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RESEARCH ON THE PREPARATION OF PURE METALS

Walter Brenner and Charles J. Marsel

Research Division, College of Engineering
New York University
University Heights
New York 53, N. Y.

Contract No. AF 19(604)4124

Project No. 5620

Task No. 56204

FINAL REPORT

March 15, 1963

Prepared for

Air Force Cambridge Research Laboratories
Office of Aerospace Research
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Bedford, Massachusetts

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I. Summary

This report summarizes the experimental studies which were carried out under Contract # AF 19(604)4124 subsequent to the work described in Scientific Report #4. The various investigations are described under two main headings reflecting the main subject matters, i.e. researches on the preparation of pure metals and researches on organic semiconductors. Some of the material included has previously been published in the form of scientific papers originally presented at various scientific meetings during the reporting period. All such material has been suitably identified. Also particular care has been taken to include the data of the latest experiments even though in certain cases no duplicate runs could be made to confirm the initially obtained results.

The syntheses of high purity tin, lead and antimony have been described in earlier issued Scientific Reports. The preparation of high purity gallium has been experimentally investigated via the synthesis and subsequent decomposition of lithium gallium hydride. This intermediate was obtained from the reaction of gallium trichloride with lithium hydride. Data were obtained which show the mechanism of purification. Product quality has been characterized in terms of emission spectrographic analyses. It was found possible to prepare by a sequence of rather simple low temperature reactions gallium metal with a total metal impurity content in the order of 5 ppm.

Some experiments were also carried out on the reduction of gallium trichloride with lithium aluminum hydride. As the reaction products include aluminum and lithium as well as gallium, this reaction does not appear to have much promise for the preparation of high purity gallium metal.

The reduction of bismuth trichloride by lithium aluminum hydride has been experimentally investigated for the preparation of high purity bismuth metal. Pyrex glass equipment was employed throughout these experimental studies. Product purity was ascertained by emission spectroscopic analyses. Bismuth ingots with an impurity content of 5 ppm were obtained rather readily. Yields of bismuth metal were 60-70% based on the bismuth trichloride used. The preparation of high purity bismuth metal by this reaction has the major advantage of requiring only low temperature processing conditions.

A considerable amount of experimental work was conducted for the development of a purification scheme suitable for the preparation of barium metal. The use of barium hydride as a reaction intermediate did not prove promising. Preliminary experiments relating to organobarium compounds proved likewise to present formidable difficulties.

After extensive experimentation barium azide was selected as a thermally unstable intermediate for the preparation of high purity barium metal. First barium hydroxide was reacted with hydrazoic acid to form barium azide in aqueous solution. Next barium was separated from the other alkaline earth metals, calcium and strontium, by chelation with 1,2-diaminocyclohexane tetraacetic acid. This chelating agent exhibits significant differences in the equilibrium constants when complexes are formed with barium, calcium and strontium. Barium azide was precipitated by adding alcohol. The dried barium azide was put under anhydrous decalin. It was found that barium azide decomposes smoothly under decalin near the boiling point to produce a new compound, barium pernitride, and nitrogen gas. Barium pernitride was then decomposed in turn at 850-900°C under 0.2 to 1 mm Hg pressure in a pure iron tube which was fully enclosed by a stainless steel tube. A final preparatory step consisted of the

reaction of the barium pernitride decomposition product in a titanium crucible at 900°C-950°C in vacuo for 10-12 hours. Decompositions were also effected only in a titanium crucible. Barium metal has no solubility in titanium and the titanium reacts preferentially with any nitrogen.

Barium metal samples were subjected to appropriate spectroscopic analyses. Samples with a total impurity content in the order of 30 ppm or less were repeatedly prepared. One such sample was submitted to Cambridge Air Force Research Laboratories. The starting material, barium hydroxide, had an approximate impurity content in the order of 2000 ppm. and higher.

The preparation of high purity yttrium metal has proven to be a difficult task indeed. Yttrium metal has a high order of thermal stability and is highly reactive with oxygen, water, etc. The synthesis of yttrium azide was attempted as a possible intermediate for the production of the pure metal similar to the above described barium purification processes. The reaction of yttrium hydroxide with hydrazoic acid did not result in the isolation of yttrium azide. Anhydrous yttrium chloride reacted with sodium azide in aqueous solutions or tetrahydrofuran, etc. did also not yield the desired product. The reaction of yttrium chloride with silver azide proved also unsuccessful. There are no published literature references which describe a successful synthesis of yttrium azide.

The application of organometallic yttrium compounds to the preparation of high purity yttrium metal was also investigated. Yttrium chloride was unsuccessfully reacted with n-butyl bromide, ethyl magnesium bromide, etc. Yttrium chloride was also reacted with sodium cyclopentadiene in tetrahydrofuran to produce tricyclopentadienyl yttrium. Under certain reaction conditions a hitherto unreported organic yttrium derivative, yttrium dicyclopentadienyl chloride, was obtained. The latter compound appeared attractive because it could be readily

purified by sublimation. Experiments designed to reduce these organoyttrium compounds have thus far been unsuccessful. Reducing agents which have been used to date include lithium metal, lithium hydride, lithium aluminum and lithium borohydride. Reduction in an autoclave at elevated temperatures and high hydrogen pressures was also attempted.

The reduction of yttrium halides with lithium hydride and lithium metal is being explored. Experimental studies on the purification of yttrium metal have been continued.

A second major area of research was concerned with the electronic behavior of certain organic solids. Many organic solids, formerly considered as dielectric materials, are currently being studied for their possible semiconductive behavior. For purposes of the subsequent summary, semiconductors may broadly be defined as materials having room temperature resistivities in the order of 10^{+3} to 10^{+10} ohm cm which decreases logarithmically with temperature. The temperature dependence, according to band theory is $\rho = \rho_0 e^{E/KT}$ where ρ and ρ_0 are the resistivities at $T^\circ K$ and $0^\circ K$ respectively, K is Boltzmann's constant, and E is one half the energy gap between the highest occupied band and the conduction band.

Previously rather extensive studies have been made on many different organics, particularly solid polycyclic hydrocarbons. Measurements have been made on different physical forms of these materials such as single crystals, smeared or evaporated films, and compressed polycrystalline powders. Significant differences in resistivity and energy gap were obtained by different workers on the same compound using the same or different methods for measurement. However the purity of the compounds studied was either incompletely

specified or not reported. Considering that one part per billion of boron increases the room temperature resistivity of silicon by a factor of 10^6 , one cannot, a priori, exclude the possibility of a similar occurrence in organic systems.

Experimental investigations on the electrical conductivity of various polycyclic aromatic hydrocarbons were carried out in order to determine impurity effects and, also, to ascertain the relationship, if any, between structure and conductivity. The compounds naphthalene, anthracene, tetracene, pentacene and hexacene were variously purified by vacuum sublimations, acid treatment, etc. Electronic properties were measured on pressed powder specimens. Data were obtained which illustrate the effect of different levels of metallic impurities on compound electronic properties. Samples of the same compound with different metallic impurity concentrations showed significant differences in both the measured values of ρ and E and in calculated values of ρ_0 and E. However the effects of specific impurities or whether the impurities were present as the free metal or chemically combined were not ascertained as yet.

It was also established that the electrical conductivity increases quite markedly as the number of fused rings in the series naphthalene to hexacene increases. Also the conduction energy gap decreases with increases in the number of fused rings. Electrical conductivity and energy gap measurements have been related to the ultra-violet B band absorption maxima of these aromatic hydrocarbons. The resistivities and energy gaps vary from $\rho_{50} = 6 \times 10^{14}$ ohm cm and 2.33 eV for naphthalene to $\rho_{50} = 3.8 \times 10^{10}$ and .566 eV for hexacene. The preparation of heptacene is in progress.

Certain heterocyclic compounds have also been purified and their electronic properties measured. These include dibenzofuran, dibenzothiophene,

carbazole, biphenyl and fluorene. The following list gives their resistivities and E values.

<u>Compound</u>	<u>E values (eV)</u>	<u>ρ 50 ohm cm</u>
Biphenyl	1.46	1.7×10^{15}
Fluorene	1.05	2.0×10^{15}
Dibenzothiophene	0.856	1.0×10^{15}
Dibenzofuran	0.445	7.75×10^{14}
Carbazole	0.586	2.5×10^{15}

The effect of the introduction of heteroatoms such as sulfur and nitrogen, compared to the carbon atom is to decrease the energy gaps.

It has previously been assumed that given "sufficient" pressure in the compaction of polycrystalline samples, pertinent electronic properties are not significantly affected by further pressure gains. A typical "sufficient" pressure has been defined as 80 Kg/cm^2 or $\sim 1200 \text{ psi}^*$. In one series of experiments it was found that certain compounds apparently do not conform to this generalization. Dibenzothiophene samples, for example, experience a 30% change in resistivity(decrease)when the pressure used for sample preparation was increased from 8060 to 24,180 psi. Further work along these lines is in progress.

Experiments were also carried out on the polymerization of acetylene and certain derivatives thereof to give long conjugated chain structures which might be expected to show enhanced electrical conductivity characteristics. The polymerization of acetylene was attempted by a number of different catalyst systems. Black infusible and insoluble, presumably cross linked polymeric

* Akamustu and Inokuchi - Proceedings of the 3rd Conference on Carbon, London, 1959.

products were obtained. Analyses showed the approximate gross composition of polyenes but these products contained substantial amounts of inorganic chemical constituents which were probably initially introduced as catalyst components. Attempts at purification to remove these constituents were unsuccessful. IR spectra did not contribute to much needed structural information.

The polymerization of phenyl acetylene was investigated using both ~~thermal~~ and catalytic initiation. Polyphenylacetylene is of interest because the alternating phenyl rings and conjugated double bonds create a decrease in the system's internal energy and should allow electron transfer for electronic conduction. Also polyphenylacetylene is soluble in various organic solvents which fact makes purification feasible.

Bulk and solution polymerization of polyphenylacetylene gave colored low molecular weight (500-1000) materials in almost quantitative yield. Reaction temperatures ranged from 130 to 200°C. The resistivities measured on compressed powder pellets were in the order of 10^{16} at ambient temperatures. The polymers obeyed the usual exponential law for semiconductors $\rho = \rho_0 e^{E/KT}$.

Pyridine acetylene monomers were synthesized. One pyridine acetylene polymer has been prepared and found to exhibit a significantly lower resistivity than polyphenylacetylene. This may be related to the introduction of the heteroatom in the phenyl ring. This pyridine acetylene polymer is water and alcohol soluble. A nickel complex which shows further reduced resistivity, has been prepared.

II. Researches On the Preparation of Pure Metals

II-1. The Preparation of High Purity Gallium by Hydride Reductions*

That class of inorganic substances known as intermetallic compounds is being increasingly researched for their possible utility as semiconductor materials. In the recent past particular emphasis has been given to the study of gallium arsenide. Because of the greater band gap and potentially greater mobility of this intermetallic compound, it could offer very distinct advantages for both high frequency and high temperature performance over such established semiconductor materials as silicon and germanium. It is generally recognized that our knowledge of the characteristics of gallium arsenide - as well as other intermetallic semiconductor materials - lags far behind that of germanium and silicon. It has been stated correctly that "this is due in part to the great difficulties involved in both the purification and growth of large single crystals⁽¹¹⁾". The importance of adequate raw materials purification techniques on pertinent device properties has been amply demonstrated with the elemental semiconductors silicon and germanium and is especially critical with the newer intermetallic compounds requiring multiple element purifications.

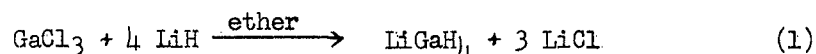
The subsequent paper is concerned with the preparation of high purity gallium for possible semiconductor applications. Previously reported experimental studies on the synthesis of pure gallium have been limited in both number and scope. Purification methods have been described by Hoffman and Scribner⁽⁵⁾, Detricler and Fox⁽³⁾, and Richards⁽¹⁰⁾. Electrolytic techniques which were first studied at the National Bureau of Standards in 1935⁽⁵⁾, have

* Y. Okamoto, E. Bierig, W. Brenner and C.J. Marsel; New York University, New York 53, N.Y., presented at the Conference on Ultrapurification of Semiconductor Materials, April 11-13, 1961, Boston, Mass.

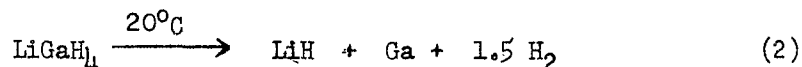
also been investigated at Lincoln Laboratories⁽⁷⁾. Gallium purification methods have been studied at RCA⁽⁹⁾, Bell Telephone Laboratories⁽¹²⁾, etc. One important consideration is that conventional zone refining is known to be inefficient in removing impurities which have segregation coefficients > 1 ⁽¹¹⁾. The reported segregation coefficients of many of the most significant impurities are greater than 1 necessitating therefore the use of other purification techniques for the optimization of gallium purity⁽²⁾.

In view of the considerable measure of success attained in the preparation of various high purity metals by hydride reductions^(1,8), it was decided to evaluate this approach experimentally for the synthesis of pure gallium metal. The careful study of pertinent literature references revealed that the compound lithium gallium hydride was reported to decompose rather readily to gallium metal and could therefore be a useful intermediate for the preparation of the pure metal^(4,13). Accordingly an experimental investigation was carried out on the synthesis of pure gallium metal via the formation and subsequent decomposition of lithium gallium hydride.

Lithium gallium hydride was first prepared by A.E. Finholt et al. who reduced gallium chloride with lithium hydride as shown⁽⁴⁾:



This compound was also synthesized by Wiberg and Schmidt who found that lithium gallium hydride decomposes, even at ambient temperatures, slowly into lithium hydride, gallium and hydrogen⁽¹³⁾:



It has been speculated that the decomposition of lithium gallium hydride is autocatalytically hastened by the presence of any finely divided gallium.

The apparently limited thermal stability of lithium gallium hydride was considered to offer a definite advantage for the preparation of gallium metal. A successful low temperature synthesis would of course minimize container contamination problems which become increasingly serious when reactions have to be carried out at elevated temperatures. It also renders more convenient certain chemical processing operations associated with decomposition reactions.

The gallium purification methods developed in this laboratory are based on the formation and subsequent thermal decomposition of the intermediate lithium gallium hydride. The synthesis of this compound was accomplished by suitable modifications of the reaction between gallium trichloride and lithium hydride in diethyl ether which was first described by Finholt et al.⁽⁴⁾. Appropriate methods for the decomposition of lithium gallium hydride and the recovery of purified gallium metal were then developed after extensive laboratory studies of various pertinent processing conditions. Spectroscopic analyses were employed throughout these studies to help ascertain impurity levels.

The starting materials for these purification studies were either gallium chloride or gallium metal. Gallium chloride was obtained both from a commercial supply house and by the chlorination of gallium metal, also procured from a commercial source. A spectrographic analysis of a typical batch of gallium chloride is shown in Table I. The total impurity content was in the order of 7000 ppm with iron and silicon most prominent.

Table I.

Spectrographic Analysis of Gallium Trichloride in ppm

Gallium	major
Iron	2500
Silicon	2500
Sodium	700
Aluminum	730
Calcium	680
Cadmium	70
Magnesium	90
Manganese	9
Lead	10
Tin	8
Silver	2
Zinc	80

With a commercial grade (purity > 95%) gallium metal as the starting material, conversion to the trichloride was first carried out. This was accomplished essentially as reported in the literature⁽⁶⁾. Commercial grade chlorine gas was passed through a concentrated sulfuric acid scrubber and then through calcium chloride. Gallium metal contained in a porcelain boat was heated gently with a Bunsen burner while dried chlorine gas was passed over it. Gallium trichloride was formed and collected in the colder region of the tube. A sketch of the equipment (Pyrex glass) set up is shown in Fig. 1. This gallium chloride was also subjected to emission spectroscopic analysis before use.

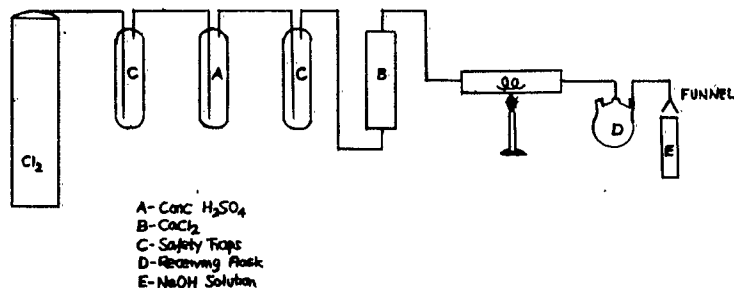


Figure 1. Diagram for Gallium Trichloride Synthesis

The reduction of gallium trichloride with lithium hydride was carried out at -80°C . Finely divided lithium hydride was reacted in a diethyl ether solution of gallium chloride. A two-fold molar excess of lithium hydride was used in many of the more successful experiments. The reaction mixture was then allowed to warm up to ambient temperatures.

Two grades of lithium hydride were experimentally investigated as a reducing agent for gallium chloride. Preliminary experiments were carried out with a 95% (nominal purity) grade of lithium hydride supplied by Maywood Chemical Co., Maywood, N.J. A spectroscopic analysis of this reagent is shown in Table II.

Table II.

Spectroscopic Analysis of 95% Maywood Lithium Hydride (in %)

Lithium	major
Sodium	0.6
Calcium	0.07
Potassium	0.05
Strontium	0.006
Barium	0.004
Copper	0.003
Silicon	0.001
Aluminum	0.003

Later work was carried out with a "purified" grade of lithium hydride. This material, designated as "99% lithium hydride", was also procured from Maywood. A spectrographic analysis is given in Table III.

Table III.

Spectrographic Analysis of 99% Maywood Lithium Hydride (in %)

Lithium	major
Calcium	0.2
Sodium	0.006
Potassium	0.04
Magnesium	0.04
Aluminum	0.03
Copper	0.03
Iron	0.005
Lead	0.005
Barium	0.004
Silicon	0.001

The spectrographic analysis did not in fact show a lower impurity level for the 99% material than for the so-called 95% grade. The main difference was found to be the amount of active material, as determined by hydrogen evolution. On this basis the 99% lithium hydride was found to contain substantially more active material - close to 99.24% as against 88.62% for the initially used 95% grade.

The reaction mixture resulting from the gallium chloride-lithium hydride interaction was filtered in an inert atmosphere, and ether was evaporated under vacuum at room temperature. As the evaporation of the ether proceeded, a white powder precipitated from the solution. A greyish colored solid precipitate remained after removal of ether had been completed.

A quantitative analysis of this precipitate agreed with the formula composition for lithium gallium hydride, LiGaH_4 . This is shown in Table IV. Repeated runs gave average yields above 95% for the lithium gallium hydride obtained (weight basis!).

Table IV.

Quantitative analysis of the LiGaH_4 precipitate

<u>Element</u>	<u>Molar Ratios</u>	
	<u>Experimental</u>	<u>Theoretical</u>
Lithium	1.02	1
Gallium	0.98	1
Hydrogen	2.04	2

This lithium gallium hydride was then decomposed thermally. A wide range of temperatures was experimentally investigated in order to ascertain optimum decomposition conditions. Temperatures in the order of 100-200°C were found to be quite satisfactory. The thermal decomposition products were then carefully treated with water, followed immediately with 3N hydrochloric acid. The resulting gallium metal was then thoroughly washed with water, acetone, etc. and transferred into Teflon containers.

Spectroscopic analyses were performed on representative samples of thusly purified gallium metal products. The results of three typical runs are summarized and also compared with a sample of commercially procured electronic grade gallium in Table V. The starting material used was the batch of gallium chloride whose spectroscopic analysis was shown in Table I.

Appropriate materials balances showed that based on the starting material gallium chlorides, the yields of purified gallium metal were in the 50-60% range. Since - as noted previously - the intermediate lithium gallium hydride could be prepared in almost quantitative amounts, losses of gallium metal must occur in the processing steps following thermal decomposition, i.e., hydrolysis, etc. This was confirmed when quantitative analyses indicated that the missing 40-50% of the gallium was indeed present in the aqueous hydrolysis solution.

Table V.

Typical Spectroscopic Analyses of Gallium Metal Obtained by Hydride
Reduction in ppm

	<u>Run #E 115B*</u>	<u>Run #E 36C</u>	<u>Run #E 36</u>	<u>Alcoa</u>
Ni	5	1	1	<1
Fe	7	1-2	<1	<1
Cr	1	2-3	1	1-2
Cu	3	.5	2-3	0.5-1
Mg	.2	1	1	1
Ag	<0.1	<0.5	<0.5	<0.5
Ca	NF	<2	<2	<2
Pb	NF	<2	<2	<2
Zn	NF	<2	<2	<2
Al	4	<1	<1	<1
Si	<1	NF	NF	NF

Elements checked but not found: As, Co, In, Mo, Sb, Th, Va, W,
Zr, Zn

* Air Force Cambridge Research Laboratories Analysis

Some experiments were carried out in order to study the feasibility of the recovery of the gallium contained in these hydrolysis solutions. It was found possible to convert this metal rather readily to sodium gallate and then recover it via electrolysis on the cathode.

It has been speculated that during the thermal decomposition of lithium gallium hydride some polymeric gallium hydride $(GaH)_x$ may be formed which in turn is hydrolyzed by the dilute aqueous hydrochloric acid solution to water soluble gallium compounds. Experimental studies are in progress to gain a better understanding of the hydrolysis reaction in order to minimize, if possible, the loss of gallium due to this reaction step.

As the above described procedures consistently resulted in a substantial reduction of the impurity level of gallium metal it was considered

of interest to investigate more closely the nature of the purification processes involved in this process. Accordingly gallium metal was chlorinated, the trichloride reduced with lithium hydride to lithium gallium hydride and the lithium gallium hydride decomposed back to the metal with spectroscopic analyses carried out at every step of the way. Electronic grade gallium metal procured from Alcoa was the starting material. A porcelain boat was used to contain the gallium during chlorination.

The analytical sequence shown in Table VI indicates rather clearly that the major purification step occurs in the preparation and subsequent sublimation of the gallium trichloride. The subsequent low temperature reduction of the gallium trichloride by the hydride reductant results in the introduction of only small quantities of additional impurities because container contamination etc., are minimized at these reaction conditions.

Also these data show that during chlorination all impurities present in the gallium starting material were either eliminated (lead, tin) or reduced (copper) but that an additional impurity, namely aluminum, was introduced - almost certainly from the boat material used. In the reduction of the halide the reducing agent effectively removes this aluminum impurity but reintroduces rather small amounts of copper and lead. The impurities are seen to concentrate in the gallium metal residue in the boat after completion of the chlorination reaction. In view of these results the suitability of other boat materials for the chlorination, particularly high purity graphite, deserves experimental evaluation.

Some experimentation was also carried out to ascertain the effects, if any, of a secondary purification, i.e., secondary chlorination and subsequent reduction of the chloride starting with a gallium metal obtained by the same process sequence. Analyses of the product of one such series of runs (E 38) follows in Table VII.

Table VI.

Qualitative Spectroscopic Analyses of Gallium Purification Process

(Run E 36)

	<u>Gallium metal supplied (ALCOA)</u>	<u>Gallium chloride produced from ALCOA gallium</u>	<u>Gallium metal left in the chlorination boat</u>	<u>Gallium metal product</u>
Boron	NF	NF	NF	NF
Gallium	major	major	major	major
Copper	0.00X	0.000X	0.0X	0.000X
Lead	0.00X	NF	0.0X	0.000X
Tin	0.00X	NF	0.0X	NF
Iron	NF	NF	0.00X (low)	NF
Aluminum	NF	0.00X (low)	NF	NF

Elements checked but not found: Ag, As, Bi, Cd, Co, Cr, Ge, In, Mg, Mn, Mo, Ni, Sb, Si, Ti, Th, V, W, Zn, Zr.

0.000X = 0.001 ~ 0.0009% estimated

0.000X (low) = 0.0001 ~ 0.0005% estimated

Table VII.

Effect of Secondary Purification of Gallium Metal on Impurity Concentrations

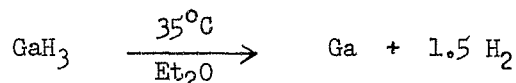
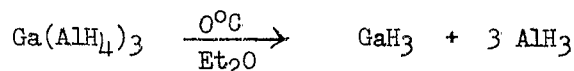
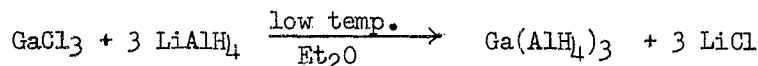
	<u>Gallium metal supplied (ALCOA)</u>	<u>Gallium metal obtained from first reduction</u>	<u>Gallium metal obtained after second reduction</u>
Boron	NF	NF	NF
Gallium	major	major	major
Copper	0.00X	0.000X	0.000X
Lead	0.00X	NF	0.000X
Tin	0.00X	NF	NF
Iron	NF	NF	NF
Aluminum	NF	0.000X (low)	0.000X
Silver	NF	NF	0.000X (low)
Magnesium	NF	NF	0.000X (low)

Elements checked but not found: As, Bi, Cd, Co, Cr, Ge, In, Mn, Mo, Ni, Sb, Si, Ti, Th, V, W, Zr, Zn.

It is apparent that at least in this series of experiments the secondary reduction not only did not improve product purity but resulted in the introduction of additional trace impurities. Further experiments are planned to obtain the additional data which are considered necessary before any conclusions can be drawn. The additional trace impurities found after the second reduction may, for example, have been introduced in the necessarily more extensive handling of the samples.

Gallium Chloride -
Lithium Aluminum Hydride Reaction

Experiments were also carried out to study the possible use of lithium aluminum hydride as a reductant for gallium chloride. The reaction of gallium trichloride with this complex metal hydride has been reported previously by Wiberg et al. to result in the preparation of a thermally unstable gallium aluminum hydride which at 0°C decomposes to gallium hydride etherate. The gallium hydride etherate was reported to break down to the metal above 35°C⁽¹⁴⁾:



Accordingly gallium trichloride in diethyl ether solutions were reacted with lithium aluminum hydride, also in diethyl ether, at -80°C. The resulting solutions were filtered and ether removed under reduced pressure. The product melted at 20 ~ 25°C and decomposed between 125-130°C, even below 1 mm Hg pressure. Analysis of the gray colored decomposition products showed substantial amounts of aluminum and lithium as well as gallium. A rather extended further

study of the gallium trichloride-lithium aluminum hydride reaction fully confirmed these results. No further work is therefore planned along these lines.

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II-2. The Preparation of High Purity Bismuth by the
Reduction of Bismuth Trichloride with Lithium Aluminum Hydride *

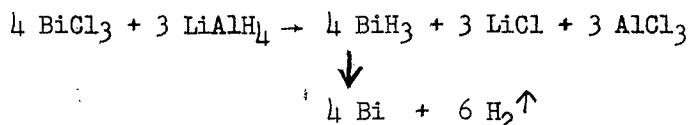
In view of the considerable amount of success obtained on the purification of metals by means of hydride reductions^(1,3), it was desired to investigate this technique for the preparation of high purity bismuth metal. Commercial production of bismuth metal has been described in the literature^(1,2,7). While both pyrometallurgical and electrochemical processes have been developed, the former are apparently in wide use and capable of yielding quite pure metal on an industrial scale^(4,6). More recently the zone refining of bismuth metal has also been investigated⁽⁵⁾. Hydride reductions are of definite interest because they offer the possibility of obtaining high purity metal by a simple low temperature reaction instead of the rather complex multi-step pyrometallurgical processes now employed.

Commercial reagent grade bismuth trichloride was reduced by lithium aluminum hydride in order to ascertain the feasibility of preparing high purity bismuth metal via hydride reductions. The reaction was studied by adding diethyl ether solutions of bismuth trichloride dropwise to an excess of lithium aluminum hydride, also in diethyl ether solution. While this reduction of the bismuth trichloride was carried out at a rather wide range of temperatures, a majority of the runs were performed under ambient conditions. Under these conditions, rapid reduction of the trichloride took place with the formation of a very finely divided black powder. The reactions were carried out in a nitrogen atmosphere. However, this precaution may not be necessary as

* W. Brenner, C.G. Kumar, H. Hellman and C.J. Marsel, New York University, New York, N.Y., presented at the Conference on the Ultrapurification of Semiconductor materials, April 11-13, 1961.

some reductions have yielded equivalent results without this precaution.

It is believed that the reduction of bismuth trichloride to the metal with lithium aluminum hydride may occur via an unstable intermediate hydride, bismuthine, as follows:



Low reaction temperatures would appear to be conducive for the isolation of bismuthine. However, under the reaction conditions investigated, no evidence for the existence of bismuthine was obtained even below -80°C .

After completion of the addition of the bismuth trichloride the reaction mixture was then hydrolyzed carefully in an acid medium. Thus unreacted lithium aluminum hydride was decomposed under acid conditions to soluble reaction products. The resulting bismuth metal powder was then washed successively with 6N hydrochloric acid, water, and absolute alcohol. The final processing steps consisted of heating this powder in a quartz tube under a helium atmosphere and casting to produce ingots. Portions of the ingots were subjected to emission spectrographic analysis. Yields of bismuth metal were in the order of 60-70% based upon the bismuth trichloride used.

Typical semiquantitative emission spectrographic analyses are shown in Table 1. The data show that the simple reduction of bismuth trichloride to the metal eliminated iron, magnesium and chromium as contaminants and either reduced or removed other interfering metal elements, i.e. silicon, copper, silver. No additional impurities were introduced during the reduction.

Table 1.

Spectrographic Analysis of Bismuth Samples

Impurities	Bismuth Chloride Starting Material	Bismuth Metal Powder Form	Bismuth Metal Ingot Form
Bi	major	major	major
Fe	0.0X (low)	NF	NF
Si	0.00X	0.000X (low)	NF
Cu	0.000X	0.000X (low)	NF
Ag	0.000X	0.000X (low)	0.000X
Mg	0.000X	NF	NF
Cr	0.000X	NF	NF
Al	NF	NF	NF

Elements checked but not found: Mn, Pb, Sn, Ni, Cr, Co, Mo, Va, W, Sb, As, Zn, Cd, In, Th, Ga, Ge

0.000X = 0.0001 ~ 0.0009% estimated
 0.000X (low) = 0.0001 ~ 0.0005% estimated

Experiments were also carried out during which the amount of excess of lithium aluminum hydride used was varied. No substantial improvements in product quality were obtained beyond a 3/1 molar ratio of $\text{LiAlH}_4/\text{BiCl}_3$.

Pyrex glass equipment was employed throughout these experimental studies. Care was taken to avoid the use of silicone grease in the apparatus as it was found that such grease could result in silicon contamination of the product. It was also essential to carry out the hydrolysis of the reduction mixture promptly under acid conditions in order to avoid possible reaction of lithium hydroxide upon the Pyrex glass reaction vessels.

The reduction of bismuth trichloride with lithium aluminum hydride offers a promising low temperature route for the preparation of high purity bismuth.

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II-3. Preparation of High Purity Barium

As has previously been described (*) preliminary experiments were carried out on the preparation of barium hydride as a possible intermediate for barium metal production. Two techniques were investigated for barium hydride synthesis, i.e. the direct hydrogenation of molten barium metal and spraying molten barium through an atomizing nozzle where it would be contacted by and atomized with gaseous hydrogen. A barium amalgam rather than barium metal was employed for the latter method in order to attempt to minimize certain expected experimental difficulties. However the experiments relating to the direct hydrogenation of barium were so successful that work on the spraying of the barium amalgam was discontinued. A total of six runs were carried out on the barium amalgam approach with an additional 10 runs made on the hydrogenation of molten barium.

In the first method atomized barium amalgam was contacted by hydrogen gas at 400-450°C. The products included some gray-white powder - presumably barium hydride - but upon analysis were not found to contain any significant amounts of hydrogen. When the experiments were repeated at 600-650°C, the products contained a larger amount of this gray-white powder but again did not indicate any significant hydrogen content. For one run which was carried out around 800°C, the hydrogen content was determined as 0.17%. The theoretical amount of hydrogen in barium hydride is 1.44%.

The hydrogenation of molten barium was studied at a number of different reaction conditions. The best results were obtained at 900-950°C and 20 psig hydrogen, i.e. above the melting point of the barium (850°C). Chemical analysis of the white powder which was obtained showed approximately 85% con-

* "Research on the Preparation of Pure Metals", Scientific Report #3, New York University, New York, N.Y.

version to barium hydride based on the amount of barium originally present. In one run a slightly higher yield was obtained.

Further experiments on the possible decomposition of the typically saline barium hydride proved discouraging. Also the separation of unreacted barium metal from the barium hydride presented additional difficult problems. Review of these experiments brought about the decision to discontinue further work on this approach.

Other preliminary experimental work made it apparent that the separation of calcium and strontium from barium would be an important consideration for the preparation of high purity barium metal. These two other alkaline earth metals are generally associated in small though varying amounts with commercially available barium compounds. The separation problem arises on account of the great similarity in both chemical behavior and even physical properties of the three alkaline earth elements. Two approaches were considered for effecting such separations, i.e. pre-purification of a barium compound before reduction to the metal, and post-purification by distillation, etc. after the metal has been obtained. The subsequent discussion describes exploratory studies on the pre-purification approach using barium chloride as the primary reactant.

A number of different possible separation methods were considered. The extraction of barium chloride with a mixture composed of equal volumes of ethyl alcohol and ether, for effecting separation on the basis of solubility differences was experimentally studied.

In one such typical experiment a sample of barium chloride was refluxed for 16 hours in a Soxhlet extraction apparatus. Analyses of the original and extracted barium chloride samples are shown in Table 1.

Table 1.

Extraction of Barium Chloride with Alcohol-Ether Mixtures

(Spectroscopic semi-quantitative analyses)

amounts in %

	<u>original sample</u>	<u>extracted sample</u>
barium	major	major
calcium	0.X (low)	0.0X
strontium	0.X (low)	0.X (low)
silicon	0.X (low)	0.00X
magnesium	0.0X (low)	0.00X
lead	0.00X	0.000X
potassium	0.00X	0.00X
aluminum	0.00X	0.00X
iron	0.000X	0.000X
copper	0.000X	0.000X (low)

Elements checked but not found: Ag, Mn, Ni, Cr, Co, Mo, Va, N, Bi, Sb, As, P, Sn, Zn, Cd, In, Ti, Zr, Na, Li

Since it was evident that no appreciable separation was effected, this method was abandoned.

Next experiments were carried out to remove calcium and strontium from barium chloride by the formation of insoluble chelates. The chelating agent was 1,2 diaminocyclohexane tetraacetic acid which is sold commercially by Geigy Industrial Chemicals (Ardsley, N.Y.) under the trade name CHEL-600. This chelating agent was chosen because published data show very appreciable differences in the equilibrium constants when complexes are formed with barium, calcium and strontium:

calcium	log K_2	= 12.50
barium		7.99
strontium		10.0

In a simple experiment a solution of 2 grams of CHEL-600 in a minimum quantity of NH_4OH and 10 ml. water was added dropwise to a stirred solution consisting of 20 grams of barium chloride dissolved in 100 ml. of pure distilled water. The precipitate was allowed to settle for two hours prior to filtration through a Whatman No. 42 filter paper. The filtrate was evaporated to dryness and subjected to spectroscopic analysis with the results of one typical run summarized in Table 2 below:

Table 2.

Analysis of Filtrate from Chelation of BaCl_2 with CHEL-600

(spectrographic semi-quantitative analyses)

	<u>original sample</u>	<u>product</u>
barium	major	major
calcium	O.X (low)	O.OX
strontium	O.X (low)	NF
silicon	O.X (low)	O.OOX (low)
magnesium	O.OX (low)	O.OOX (low)
lead	O.OOX	O.OOOX
potassium	O.OOX	NF
aluminum	O.OOX	O.OOX (low)
iron	O.OOOX	NF
copper	O.OOOX	O.OOOX

Checked but not found: Ag, Zn, Cd, In, Bi, As, Sb, Sn, Ga, Th, Ge, Ti, Mn, Ni, Cr, Co, Mo, Va, W, Zr, Na, Li

It is apparent that this simple experiment resulted in the elimination of strontium. It is also quite clear that the chelating agent effectively removed several other minor impurities. Calcium however was not eliminated although the amount present was cut by roughly one order of magnitude. Additional experiments closely confirmed this analysis and also showed that the reason for the inability of this chelating technique to remove calcium was the water solubility of the calcium chelate.

After it had been established that calcium chelates with CHEL-600 are water soluble, experiments were performed to evaluate the feasibility of isolating barium as a CHEL-600 chelate after removal of the strontium had been effected as described above. Accordingly a sample of barium chloride was treated with CHEL-600 and the resulting precipitate filtered. Analysis of the filtrate showed absence of strontium. Additional CHEL-600 (20 gms per 100 gms BaCl₂ solution) was then added and the precipitate thusly formed filtered, washed and dried (100°C.). Analysis of the filtrate gave the data shown in Table 3. The data show a further reduction of the calcium content as well as the elimination of the impurities aluminum, lead and silicon.

Table 3.

Analysis of Precipitate Obtained in Chelation of Barium Chloride

with CHEL-600

(Semi-quantitative spectroscopic analysis)

barium	major
calcium	0.00X (low)
magnesium	0.00X (low)
silver	0.000X
copper	0.000X
iron	0.000X

Checked but not found: Si, Al, Ti, Zr, Zn, Cd, In, Pb, Sn, Bi, Sb, As, P, Th, Ga, Ge, Mn, Ni, Cr, Co, Mo, Va, W, Na, Sr, K, Li

A considerable amount of additional chelating studies resulted in significantly improved calcium removal by effecting minor changes in the chelation procedure. Also the applicability of this separation technique to the compound barium azide was established. Additional information on the separation of calcium and strontium from barium in barium azide is discussed below.

Barium hydroxide was finally chosen as the starting material for the preparation of the thermally unstable intermediate, barium azide. Commercial grade barium hydroxide obtained from the Baker Chemical Co., Phillipsburg, N.J. was employed. The nominal analysis of this "Baker Analyzed Reagent" grade of barium hydroxide is given in Table 4, below.

Table 4.

Nominal analysis of barium hydroxide, "Baker Analyzed Reagent" grade

assay ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$)	99.5%
barium carbonate (BaCO_3)	0.29%
insoluble in HCl	0.005%
chloride (Cl)	0.001%
sulfide (S)	$\leq 0.001\%$
substances not precipitated by H_2SO_4	0.03%
heavy metals (as Pb)	0.0003%
iron (Fe)	0.0005%

"Baker Analyzed Reagent" grade barium hydroxide was recrystallized twice from distilled water. A spectrographic analysis of the recrystallized material was undertaken in order to ascertain both the identity and relative amounts of cationic impurities. The results of this analysis showed that the main impurities were strontium, calcium, lead and iron with strontium most prominent. Typical analytical data are shown in Table 5 for batch G-3.

Table 5.

Qualitative Spectrophotographic Analysis of Barium Hydroxide

<u>metal</u>	<u>amount in ppm</u>
barium	major
strontium	3000
calcium	700
lead	30
iron	7

Elements checked but not found: silicon, aluminum, sodium, magnesium, antimony, manganese, silver, nickel, chromium, cobalt, molybdenum, vanadium, tungsten, gallium, thallium, germanium, zinc, cadmium, indium, bismuth, arsenic, phosphorus, tin, zirconium, titanium, potassium, lithium.

This recrystallized barium hydroxide was reacted with aqueous hydrazoic acid. The hydrazoic acid was prepared by the controlled reaction of sodium azide in the presence of alkali with sulfuric acid at a suitably elevated temperature. (1) A sketch of the equipment used is shown in Fig. 1 below.

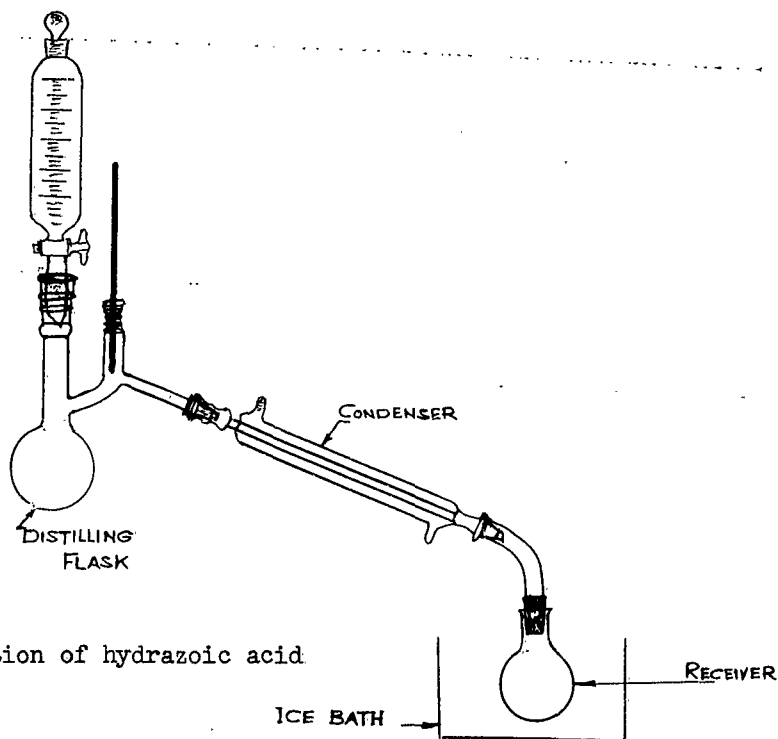


Fig. 1. Preparation of hydrazoic acid

In a typical preparation 30 grams of sodium azide (Purified Grade Fischer Scientific Co., Fairlawn, N.J.) and approximately 10 grams of sodium hydroxide crystals (Baker Analyzed Reagent Grade, Baker Chemical Co., Phillipsburgh, N.J.) were dissolved in 300 ml of distilled water. This solution was heated in a 500 ml distilling flask to which had been fitted a dropping funnel and, separately, a water cooled condenser. As shown in Fig. 1, the other end of the condenser was connected by means of an adapter to 500 ml flask containing approximately 200 ml of distilled water and cooled externally with an ice-water mixture. 180 ml of 40% sulfuric acid solution were then added dropwise to the boiling alkaline sodium azide solution. Hydrazoic acid formed and distilled into the condenser (B.P. 37°C.) to be collected in the ice water cooled flask. Sodium hydroxide was used purely as a precautionary measure to prevent the formation of a high concentration of hydrogen azide to the hot solution.

Barium azide was obtained in solution by reacting barium hydroxide with hydrazoic acid. Specifically a saturated solution of barium hydroxide was added slowly with vigorous stirring to the above prepared hydrazoic acid solution until the solution was faintly acidic as shown by a suitable indicator. Generally clear solutions were obtained. In certain runs some turbidity developed presumably due to some barium sulfate formation. When this occurred filtration readily restored the clarity of the aqueous barium azide solution.

This aqueous barium azide solution was vacuum concentrated to around one third of its original volume. Barium azide was precipitated by the addition of ethyl alcohol. The wet crystals were vacuum dried and stored in a dessicator at ambient temperatures, away from light, etc.

Prior to attempts at the further purification of barium azide including the separation of calcium and strontium, exploratory studies were made on its

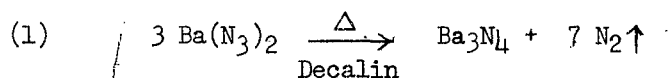
thermal decomposition. Initial decomposition experiments were conducted by irradiating dry barium azide powder under nitrogen with a 275 watt GE Sunlamp operated at 110 V. This procedure initiated decomposition even at ambient temperatures. However the decomposition reaction could not always be suitably controlled with several small explosions occurring. It was therefore decided to investigate the decomposition of barium azide under inert solvents in order to moderate this reaction.

Various inert solvents were investigated for this purpose. Barium azide did not decompose under cyclohexane. Decomposition occurred however in both xylene and decalin solvents. Excellent results were obtained when barium azide was decomposed under decalin near its boiling point. Heating proved to be as effective as U.V. irradiation and was therefore used in all later decomposition experiments. With the barium azide under decalin solvent as much as 10-20 grams of barium azide could be smoothly decomposed in less than 30 minutes. In most decomposition reactions the nitrogen gas produced was collected and measured. The black precipitate remaining under the decalin layer proved to be highly reactive with air and water. Suitable elemental analysis of the reaction products were carried out. Infrared spectra of the decalin before and after barium azide decomposition were identical. This indicates that the decalin did not take part in the barium azide decomposition.

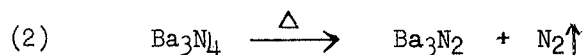
As the nitrogen gas measurements gave results which were substantially less than the theoretical amount present in barium azide, nitrogen analyses were carried out on the black precipitate using the Kjeldahl method. Nitrogen contents of 12.49% and 12.72% were found corresponding to the nitrogen content of a hypothetical barium pernitride, Ba_3N_4 (11.95% N_2), the strontium analogue of which is however known.

This black precipitate was washed with ether, vacuum dried and heated further in vacuo up to 250°C. Additional nitrogen gas was collected during this second heating. Nitrogen analyses of the resultant black product gave values in the order of 6.50%. This corresponds well with the theoretical amount of nitrogen in barium nitride, Ba₃N₂, which is 6.36%.

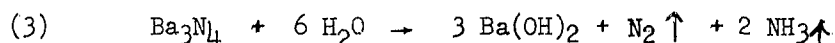
The results of a considerable number of experiments confirmed that barium azide under decalin does indeed decompose to barium pernitride rather than barium metal as had been supposed. This reaction is believed to take place as shown in the following equation (1):



Upon further heating under a low vacuum atmosphere barium pernitride decomposed into barium nitride and gave off additional nitrogen gas. This decomposition is shown by equation (2):



In water barium pernitride was rapidly converted to barium hydroxide. Nitrogen gas and ammonia were produced also. Equation (3) expresses this reaction:



The barium pernitride was found to have a hexagonal structure. This type of structure has not been previously reported for any nitrogen compound of barium. Additional details on the decomposition of barium azide and analogous exploratory experiments on the decomposition of calcium azide are described in an attached paper which was delivered at the 1962 Washington Meeting of the American Chemical Society.

Further studies were carried out on the thermal decompositions of barium pernitride because it was desired to obtain the metal and not the nitrides. It was found that when thermal decompositions of barium pernitride were carried out at 850° - 900° C under 0.2 to 1.0 mm Hg pressure, the metal was obtained. For these decomposition reactions the barium pernitride was placed in a pure iron tube approximately 1" diameter and 12" long, which in turn was enclosed by a stainless steel tube. A sketch of the experimental setup is shown in Fig. 2.

This assembly which was found necessary to prevent attack of the barium metal on container materials such as stainless steel, was then heated in a Lindberg furnace. Chemical analysis showed that the decomposition product contained 1-2% nitrogen as the major impurity. This nitrogen is apparently present in the form of a barium nitride.

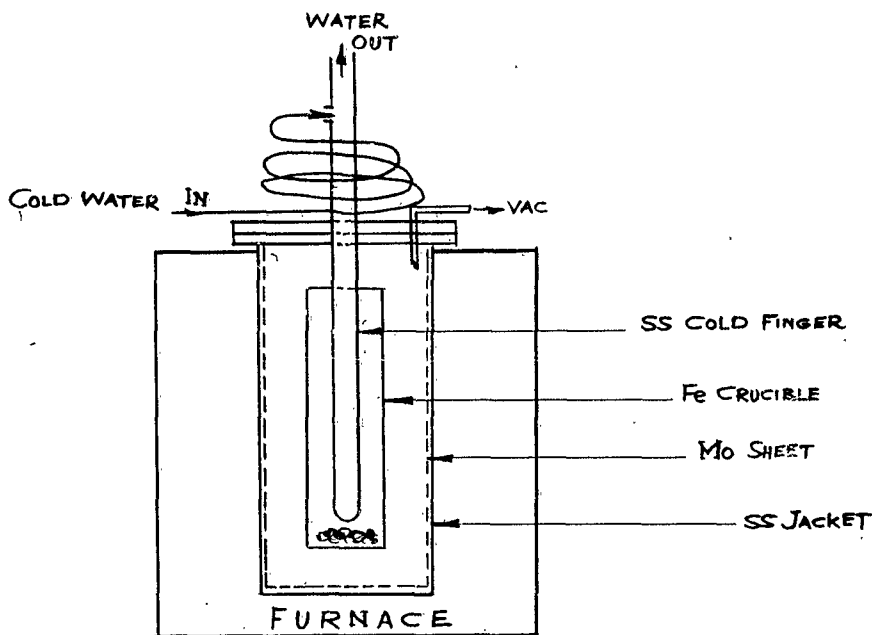


Fig. 2 - Distillation of Barium

Various methods were considered in order to eliminate this nitride impurity. The most effective means developed consisted of further heating this initial barium pernitride decomposition product in a titanium crucible at 900-950°C in vacuo for 10-12 hours. Barium metal has no solubility in titanium and the titanium reacts preferentially with the evolved nitrogen. Chemical analysis could not discern any detectable amounts of nitrogen in the metal product after reaction.

Chemical analysis did however show contamination of the barium with titanium in the order of 0.0X%. Thus distillation was indicated as a final purification step in view of the differences in melting points, etc.⁽²⁾. A suitable temperature has been found to be 1000°C. Such distillations were carried out in titanium crucibles. These crucibles were wrapped with thin molybdenum foil and then placed inside of a stainless steel container, the function of the molybdenum foil being to prevent direct contact of the titanium crucible with the stainless steel. A cold finger (stainless steel) extended into the center of the titanium crucible for the deposition of distilled barium. A sketch of this experimental setup is shown in Fig. 3.

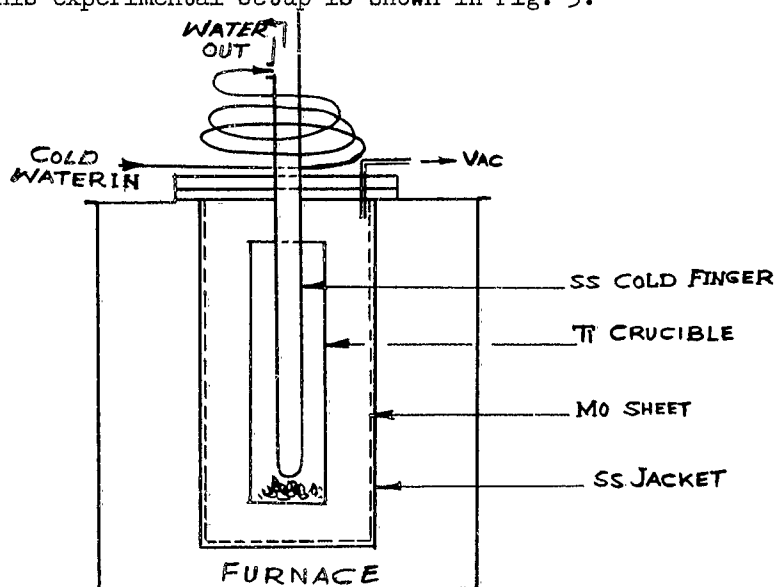


Fig. 3. Distillation of Barium

These processes were later somewhat simplified by utilizing the same titanium crucible both for the high temperature thermal decomposition of the barium pernitride into barium metal and its subsequent distillation to minimize container derived impurities, etc. The distilled barium metal was highly reactive to oxygen, water, alcohol and so on.

After the above described procedure for the preparation of barium metal had been established, major emphasis was put on the purification thereof. The two processing steps where purification appeared to be feasible, were in the preparation of barium azide and in the final distillation of the metal. Accordingly experimental studies were carried out on the purification of barium azide in order to obtain barium metal with minimal impurity contents for the final distillation.

Preliminary experiments were carried out to ascertain the impurities present in barium azide which had been synthesized as described above. Because of the thermal instability of barium azide, spectrographic analyses were carried out on the more stable barium pernitride. A typical analysis follows (Table 6).

Table 6.-
Semi-quantitative
spectrographic analysis of Ba_3N_4 obtained from "unpurified"
 $Ba(N_3)_2$ (Sample G-1)

<u>metal</u>	<u>amount in %</u>
barium	major
strontium	.0X
calcium	.0X
silicon	.X
aluminum	.0X
sodium	.00X
iron	.00X
lead	.00X
magnesium	.00X (low)
antimony	.00X (low)
manganese	.000X
copper	.000X
silver	.000X

Elements checked but not found: nickel, chromium, cobalt, molybdenum, vanadium, tungsten, gallium, germanium, zinc, cadmium, indium, bismuth, arsenic, phosphorus, tin, zirconium, titanium, potassium, lithium, boron.

Considering the previously described promising results obtained with chelating agents for the separation of the alkaline earth metal impurities, etc. from barium chloride, it was decided to evaluate the same approach for the purification of barium azide. Thus barium azide in aqueous solutions was treated with an ammoniacal solution of 1,2 diaminocyclohexane tetraacetic acid at ambient temperature. Typical specific experiments involved the addition of 1.5 grams of chelating agent dissolved in 15-20 mls of 20% ammonium hydroxide solution to 10 grams of barium azide dissolved in the minimum amount of water. The solution was allowed to stand for a short period of time - approximately 1/2 hour - and then filtered to remove the precipitate. Reagent grade redistilled ethyl alcohol was added to the filtrate to precipitate the barium azide. Some experiments were also carried out during which a second portion of chelating agent was added to the filtrate. Typical spectrographic analysis of barium pernitride which was obtained from the decomposition of thusly purified barium azide are given in Table 7, below. It is to be noted that this barium azide was decomposed under redistilled and dried decalin.

Table 7.

~~Semi~~-quantitative spectrographic analysis of Ba_3N_4 obtained from "purified" $Ba(N_3)_2$ (Samples G-8 and G-30)

<u>Metal</u>	(amounts in %)	
	<u>Sample G-8</u>	<u>Sample G-30</u>
barium	major	major
strontium	NF	NF
calcium	.000X	.000X
aluminum	.00X	.000X
silicon	.00X	.000X
magnesium	.00X (low)	.000X
titanium	NF	NF
iron	.000X	NF
copper	.000X	NF
lead	.000X	NF
silver	.000X	.000X (low)

Elements checked but not found: nickel, manganese, cobalt, zinc, cadmium, indium, tin, bismuth, antimony, arsenic, phosphorus, chromium, molybdenum, vanadium, tungsten, thallium, gallium, germanium, sodium, lithium, potassium, boron.

A comparison of Tables 6 and 7 shows that the above described chelation step did indeed result in a significant reduction of metal impurity concentrations. Strontium was eliminated completely and calcium was greatly reduced. In addition certain other impurities such as antimony, silicon, sodium, manganese and iron were either removed or significantly reduced in concentration.

Experiments were also carried out in which an additional oxalic acid treatment was given to the filtrate in order to chelate any calcium traces remaining. The data of Table 8 show that this was not successful and that, as a matter of fact, the total impurity level increased. Work on this auxiliary treatment was therefore discontinued.

Table 8.

Semi-quantitative spectrographic analyses of Ba_3N_4 obtained from "purified" $Ba(N_3)_2$ post treated with oxalic acid (Samples G-7 and G-17)
(amount in %)

<u>Metal</u>	<u>Sample G-7</u>	<u>Sample G-17</u>
barium	major	major
strontium	.OX	.OOX
calcium	.OOX	.OOX
aluminum	.OX	.OOOX
silicon	.OX	.OX
magnesium	.OOX	.OOOX
titanium	.OOX	NF
iron	.OOOX	.OOOX
copper	.OOOX	.OOOX
silver	.OOOX (low)	NF [~]

Elements checked but not found: nickel, manganese, cobalt, zinc, cadmium, indium, tin, bismuth, antimony, arsenic, phosphorus, chromium, molybdenum, vanadium, tungsten, thallium, gallium, germanium, sodium, lithium, potassium, boron.

The analyses of three samples of distilled barium metal product are shown in Table 9 below. As has been described before a titanium crucible wrapped with thin molybdenum foil was employed for the containment of the barium prior to

distillation. Approximately 10 grams of one of these samples (G-42) were sent to the Cambridge Air Force Research Laboratories for further evaluations. The principal nonmetallic impurity was nitrogen, present to less than 0.01%.

Table 9.

Semi-quantitative spectrographic analyses of distilled barium metal samples obtained from the thermal decomposition of "purified" Ba(N₃)₂

amount in %

<u>Metal</u>	<u>Sample #G-32</u>	<u>Sample # G-34</u>	<u>Sample #G-42</u>
barium	major	major	major
strontium	.00X	.00X	.00X
calcium	.000X	.000X	.000X
silicon	.000X	.000X	.000X
aluminum	.00X	.000X	.000X
iron	.000X	.000X	.000X
magnesium	.000X	.000X	.000X

Elements checked but not found: boron, copper, silver, zinc, cadmium, indium, manganese, nickel, chromium, cobalt, molybdenum, vanadium, tungsten, lead, tin, bismuth, antimony, arsenic, thallium, germanium, gallium, titanium, zirconium, sodium, potassium, lithium.

It was surprising that small amounts of strontium reappeared as an impurity in the distilled barium as they did not show up in purified barium azide. The other elements noted as impurities are present in quite small amounts. As this strontium could come from the container material, some experiments were carried out to ascertain the possible presence of strontium in titanium. The results were inconclusive however. The analysis of the grade of commercially pure titanium used indicated that strontium is not present as a normal impurity. Further study of this problem is under consideration.

The above described purification scheme suggests a new approach for the preparation of high purity alkaline earth metals from commercially available

raw materials. While the validity of this purification concept is believed to be demonstrated by the data which have been presented above, additional experiments are suggested in order to improve upon the equipment used and also to further refine the procedures used.

References

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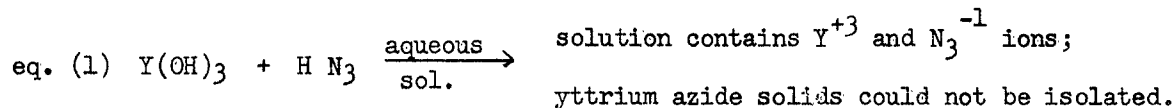
II-4. Yttrium purification studies

The preparation of yttrium metal has been investigated by Thompson⁽¹⁾, Trombe⁽²⁾, Daane and Spedding⁽³⁾, C.V. Banks and coworkers⁽⁴⁾, J.A. Haefling, F.A. Schmidt and O.N. Carlson⁽⁵⁾ as well as other workers. The high temperature reduction of yttrium fluoride with calcium metal has been rather extensively investigated. Other reductants for yttrium fluoride which have been experimentally investigated, include lithium, calcium-lithium alloys, magnesium, aluminum, sodium and zinc. Some work has also been reported on the reduction of yttrium chloride with lithium and sodium. A comprehensive review of metallothermic preparations of yttrium metal has been prepared by O.N. Carlson and F.A. Schmidt⁽⁶⁾.

Because of the high reduction temperatures required container contamination is a serious problem for the preparation of high purity yttrium metal. Yttrium metal not only is quite stable thermally but reacts readily with oxygen, water, etc. The synthesis of high purity yttrium with the semiconductor meaning of "purity" has proven to be a difficult task. The subsequent report describes preliminary experiments which were undertaken in order to develop, if possible, a low temperature process for the preparation of the high purity metal. Successful development of such a low temperature process would greatly reduce container contamination problems and also make possible the use of simpler reduction equipment, etc.

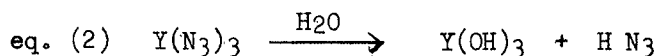
Initially experiments were carried out to produce yttrium azide as - it was hoped - an unstable intermediate for subsequent decomposition to the metal. Yttrium azide has not been reported in the chemical literature. Later work was carried out on the preparation of organo-yttrium compounds for use as intermediates in the preparation of yttrium metal.

The preparation of yttrium azide was first attempted by reacting aq. yttrium hydroxide with aq. hydrazoic acid as shown in equation (1) below. Ambient temperature conditions prevailed. The resulting solution was analytically found to contain both Y^{+3} and N_3^{-1} ions. Precipitation of yttrium azide by various organic solvents proved unsuccessful.



The results obtained when alcohol precipitation was attempted were typical. A white precipitate was gotten which did not contain azide ions. The composition was that of an yttrium hydroxide.

Evaporation of water by vacuum distillation resulted in the formation of a white solid which again did not contain any azide ions. However the evaporated liquid which was collected in a dry ice-acetone cooled vessel, did contain azide ions and was acidic. It is therefore believed that yttrium azide undergoes hydrolysis as shown in equation (2).



The same reaction between anhydrous yttrium chloride and sodium azide was attempted in organic solvents such as tetrahydrofuran. Anhydrous yttrium chloride was obtained by passing gaseous hydrochloric acid over commercially available $YCl_3 \cdot 6H_2O$ at temperatures up to $120^\circ C$. The solution contained Y^{+3} and N_3^{-1} ions. However when the solvent was removed, N_3^{-1} could not be found in the remaining solid. Complex formation is believed to have taken place.

Experiments were also carried out in which it was attempted to prepare yttrium azide by ion exchange techniques. Dowex Anion Exchange #1X8 was employed. The resin was loaded with sodium azide solution till the effluent did not contain

chloride ions. Then yttrium chloride solution was passed through the azide form of the resin. A solution was finally obtained which contained both Y^{+3} and N_3^- ions. As before, however, attempts at the isolation of the azide failed.

The reaction between yttrium chloride and silver azide was also experimentally investigated. Silver chloride precipitated and was filtered off. The solution contained both Y^{+3} and N_3^{-1} ions but isolation of the yttrium azide was unsuccessful. In view of these results further work on the preparation of yttrium azide was discontinued.

The possible use of organo-yttrium compounds as intermediates for the preparation of high purity yttrium metal was next investigated. The reactions of yttrium chloride with n-butyl bromide, ethyl magnesium bromide, etc. were unsuccessfully attempted in order to obtain alkyl yttrium compounds.

Yttrium metal was also reacted with methyl iodide in order to obtain methyl yttrium. Pyridine was used as a solvent. After 24 hours reflux, a black pasty product was obtained. This material was extracted several times with pyridine in a Soxhlet apparatus. Chemical analyses showed 10.35% yttrium, 36.02% carbon, 3.43% hydrogen, 7.03% nitrogen and 32.8% iodine. It appears that some complex was formed rather than the desired methyl yttrium.

Yttrium chloride was reacted with sodium cyclopentadiene in tetrahydrofuran. Tricyclopentadienyl yttrium was obtained in moderate yield. However, under certain reaction conditions the hitherto unreported organic yttrium derivative, yttrium dicyclopentadienyl chloride, was obtained. This compound could be readily sublimed and being capable of purification appeared to be of interest as intermediate for the preparation of yttrium metal.

A considerable amount of experimentation was carried out on the reduction of both the tricyclopentadienyl yttrium and the dicyclopentadienyl yttrium chloride. Reducing agents which have been experimentally evaluated, include hydrogen, lithium, lithium hydride, lithium aluminum hydride and lithium borohydride. A re-evaluation of this approach has resulted in the decision to discontinue further studies in favor of the reduction of yttrium halides by hydrides, etc.

A detailed report on the organoyttrium work is presented in the following paper which will be presented at the Third Rare Earth Conference in April 1963.

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- (5) J.A. Haefling, F.A. Schmidt and O.N. Carlson; "A Study of Several Metals as Reductants for Yttrium Fluoride," Report IS-374, Sept. 1961 (Ames Laboratory, Ames, Iowa).
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ORGANO RARE EARTH COMPOUNDS
ORGANO YTTRIUM COMPOUNDS*

Abstract:

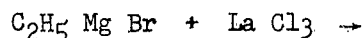
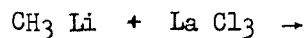
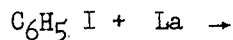
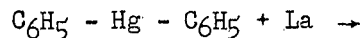
The literature of the preparation and characterization of organo rare earth compounds is reviewed with special emphasis on organo yttrium compounds. The synthesis of tricyclopentadienyl yttrium is described by known methods. A new surprisingly volatile compound dicyclopentadienyl yttrium chloride has been obtained from the reaction of anhydrous yttrium trichloride with sodium cyclopentadiene. Pertinent physical and chemical properties of dicyclopentadienyl chloride are discussed. Similar preparations with other rare earth metals are considered.

Introduction:

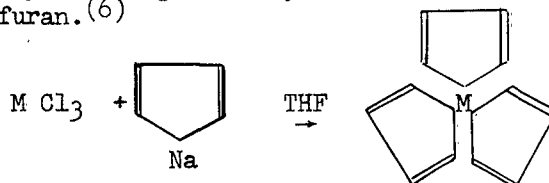
Cerium, the first accurately identified rare earth element, was discovered about 160 years ago. Since that time steadily increasing emphasis has been given to studies related to the preparation and properties of rare earth elements, alloys, compounds and also solutions. Very little published information is available however on the preparation and properties of organo rare earth compounds.

The first organo rare earth compounds were reported in 1938.⁽¹⁾ Triethyl scandium and triethyl yttrium were synthesized in the form of etherates, $(C_2H_5)_3M O(C_2H_5)_2$ which compounds distilled at about 220°C. However the validity of this work has been questioned on good grounds.⁽²⁾ Attempts to prepare erbium and lanthanum alkyls from the reaction of the rare earth metal chlorides with alkyl magnesium halides proved unsuccessful.⁽³⁾ Gilman and Jones reported on an intensive study of the preparation of the alkyl and aryl lanthanum compounds in 1945.⁽⁴⁾ The following reactions were experimentally investigated but to no avail:

* Y. Okamoto, W. Brenner, J.C. Goswami, Research Division, College of Engineering New York University, New York 53, N.Y.; and A. Rubin, A. Armington, Cambridge Air Force, Research Laboratories, Bedford, Massachusetts.



Probably the best positive evidence for the formation of organic rare earth compounds is the reaction of methyl radicals with a lanthanum metal mirror. This experiment was carried out employing the so-called Paneth technique.⁽⁵⁾ More recently Birmingham and Wilkinson attempted the preparation of tricyclopentadienyl rare earth compounds by reacting the anhydrous metal halides with cyclopentadienyl-sodium in tetrahydrofuran.⁽⁶⁾



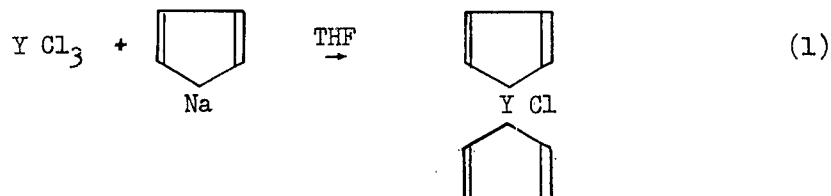
where M = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Yb.

The tricyclopentadienyl rare earth compounds were found to exhibit rather similar chemical properties. Their comparatively low melting points and fair volatilities suggest that structurally they can be considered as ionically bonded molecular entities, even in the solid state.

Experimental and Discussion

A. Dicyclopentadienyl yttrium chloride

A hitherto unreported compound, dicyclopentadienyl yttrium chloride, was repeatedly and reproducibly synthesized and isolated in 10-20 Wt.% yields from the reaction of anhydrous yttrium trichloride with cyclopentadienyl sodium at ambient temperatures. The reaction is shown by the following equation (1):



A slight excess of cyclopentadienyl sodium was employed over the theoretical 3 moles required per mole of yttrium chloride. The reactions took 15-20 hours at room temperature under argon atmosphere. No data are as yet available on the effect of longer reaction periods on product yields. Sodium chloride produced as indicated in equation (1) was removed by filtration under vacuum. The solvent, tetrahydrofuran, was removed by vacuum distillation. The residue was sublimed in a stream of purified hydrogen or argon at approximately 250°C.

A microanalysis of this compound is shown in Table 1 and apparently confirms the composition as dicyclopentadienyl yttrium. The white sublimate darkens slightly upon heating to 300°C in a sealed tube and did not melt at 400°C. Dicyclopentadienyl yttrium chloride is stable in nitrogen, argon, etc. for prolonged time periods but reacts rapidly with air to produce cyclopentadiene and yttrium chloro hydroxides.

Table 1.

Micro-Analysis of Dicyclopentadienyl Yttrium Chloride

	C	H	Y	Cl
found %	47.78	4.44	34.6	14.05
			34.7	14.30
theoretical %	47.17	3.92	34.9	13.95

The infrared and nuclear magnetic resonance spectra together with the established ready volatility suggest that dicyclopentadienyl yttrium chloride is ionically bonded, even in the solid state.

Dicyclopentadienyl yttrium could be readily purified by distillation. Needle-like white crystals were obtained upon sublimation. The ready volatility of dicyclopentadienyl yttrium chloride suggests that this compound may be of interest as an intermediate for the preparation of high purity yttrium compounds, including possibly the metal. A spectrographic analysis of once sublimed dicyclopentadienyl yttrium chloride is shown in Table 2. This compound was synthesized from commercially available yttrium chloride and unpurified cyclopentadienyl sodium. The results show a surprisingly good purity even though no special precautions were taken during the synthesis. It is believed that significantly lower impurity levels can be achieved by repeated sublimations.

Table 2.

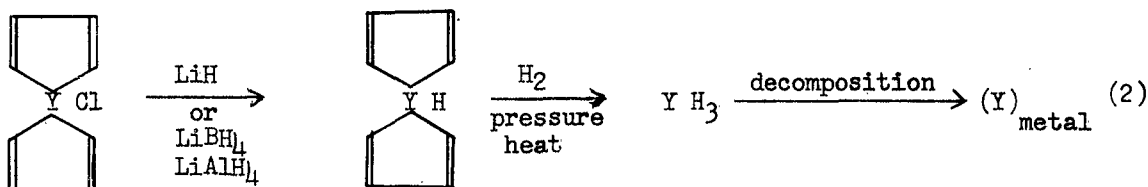
Semi-quantitative Spectrographic Analysis

yttrium	major
copper	0.0X *
silver	0.0X
aluminum	0.00X-0.000X
iron	0.000X
lead	0.000X
silicon	0.000X

Elements checked but not found: zinc, cadmium, indium, bismuth, antimony, arsenic, phosphorus, tin, thallium; gallium, germanium, manganese, nickel, chromium, cobalt, molybdenum, vanadium, tungsten, titanium, zirconium, magnesium, calcium, barium, sodium, strontium, potassium, lithium.

* .0X = 0.01 - 0.09% estimated.

The following reactions have been carried out and are being further studied with dicyclopentadienyl chloride with the purpose of preparing other organic yttrium compounds and also the rare earth metal itself (equation 2)

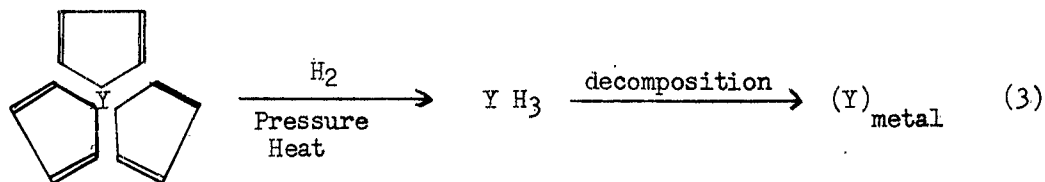


In general, the reduction with LiH and LiAlH₄ appears to be very slow at ambient temperatures in tetrahydrofuran. Elevated temperature reductions are under study.

B. Tricyclopentadienyl yttrium

Tricyclopentadienyl yttrium was prepared in accordance with the methods described by Birmingham and Wilkinson.⁽⁶⁾ Yields of less than 10% were obtained. The melting point of tricyclopentadienyl yttrium was found to be 280-290°C. This value agrees fairly well with the previously published report of 295°C.⁽⁶⁾ However no full characterization of tricyclopentadienyl yttrium obtained has as yet been carried out.

Hydrogenation of sublimed tricyclopentadienyl yttrium under high pressure is being investigated in order to possibly obtain the hydride intermediate as a precursor for the preparation of yttrium metal. This reaction sequence is shown in equation (3):



References

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- (2) F.A. Cotton, *Chem. Reviews* 55, 551 (1955); also unpublished work by F.A. Cotton. See also note below.
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- (5) F.D. Rice and K.K. Rice; "The aliphatic free radicals"; John Hopkins Press, Baltimore, Md. (1935).
- (6) J.M. Birmingham and G. Wilkinson, *JACS* 76, 6210 (1954); see also *ibid.* 78, 42 (1956).

Note to reference (2):

An attempt to reproduce Pletts' work for yttrium was made by Okamoto and Goswami. The reaction between anhydrous yttrium chloride and ethyl magnesium bromide was repeatedly investigated experimentally in diethyl ether. However the expected product, triethyl yttrium etherate could not be isolated.

III. Researches on Organic Semiconductors

III-1. Investigations of Polycyclic Aromatic Hydrocarbons

Experimental studies were carried out in order to ascertain the effects of structure and metallic impurities on the electrical resistivity and related properties of the series of polycyclic aromatic hydrocarbons, naphthalene to hexacene. While the electronic properties of polycyclic aromatic hydrocarbons have been investigated in the past, a review of such studies has shown significant differences in the magnitude of the values obtained by different workers with the same chemical compound, with little if any agreement among the data reported to date. The initial studies on naphthalene and anthracene are fully described in a paper entitled "Effect of Impurities on the Electrical Conductivity of Simple Polycyclic Hydrocarbons" which was delivered at the Inter-Industry Conference on Organic Semiconductors, April 1961, Chicago, Ill.⁽¹⁾ Additional information and data on tetracene, pentacene and hexacene are given in a report entitled "Electronic Conductivity of Polyaromatic Hydrocarbon Compounds: Structural Relationships and Impurity Effects".⁽²⁾

(1) Also published in J.J. Brophy and J.W. Buttrey, "Organic Semiconductors", Macmillan Co., New York, N.Y. 1962.

(2) To be delivered at September 1962 ACS meeting.

EFFECT OF IMPURITIES ON THE ELECTRICAL CONDUCTIVITY
OF SIMPLE POLYCYCLIC AROMATIC HYDROCARBONS*

Introduction

Electrical properties including conductivities of various polycyclic aromatic hydrocarbons have been measured by a number of investigators (1-8). A review of these studies points out significant differences in the magnitude of the values obtained by different workers with the same chemical compound, with little if any agreement among the data reported to date. Also purity of the compounds being studied was either incompletely specified or not determined altogether. This investigation was undertaken in order to ascertain the effect of metallic impurities on the electrical resistivity and related properties of a series of simple polycyclic aromatic hydrocarbons. One measurement technique was developed and employed to obtain all the data reported below in an attempt to minimize the role of this variable as much as possible.

Experimental

1. Apparatus. Resistivity measurements were performed with a Keithley Model 610-A Electrometer with accompanying power supply and shunt. Measurements were made in accordance with the techniques developed by Brown and Aftergut⁽²⁾. All measurements were carried out in an atmosphere of dried air, on discs which had been compacted under pressure (8050 psi). The thickness of disc ranged from 0.10 to 0.17 cm.

2. Materials. Naphthalene and Anthracene were obtained from E.H. Sargent Co. and Eastman Organic Chemicals, respectively. The commercially available products were purified by the following methods:

* Y. Okamoto, F. T. Huang, A. Gordon, Research Division, College of Engineering, New York University, New York, New York; and B. Rubin, Air Force Cambridge Research Laboratories, Bedford, Massachusetts.

Method 1: Acid Treatment and Sublimation. Saturated solutions of the various hydrocarbons in electronic grade benzene (Fisher Scientific Co.) were prepared and then refluxed with 10 percent aqueous hydrochloric or sulfuric acid for several hours. After cooling to room temperature, the benzene layer was decanted and thoroughly washed repeatedly with distilled water. The remaining solvent was then removed by distillation. The solids were dried under vacuum at room temperature. Further purification was effected by two successive sublimations under reduced pressure (5-20 mm Hg).

Method 2: Multiple Sublimations. The materials obtained commercially were purified directly by means of multiple vacuum sublimation. After purification of the hydrocarbons, the metallic impurity content in the samples were obtained by emission spectroscopic analysis. The spectrograph is a large Littro quartz prism, manufactured by Bausch and Lomb, Inc. A weighed portion of the samples is burned to completion in a high purity graphite electrode, using a 10-amp d-c arc.

Results and Discussion

A plot of $\log \rho$ vs $1/T$ of the compounds investigated obeyed the equation $\rho = \rho_0 \exp (E/kT)$, where ρ is the specific resistivity at T degree absolute temperature, ρ_0 is a constant referred to as the resistivity at infinite temperature, E is the conduction energy gap, and k is Boltzmann's constant. Typical temperature resistivity profiles obtained on heating naphthalene and anthracene discs are shown in Figures 1 and 2. The values computed for E and ρ_0 are shown in Tables I and II together with the qualitative spectrographic analyses. For comparison purposes, the data obtained by the various investigators on naphthalene and anthracene are summarized in Table III.

The results (e.g., A-4) show that the reproducibility of measurements carried out by the above described technique is of the order of ± 3 percent. Samples of the same chemical compound with different metallic impurity concentration showed significant differences both in the measured values of ρ and in calculated values of ρ_0 and E . However, it was not determined whether the metallic impurities were present as the free metal or chemically combined. Also the effect of a specific impurity (as free metal or metallic compound) has not yet been determined. Additional experiments are now in progress to further clarify the effects of both metallic and organic impurities in these and related hydrocarbons.

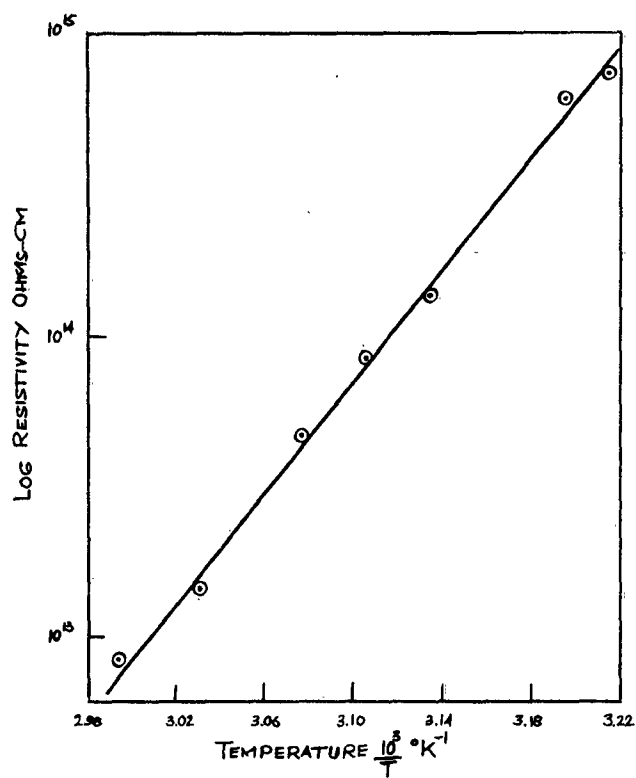


Fig. 1. Resistivity -- temperature profile of naphthalene (NA-5)

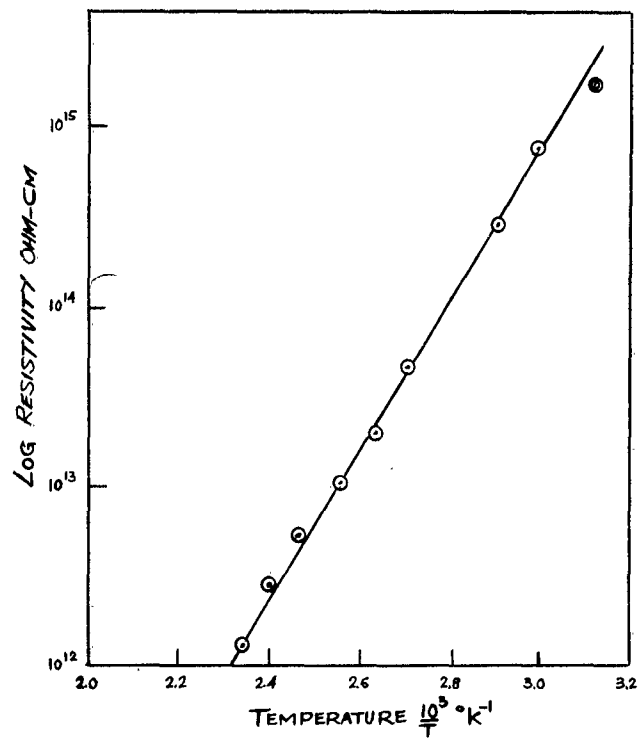


Fig. 2. Resistivity -- temperature profile of anthracene (A-3)

Table I.

Effect of Metallic Impurities on the Resistivity
of Naphthalene

Sample Number and Purification Method	NA 2 as obtained	NA 5 2 vacuum sublimations	NA 6 4 vacuum sublimations	NA 4 sulfuric acid treatment and 2 vacuum sublimations
	Spectrographic Analysis			
Si	0.00X	0.000X ^a	0.0000X	NF
Mg	0.00X	0.000X	0.0000X	0.000X
Ag	0.00X	NF ^b	NF	NF
Fe	0.00X	0.0000X	NF	NF
Ca	0.000X	0.000X	NF	NF
Cu	0.0000X	0.0000X	NF	NF
Al	0.000X	0.000X	NF	NF
Calculated ρ_0 (ohm-cm)	1.0×10^{-33}	1.40×10^{-15}	1.50×10^{-9}	3.66×10^{-16}
Calculated E (ev)	3.00	1.84	1.49	2.33
Temperature Range ($^{\circ}$ C)	40-70 $^{\circ}$	40-70 $^{\circ}$	40-70 $^{\circ}$	40-70 $^{\circ}$

^a Estimated value: 0.00X = 0.001 - 0.009%

^b Elements are checked but not found.

Table II
Effect of Metallic Impurities on the Resistivity of Anthracene

Sample Number and Purification Method	A-1 as obtained	A-2 2 vacuum sublimations	A-3 4 vacuum sublimations	A-4a Hydrochloric acid treatment and 2 vacuum sublimations	A-5 Hydrochloric acid treatment and 2 vacuum sublimations
Spectrographic Analysis					
Mg	0.00X	0.00X (low)	0.000X	0.000X	0.000X
Si	0.00X	0.00X (low)	0.000X	0.000X	0.000X
Al	0.00X	0.00X (low)	NF	0.000X	NF
Ni	0.00X	0.000X	NF	NF	NF
Ca	0.00X	0.00X	0.000X	0.00X (low)	0.000X
Fe	0.00X (low) ^b	0.000X	0.000X	0.000X	0.000X
Cu	0.000X	0.000X (low)	NF	0.000X	NF
Cr	0.000X	NF	NF	NF	NF
Pb	0.000X	0.0000X ^a	NF	NF	NF
Na	0.000X	0.000X	0.000X (low)	0.0X	NF
K	0.000X	0.000X	NF	0.00X	NF
Ag	0.0000X	0.0000X	NF	NF	NF
Sn	0.0000X	NF	NF	NF	NF
Mn	0.0000X	NF	NF	NF	NF
Calculated ρ (ohm-cm)	4.58×10^{-3}	1.70×10^2	5.62×10^2	9.48×10^c 1.06×10^{2d} 1.85×10^{2e} 9.66×10^f	5.34
Calculated \bar{E} (ev)	1.13	0.832	0.812	0.860 ^c 0.846 ^d 0.859 ^e 0.866 ^f	0.946
Temperature Range, °C	45-160°	45-160°	45-160°	45-160°	45-160°

^a The surprisingly high contents of sodium and potassium may have been introduced inadvertently during the washing process by water.

^b Estimated value: $0.00X$ (low) = $0.001 - 0.005\%$.

^c Normal.

^d Same material (A-4) different pellet.

^e Repeat run on same pellet as (c).

^f Same material, different pellet measured under oxygen and moisture free nitrogen atmosphere.

Table III.

Conduction Energy Gap (E) of Naphthalene and Anthracene

Author	Temperature Range, °C	E (ev)	Comments
Naphthalene Pick and Wissman ⁽³⁾	60-75	1.85	single crystals (in vacuo)
Riehl ⁽⁴⁾	20-75	0.70	single crystals (in dry air)
Brown and Aftergut ⁽²⁾	46-63	1.35	disc (in N ₂ atmosphere)
	36-63	1.40	disc (in air)
Anthracene Mette and Pick ⁽⁵⁾	80-200	0.83	single crystal
Inokuchi ⁽⁶⁾	50-150	1.35	single crystal
Riehl ⁽⁴⁾	20-60	0.75	single crystal
Northrop and Simpson ⁽⁷⁾	25-80	0.97	films
Eley, Parfitt, Perry and Taysun ⁽⁸⁾	70-204	0.83	polycrystalline

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Electronic Conductivity of Polycyclic Aromatic Hydrocarbon

Compounds: Structural Relationships and Impurity Effects*

Certain organic solids, formerly considered as dielectric materials, are currently being studied for their semiconducting behavior. Semiconductors may broadly be defined as materials having room temperature resistivities of $10^{-3} - 10^{10}$ ohm-cm., which decrease logarithmically with temperature increase. The temperature dependence according to band theory is: $\rho = \rho_0 e^{E/kT}$, where ρ and ρ_0 are the resistivities at $T^\circ\text{K.}$ and 0°K. , respectively, k is Boltzmann's constant, and E is one half the energy gap between the highest occupied band and the conduction band.

Extensive studies have been made on solid polycyclic aromatic hydrocarbons in different physical forms, such as single crystals, smeared or evaporated films, and compressed polycrystalline powders⁽¹⁻⁹⁾. Significant differences in resistivity and energy gap were obtained by different workers on the same compound by the same or a different method. However, the purity of the compounds studied was either incompletely specified or not reported. Considering that one part per billion of boron increases the room temperature conductivity of silicon by a factor of 10^6 , one cannot, a priori, exclude the possibility of a similar occurrence in organic substances.

Benzene solutions of naphthalene, anthracene, tetracene, and pentacene containing 5 or 10 percent aqueous hydrochloric or 10 percent aqueous sulfuric acids, were refluxed for several hours. After repeated washings of the benzene layer with distilled water, the remaining solvent was removed by vacuum distillation. Various purity grades of each compound were prepared by two, three, or

* Y. Okamoto, A. Gordon, F. T. Huang, W. Brenner, Research Division, College of Engineering, New York 53, N.Y.

four successive vacuum sublimations, and each sample was analyzed for metallic content by emission spectroscopy. The ultra-violet spectra were also recorded. Gas chromatograms of the relatively volatile naphthalene and anthracene were obtained.

Hexacene was prepared by dehydrogenating dihydrohexacene.* This compound was refluxed in *o*-methyl naphthalene with palladium/charcoal catalyst under a nitrogen atmosphere. The hexacene was purified by vacuum sublimation. The very small amount of material did not permit spectrographic analysis.

Because of the great difficulty in preparing single crystals of these polycyclic aromatic hydrocarbons, it was found convenient to perform measurements on the bulk materials in the form of compressed cylindrical discs from 0.05-0.3 cm. thick. Pressures ranging from 530-1700 atmospheres were employed. Other investigators have found the resistivities to be independent of the applied pressure if it is greater than 77 atmospheres (80 kg./cm²). The cell consisted of two standard taper glass socket joints, between which a pellet was sandwiched; mercury served as the contact electrodes. The entire cell was housed in a sealed glass vessel in which the temperature and atmosphere could be regulated. Measurements were made with a Keithley Model 610A high impedance electrometer during heating and cooling from 20°C. to 200°C.

Spectroscopic impurity analyses and corresponding ρ and E values are shown in Table I for samples of naphthalene compressed under 550 atmospheres. Interpretation of these and other results is difficult, since it is unknown whether the impurity is present as the free element or in chemical combination. The effect of a specific impurity is also unknown, but studies in that direction are in progress. For comparison, the values of E obtained by other investigators are summarized in Table II.

* Obtained from Rutgerswerke - Aktiengesellschaft in Germany

Table I.

Effect of Inorganic Impurities on the Resistivity of Naphthalene Samples^a

Impurity	1	2	3	4
Si	0.00X	0.000X	0.0000X	-
Mg	.00X	.000X	.0000X	0.000X
Ag	.00X	-	-	-
Fe	.00X	.000X	-	-
Ga	.000X	.000X	-	-
Cu	.0000X	.0000X	-	-
Al	.000X	.000X	-	-

$\rho_{50^\circ\text{C.}}^b$, ohm-cm. 1.05×10^{11} 0.65×10^{11} 2.80×10^{11} 6.00×10^{11}

E^b , eV. (40-70°C.) 3.00 1.84 1.49 1.93

^a Purification Methods:

- Sample 1 - reagent grade
- Sample 2 - two vacuum sublimations
- Sample 3 - four vacuum sublimations
- Sample 4 - 10% H₂SO₄ washing in two vacuum sublimations

^b Measurements obtained upon heating

Table II.

Energy Gap (E) of Naphthalene

Method	E, eV*	Temperature Range, °C.	Reference
Single crystal in vacuo	1.85	60-75	3
Single crystal in dry air	0.70	20-75	4
Compressed pellet in Nitrogen	1.35	46-63	2
Compressed pellet in air	1.40	36-63	2

* Based on Boltzmann expression E/kT ; values also found reported in terms of $E'/2kT$, where $E' = 2E$

The temperature dependence of the electronic conductivities of naphthalene, anthracene, tetracene, pentacene and hexacene are plotted in Fig. 1. The results are seen to obey the above referred to basic semiconductor relationship $\rho = \rho_0 e^{E/kT}$. The conductivity of hexacene approaches values which might be expected for semiconductor materials. Electronic properties of this series of aromatic polycyclic hydrocarbons are summarized in tabular form below.

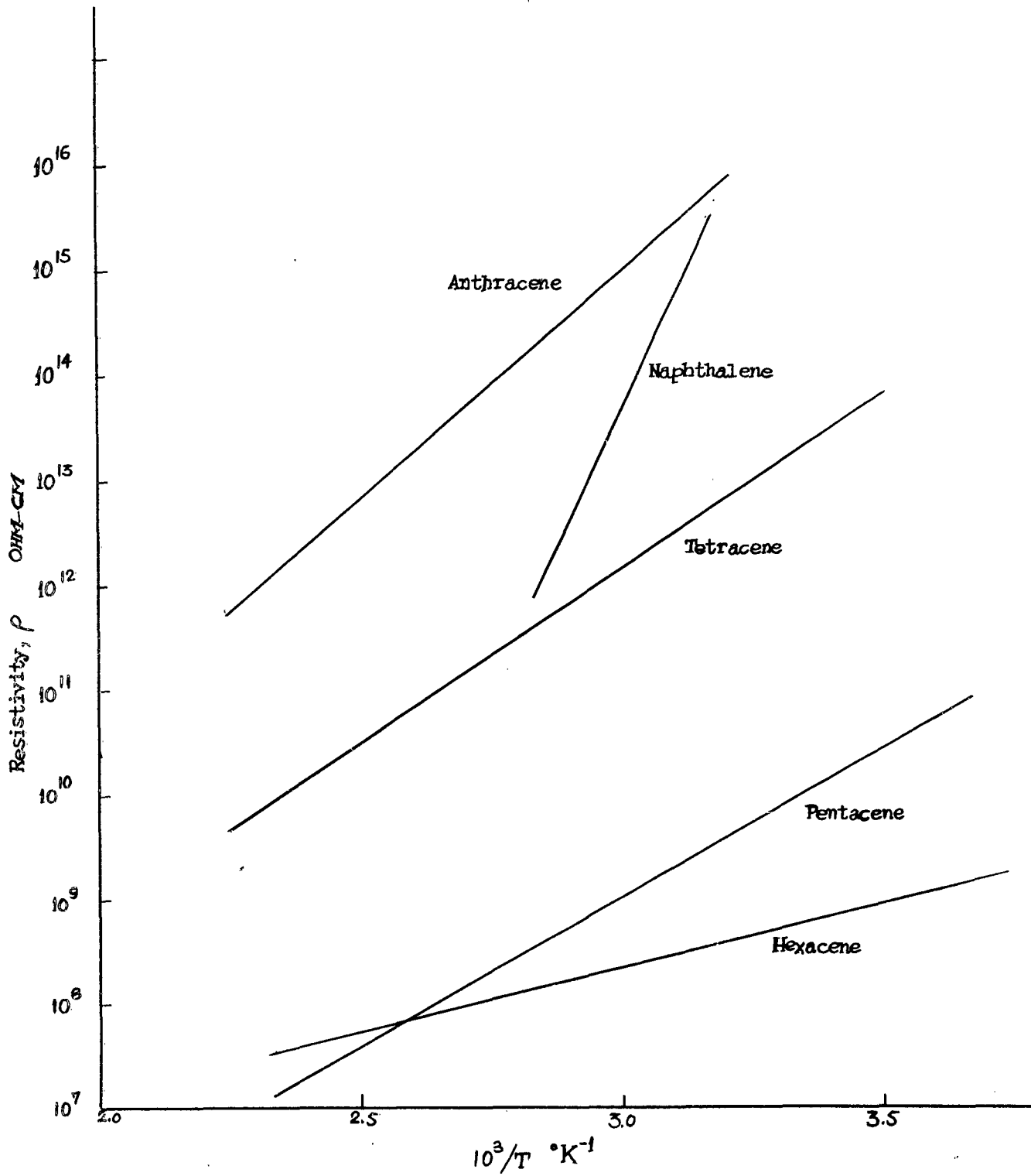
Table III.
Electronic Properties of Polycyclic Aromatic Hydrocarbons

	ρ_{50} ohm-cm	E, eV
naphthalene	6×10^{14}	2.33
anthracene	6.7×10^{15}	0.968
tetracene	1.9×10^{12}	0.690
pentacene	1.0×10^9	0.660
hexacene	3.8×10^{10}	0.566

A regular decrease in the conduction energy gap is observed as the number of fused rings increases in the series naphthalene through pentacene. However, at a given temperature one finds the resistivity of anthracene to be higher than that of naphthalene, whereas the opposite is expected. This apparent anomaly disappears and the expected increase in conductivity is observed in the series anthracene, tetracene, pentacene. No explanation for this phenomenon is available, although it may be related to crystal anisotropy.

If one plots the energy gap, E, obtained for the purest samples of each material, versus the ultra-violet absorption maxima of the B-band (benzenoid absorption), an asymptotic relationship is observed approaching $E = 0$ with an

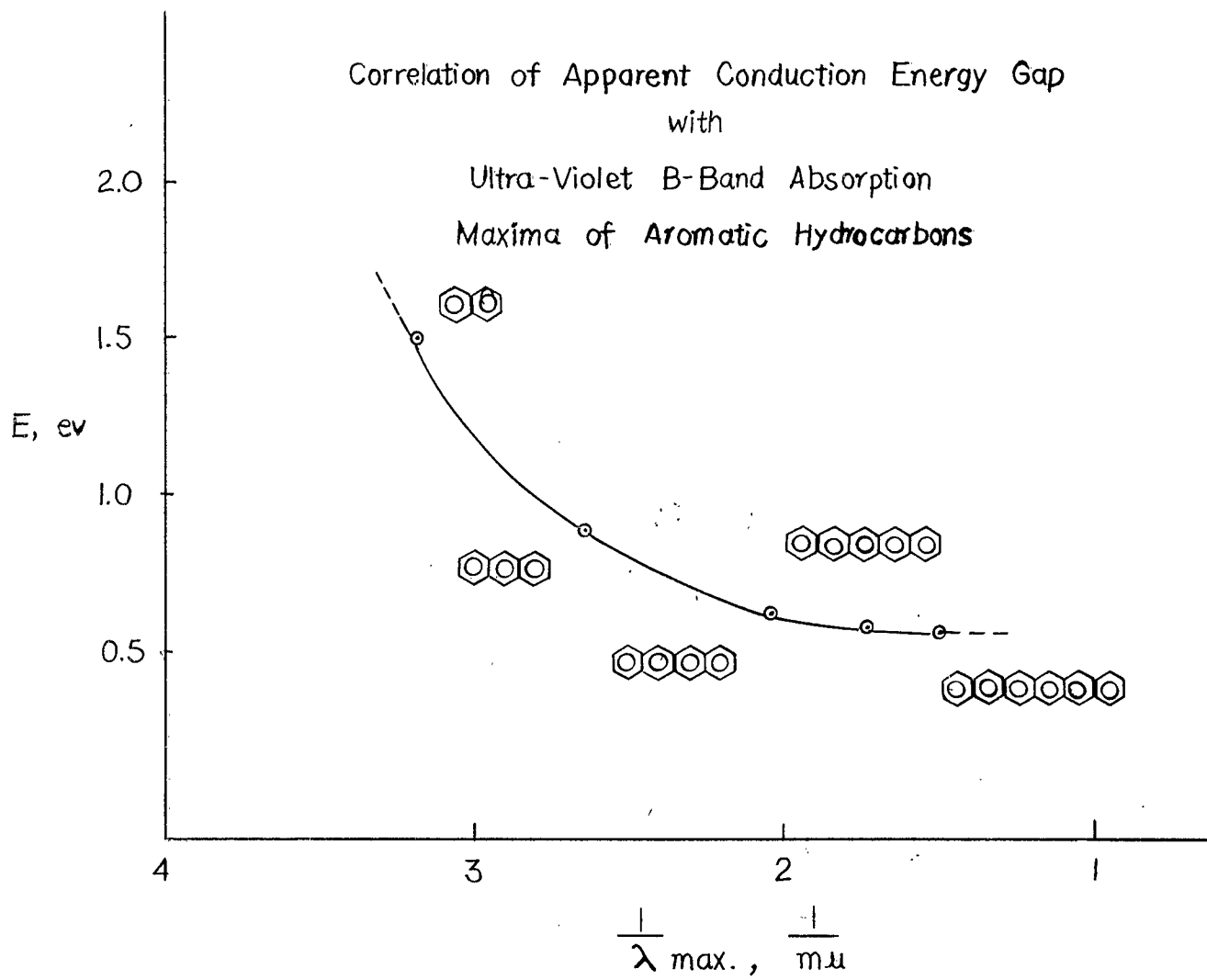
TEMPERATURE DEPENDENCE OF ELECTRONIC CONDUCTION OF AROMATIC
HYDROCARBONS



increase in the number of fused rings toward a graphite-like structure. From the curve (Fig. 2) one can predict the energy gap for higher homologues, such as heptacene. This hypothesis is currently being studied. The band theory of conduction is strongly supported for these π -electron systems, rather than a radical or charge transfer mechanism⁽²⁾ or triplet state activation⁽¹⁰⁾. Recent theoretical treatments for anthracene by LeBlanc⁽¹¹⁾ and Kepler⁽¹²⁾ on hole and electron mobility are in good agreement with experiment, and corroborate the band theory.

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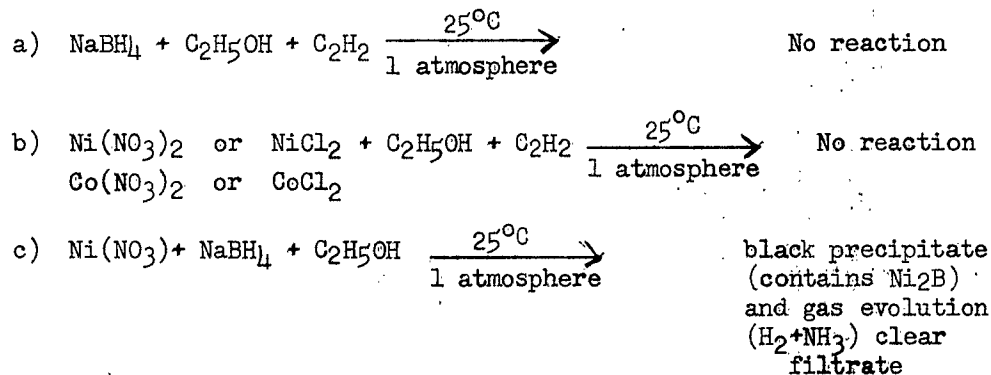


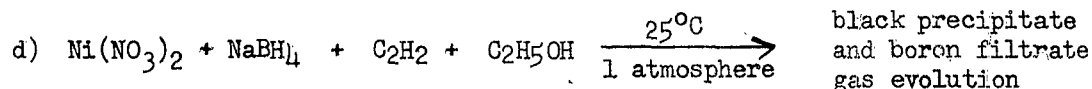
III-2 Polymerization of Acetylene and Derivatives Thereof

III-2.A Polymerization of acetylene

The polymerization of acetylene is of definite interest for the preparation and study of organic semiconducting polymers. The resulting macromolecules would be expected to possess the theoretically rather desirable polyene conjugated structure. In reports of three recent investigations the preparation of such polyene structures from acetylene has been claimed^(1,2,3). It was therefore decided to undertake the synthesis of such macromolecules and to study their pertinent electronic and physical properties.

Preliminary experiments were carried out with the Luttinger catalyst system⁽²⁾, which has been reportedly capable of effecting stereospecific acetylene polymerization at low temperatures. Theoretically this has the advantage of eliminating complicating thermal effects accompanying most polymerization reactions. This catalyst consists of a solution of divalent nickel or cobalt salts to which sodium borohydride is added. When acetylene is then bubbled through this solution at ambient temperatures and pressures, black precipitates are formed. Suitable solvents are said to include ethanol, water, and dimethylformamide. A rather detailed experimental study of this reaction has been carried out. The results to date can be summarized as follows:





The experiments performed to date suggest that the catalyst may well be an active form of nickel boride obtained as shown in reaction c). Analysis of the precipitate of reaction d) showed the presence of organic material having the approximate gross chemical composition of a polyene, and substantial amounts of inorganic chemical constituents including Co, Ni, Na, and Fe. Attempts at purification were generally unsuccessful due to the insolubility and infusibility of the organic material. IR spectra did not add to our knowledge of the structure of the organic portion of the product. The presence of the supposed double bonds in the organic portion of the product could not be confirmed by appropriate chemical tests. Exploratory experiments were also carried out with other potential catalysts for acetylene including chlorplatinic acid and trifluoroacetic acid. Evaluation of results showed that the polymeric products exhibited similar characterization problems.

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III-2.B Polymerization of phenyl acetylene

Phenyl acetylene has been polymerized and the products are being studied. It has been found that phenyl acetylene can be polymerized thermally as well as by the use of the Luttinger catalyst. This has the major advantage of eliminating the necessity for (catalyst metal) purification after polymerization. Also phenylacetylene polymers have solubility in organic solvents such as benzene and toluene which again simplified characterization. Information on polyphenylacetylenes is presented in the following paper (published in Chemistry and Industry, p. 2004-2006, December 1961).

On the Synthesis and Electronic Properties of Polyacetylenic Hydrocarbons*

Recently, much attention has been focused on the electronic properties of organic solids, and in particular of those exhibiting semi-conductive behavior. Most of the compounds exhibiting this phenomenon (room temperature resistivities from 10^{-3} to 10^8 ohm-cm. and a negative temperature coefficient of resistivity) contain conjugated double bonds, aromatic or olefinic, such as pentacene⁽¹⁾ and β -carotene⁽²⁾. Therefore, it was thought that the study of polymers of the form $(-\overset{\text{R}}{\underset{|}{\text{C}}}=\text{CH}-)_n$ might shed additional light on the relationship between chemical structure and electronic properties. Such straight chain polymers appear to be most easily prepared by polymerization of acetylenic compounds, most attempts at which, however, have led merely to cyclization.^(3,4) Recently, however, Natta and co-workers⁽⁵⁾ have prepared a highly crystalline, insoluble and infusible all-trans straight chain polyene by polymerizing acetylene with Ziegler-type catalysts. Luttinger⁽⁶⁾ and Green⁽⁷⁾ also report having formed similar polyenes from acetylene using nickel and cobalt salts or complexes with sodium borohydride.

Of special interest is a linear poly(phenylacetylene) structure, $(-\overset{\text{Ph}}{\underset{|}{\text{C}}}=\text{CH}-)_n$, in which the alternating phenyl rings and conjugated double bonds create a decrease in the system's internal energy, and apparently allow electron transfer for electronic conduction. Korshak⁽⁸⁾ has polymerized phenylacetylene in low yield (3-60%) in presence of peroxides under 1-6000 atmospheres pressure from 70-200°C. The structurally unidentified polymer

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was a brittle orange-red solid which became a yellow powder on reprecipitation from benzene. Berlin(9,10) has reported polymerizing phenylacetylene catalytically and thermally to a yellow solid having high thermal stability and comparative inertness in addition reactions. The assumed structure was that of a conjugated polyvinylene, based solely on chemical inactivity and E.P.R. spectra showing unpaired electrons. Champetier and Martynoff(11) have obtained presumably the same type of polymers by using organomagnesium compounds in the presence of ferric chloride or titanium tetrachloride. Again the yields were low and the structures were not identified.

In attempting to avoid catalyst contamination and to improve yields, phenylacetylene was thermally polymerized under oxygen-free, dry nitrogen at reflux temperatures for 20-65 hours in the absence of solvent as well as in 10-20 weight percent solutions of decalin, xylene, diethylene glycol dimethyl ether (diglyme), and chlorobenzene. In all cases deep red solids were obtained in near quantitative yields, which became yellow-orange powders upon reprecipitation from benzene, acetone, carbon tetrachloride, or chloroform solutions by adding methanol, ethanol, or petroleum ether. Physical properties of the various products are shown in the Table. Surprisingly, cyclization occurred only during bulk polymerization (no solvent); less than 1% 1,3,5-triphenylbenzene was obtained upon vacuum sublimation, whereas none of the "solvent" polymers were sublimable.

Upon hydrogenation (Pd/charcoal, glacial acetic acid, 8 atmospheres) the infrared spectra (in CCl_4 solution) of the polymers become essentially identical with that of linear polystyrene. The results for polymers produced in xylene are shown in Fig. 1. The small aliphatic C-H stretching vibration at 3.50μ for the polymer before hydrogenation is attributed to chain terminating solvent molecules. This peak disappears in the spectrum of the bulk polymerization product and is much more pronounced for the decalin and diglyme polymers. With infrared and also N.M.R. data, along with certain chemical evidence, we assign the polymer the expected conjugated structure, $(-\overset{\text{Ph}}{\underset{|}{\text{C}}}=\text{CH}-)_n$, in mostly trans configuration where $n = 5-10$, the terminal group being a solvent molecule, except in the case of chlorobenzene.

To determine the electroconductivity of the material, a temperature-resistivity profile was made under purified nitrogen on compressed pellets. The procedure followed is the same as outlined in a previous paper.(12) Figure 2 shows the results for the bulk polymer, which appears to obey the usual exponential law for a semiconductor, $\rho \propto \exp. (E/kT)$, where ρ = resistivity, ohm-cm.; E = apparent energy gap, eV.; k is Boltzmann's constant; and T is absolute temperature. The low molecular weight materials obtained to date do not show conductivities significantly lower than those of many other non-conjugated polymer systems. A room temperature resistivity of 10^{16} ohm-cm. and a high apparent energy gap of 0.963 eV. place the polymer in the dielectric category, even though it conducts better than linear polystyrene by a factor of 1000. Further studies on such polymers are now in progress.

The authors thank the Cambridge Air Force Research Laboratories, Bedford, Massachusetts, for financial support.

Table

Polymerization Conditions and Physical Properties of Poly(phenylacetylene)

Solvent	Reflux Temperature	Reaction Time (hours)	Melting Point of Crude Polymer	Average M.W.(a)	Found % C	Found % H
Decalin	175-195°C	22	188-195°C	550	93.32	6.29
Xylene	140-160	65	100-135	485	93.83	6.35
Diglyme	165-180	65	100-115	482	90.78 ^(b)	6.48 ^(b)
Chlorobenzene	130-145	48	145-150	1020	93.95	6.04
None (c)	145-160	18	195-205	973	93.58	5.90

(a) Cryoscopic

(b) Remaining 2.74% is oxygen from terminal ether molecules

(c) Yield based on monomer was 75%

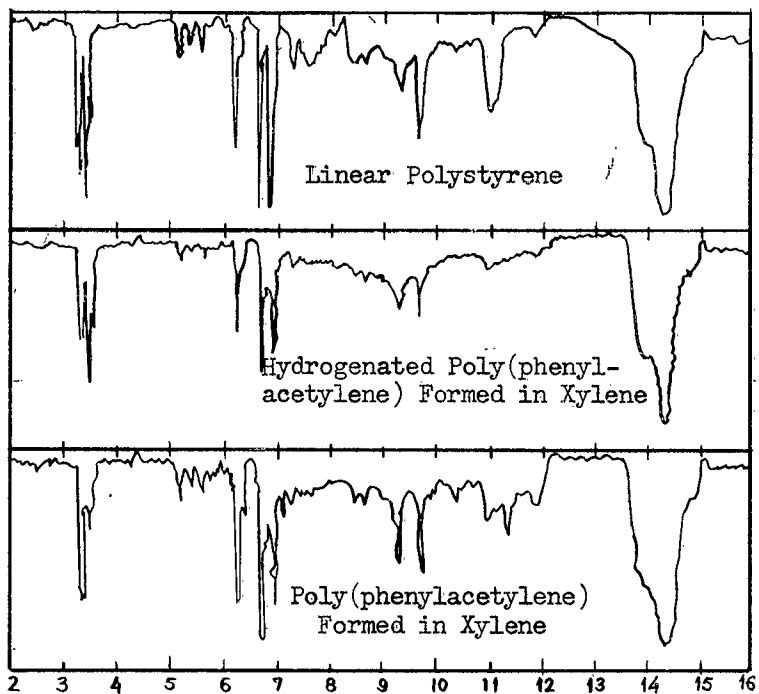


Fig. 1 Infrared Spectra of Polymers

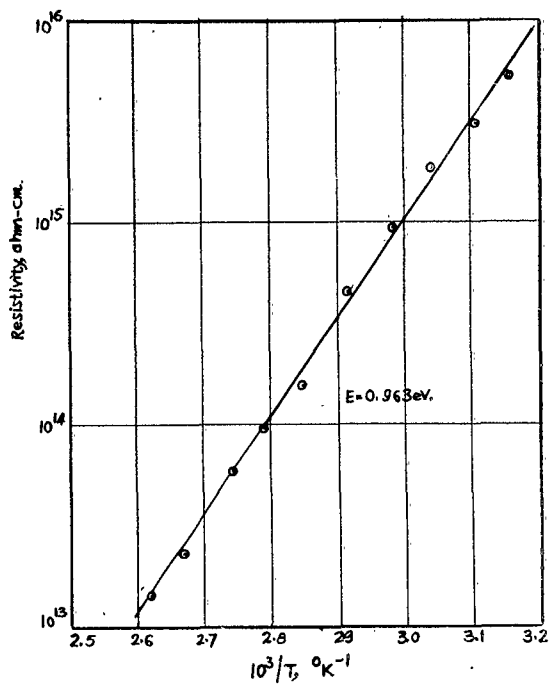


Fig. 2 Temperature-Resistivity Profile of Bulk Poly(phenylacetylene)

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III-2.C Polymerization of pyridyl acetylene

Experiments were carried out on the synthesis of polypyridyl acetylenes in order to investigate the effect of the nitrogen heteroatom in the pyridyl ring on polymer electronic properties. The results are summarized in the following paper to be presented at the September 1963 ACS meeting.

On the Synthesis and Electronic Properties of Polypyridyl Acetylenes*

Investigation relating to the study of the electronic properties of organic solids have been receiving steadily increasing attention in the past few years. The recent spectacular developments concerning both elemental and compound inorganic semiconductors have undoubtedly fanned much of the current interest in the electronic properties of organics. One area of investigation which is of fundamental importance for the study of the electronic properties of organic materials is the relationship between chemical structure and electronic properties.

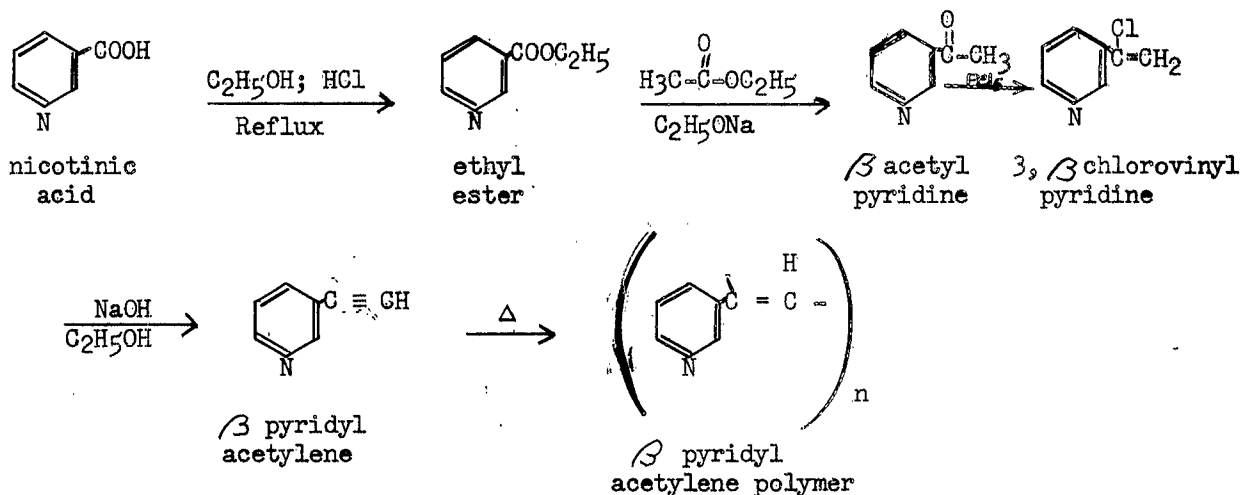
By now the electronic properties of a considerable number of organic solids have been measured. However many of the data obtained are of questionable value as the role which both inorganic and organic impurities can exert on electronic properties, has not been sufficiently recognized till quite recently. Among the many organics studied conjugated structures such as polyenes have shown outstanding interest because they exhibit lower resistivities and also an inverse temperature-resistivity relationship. Monomeric acetylenes have been particularly investigated as they offer one of the simpler routes for the synthesis of polyene structures via polymerization. Previous investigations of polyphenylacetylenes have shown that their low molecular weight polymerizates (600-1200) exhibit resistivities in the order of 10^{16} ohm-cm with apparent energy gaps of 0.96 eV. The analogous but completely saturated polystyrene structures have resistivities in the order of 10^{19} ohm-cm.

It was considered of interest to ascertain the effect of introducing a nitrogen atom in the ring of the previously studied phenyl acetylenes on their electronic properties in the solid state. It was also desired to ascertain the effect of the position of the nitrogen atom in the ring relative to the location of the acetylene group. Accordingly isomeric pyridyl acetylene monomers were synthesized as described below. Particular attention was paid to the purification of the monomers in order to minimize the effects

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of impurities on compound electronic properties. For the same reason, i.e. avoidance of catalyst contamination as a possible source of electronically active impurities, thermal polymerization techniques were employed for the preparation of the corresponding polypyridylacetylenes.

The following preparative scheme was employed for the synthesis of the isomeric polypyridylacetylenes (shown for the β isomer):



The pyridylacetylene monomers were polymerized thermally in the liquid state in bulk and in solutions of organic solvents. The bulk polymerizations of the isomeric pyridylacetylene monomers were carried out at suitably elevated temperatures in sealed tubes or under a dry and oxygen free nitrogen atmosphere in the absence of a solvent, at reflux. Solution polymerizations with 10-20 wt. % of the monomers in solvent media such as xylene and diglyme were also experimentally investigated. Typical polymerization times ranged from 20 to in excess of 60 hours. Temperatures varied from 170-210°C.

In the bulk polymerizations dark brown solid products were obtained in near quantitative yields. They were purified using organic solvent extractions. The lower molecular fraction was soluble in benzene and was subsequently precipitated with n-heptane. The color of this vacuum dried fraction which decomposed in air at 183°C, was light brown. The benzene insoluble fraction dissolved in hot chloroform and was precipitated with benzene. Dark brown material was obtained. The melting point in air exceeded 300°C. A molecular weight estimate via vapor pressure techniques was 1330.

Pertinent electronic measurements were carried out on the higher melting polymer fraction both at room and elevated temperatures. A Keithley Electrometer Model 610A was employed to make these measurements. The order of resistivities measured were in the range of 10^{12} - 10^{13} ohm-cm at ambient temperatures. The energy gap, ΔE , was determined at 1.25 eV.

The results were compared with analogous measurements for the polyphenylacetylenes previously studied. The comparison of the electronic properties of these two different polymers with roughly equivalent molecular weights is shown below and illustrates the effect of the heteroatom in the pyridyl ring:

<u>Polymer</u>	<u>ρ_{25} ohm-cm</u>	<u>ΔE, eV</u>
Polyphenylacetylene	10^{16-17}	0.96
Poly- β pyridylacetylene	10^{12-13}	1.25

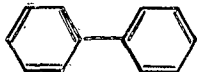
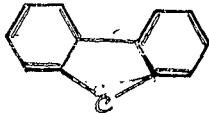
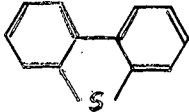
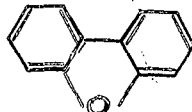

Further studies on the rather hygroscopic pyridylacetylene polymers have been planned. The effect of the position of the nitrogen atoms relative to the location of the acetylene group, on polymer electronic properties will be studied. Attempts will also be made to obtain higher molecular weight products. Complexes of such polymers with metal salts, etc. are being explored.

III-3. Investigations of miscellaneous organic compounds

In the course of the investigations which are described in this report, the electronic properties of various organic compounds were measured. The results of these studies are summarized below.

The electrical resistivity of one series of simple aromatic compounds was studied to investigate the effect of various heteroatoms in their structure on their electronic properties. These compounds included dibenzofurane, dibenzothiophene, carbazole, biphenyl and fluorene.

The following list gives their resistivities and ΔE values:

Compound	Structure	ΔE , eV	ρ_{50} ohm-cm
biphenyl		1.46	1.7×10^{15}
fluorene		1.05	2.0×10^{15}
dibenzothiophene		0.856	1.0×10^{15}
dibenzofurane		0.445	7.75×10^{14}
carbazole		0.586	2.5×10^{15}

These data show no significant resistivity differences at ρ_{50} . However the effect of the introduction of heteroatoms such as sulfur, oxygen or nitrogen compared to the carbon atom is to decrease the energy gaps.

Further investigation of this and other series as well as analogous studies of macromolecular entities are considered of interest for a better understanding of the effect of structure on electronic properties.

The reaction between hydrazine and glyoxal has been carried out repeatedly in a 95% ethanol solvent medium. The expected product should be a polymer with the interesting $(-C=N-N=C-)_n$ chain. A black solid with a melting above 360°C . was isolated which did dissolve in common organic solvents e.g. benzene, acetone, toluene, and alcohol. Elemental analyses gave the following results:

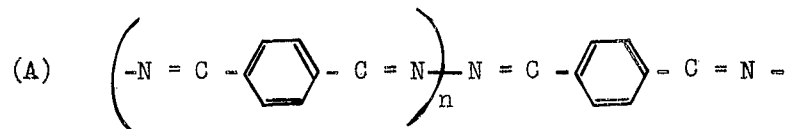
Elemental Analysis for Glyoxal-Hydrazine Condensation Products

	<u>C</u>	<u>H</u>	<u>N</u>
Found %	44.6	3.7	51.7
Calculated % as $(-C=N-N=C-)_n$	44.6	3.88	29.2

Additional experimental work was carried out using different reaction conditions in order to produce compounds whose composition would more closely correspond to the one desired. The discrepancy of the nitrogen analysis with the theoretical value of the desired structure is considered due to unreacted aldehyde groups. Particular attention has been paid to the development of reaction conditions which will permit the use of anhydrous conditions in such experiments. The results obtained to date have however not been encouraging.

Pellets have been produced from the above described black polymeric solids. Conductivity measurements have been carried out and show resistivities in the 10^8 to 10^{10} ohm-cm range at ambient temperatures.

A polyazine has also been prepared from the reaction of terephthalic aldehyde with hydrazine. The structure of this polymer is believed to be as follows in (A). The polymer is yellow, insoluble in common organic solvents and has a melting point above 360°C . Preliminary electrical measurements show a resistivity at ambient temperatures in the order of 10^{15} ohm-cm.



Further plans look to an extension of such investigations with particular emphasis on the realization of pertinent compound purities and suitable electronic data.

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Charles J. Marsel, March 15, 1963
AFCLR-63-97
79 pp.
Unclassified report

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II. C. J. Marsel

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