inactive. For this purpose an acid extraction was employed.

A spectrophotometric method, based upon the strong absorption of the hexachlororhenate ion at a wave length of 281 μ , as well as the well recognized gravimetric method, based upon the insolubility of tetraphenylarsonium chloride, were used for the analysis of the catalysts. The spectrophotometric method was shown to be suitable for obtaining an approximate analysis, but lacked the precision necessary for an ultimate analysis. To determine the exact rhenium content of the material, the gravimetric method was therefore used. The valence state of the rhenium in the catalyst material was determined by oxidizing the catalyst in acidic potassium dichromate and then back titrating the excess oxidant. The analytical data indicated that all the catalysts were identical in composition; apparently a definite compound ($ReO \cdot 2H_2O$).

The activities of the sodium-ammonia catalysts were evaluated by 69 reductions of organic substrates. The lithium-ammonia catalyst's activity was demonstrated in 24 hydrogenations, while the lithium-ethylamine catalyst was similarly used in a total of 55 reductions. Several catalysts prepared in miscellaneous systems were also evaluated. In all, a total of 161 hydrogenations were performed.

The analysis of the reduction products was performed by means of gas chromatography except in the case of simple substrates used without solvent, for which refractive indices were used.

In general the activity of the lithium-ethylamine catalyst was found to be somewhat superior to that of the catalysts prepared in ammonia. This was definitely the case in the reduction of the carbonyl group as contained in such substrates as butanone, acetone, and cyclohexanone. Acetone was reduced by the Li-EtNH₂ catalyst at about 55°C., butanone required 90°C., while cyclohexanone required a temperature of ca. 120°C. In contrast the Na-NH₃ catalyst required a temperature of 78°C. to reduce acetone, 130°C. to reduce butanone, and 160-170°C. to reduce cyclohexanone.

In the case of the olefinic bond, except when conjugated to the benzenoid structure, the Li-NH₃ catalyst was the most effective. This catalyst reduced hexene-1 at about 100°C. and cyclohexene at 105°C. Styrene on the other hand was reduced by the Li-EtNH₂ catalyst in one experiment at room temperature while the Li-NH₃ catalyst required 70°C. and the Na-NH₃ catalyst 100°C.

The Li-EtNH₂ and Li-NH₃ catalysts were about equally effective in the reduction of nitrobenzene. The temperature required was about 110°C. The Na-NH₃ catalysts in contrast required temperatures of about 175°C.

The Na-NH₃ catalyst was used in an evaluation of the ease of reduction of a series of ketones. A very interesting relationship evolved from this study. It was observed that in all but two cases, the ketones containing an even number of carbon atoms in the principal chain reduced under significantly milder conditions than their odd numbered homologs.

A number of hydrogenations were attempted on compounds containing a nitro group and another easily reducible group. In all cases, no reduction of the second group occurred until the nitro group was hydrogenated, in spite of the fact that the conditions for the reduction of the nitro group alone were more drastic than for the reduction of any of the other functions. This phenomenon has been observed in previous investigations in which selectivity of reduction, with a rhenium catalyst, involving the nitro group was attempted.

A number of compounds containing both the carbonyl group and olefinic bond, i.e., allylacetone, 2-allylcyclohexanone, were hydrogenated in attempt to obtain selective reduction. The results clearly indicated that the rhenium catalysts reduce the olefinic bond preferentially to the carbonyl group. This was also demonstrated to be the case with the "Standard" catalysts. However, in one experiment in which a partial poisoning of the catalyst from pyridine occurred, the product obtained was 5-hexene-2-ol, indicating a reversal of ease of reduction of the two groups in this case.

In the case of crotonaldehyde the carbonyl group was apparently more easily reduced than the olefinic bond by both the rhenium and "Standard" catalysts. On one occasion, however, the Li-EtNH₂ catalyst produced crotyl alcohol.

The greatest worth of the catalysts of this investigation was undoubtedly their ability to catalyze the reduction of carboxylic acids. The catalysts prepared in all three systems seemed to be equally active in this respect. It was observed in this connection that when the reduction was run without solvent, the product was a mixture of both the alcohol

and ester. However, if water was used as a solvent, the reduction yielded in most cases only the alcohol. The Li-EtNH₂ catalyst was used in the reduction of a series of carboxylic acids. Included in the series were acetic, propionic, isobutyric, valeric, caproic, caprylic, capric, and lauric. All were reduced in the temperature range of 160-180°C., except acetic which was reduced at 145°C. This catalyst, therefore, is as effective in this reaction as any rhenium catalyst heretofore studied and much superior to any other catalyst reported in the literature.