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The Use of the Neutral Bis-cyclopentadienyl Metal Compounds of Iron, Cobalt, and Nickel in the Catalysis or Hydrogenation Reactions

Andrew Jackson Chadwell Jr.
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To the Graduate Council:

I am submitting herewith a dissertation written by Andrew Jackson Chadwell Jr. entitled "The Use of the Neutral Bis-cyclopentadienyl Metal Compounds of Iron, Cobalt, and Nickel in the Catalysis or Hydrogenation Reactions." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Dr. Hilton A. Smith, Major Professor

We have read this dissertation and recommend its acceptance:

J.H. Robertson, William H. Fletcher

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

March 10, 1958

To the Graduate Council:

I am submitting herewith a dissertation written by Andrew Jackson Chadwell, Jr., entitled "The Use of the Neutral Bis-cyclopentadienyl Metal Compounds of Iron, Cobalt, and Nickel in the Catalysis of Hydrogenation Reactions." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Hilton A. Smith
Major Professor

We have read this dissertation
and recommend its acceptance:

Judson H. Robertson
William H. Fletcher
Edgar H. Cawls
A. D. Melonen

Accepted for the Council:

Alvin Wentling
Dean of the Graduate School

THE USE OF THE NEUTRAL BIS-CYCLOPENTADIENYL METAL COMPOUNDS
OF IRON, COBALT, AND NICKEL IN THE CATALYSIS
OF HYDROGENATION REACTIONS

A DISSERTATION

Submitted to
The Graduate Council
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

by

Andrew Jackson Chadwell, Jr.

March, 1958

CRANES & CREST

To Jane



ACKNOWLEDGMENT

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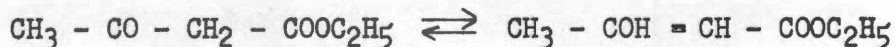
CHAPTER I

INTRODUCTION

A. Bis-cyclopentadienyl Metal Compounds

1. Metal Cyclopentadienides

Organic compounds which have a hydrogen atom attached to a carbon atom adjacent to a carbon-oxygen or carbon-carbon double bond are observed to participate in reactions which require an acidic alpha hydrogen atom. Noteworthy examples of such reactions are the condensations of diethyl malonate and of ethyl acetoacetate with alkyl halides. The aldol condensation requires such an acidic alpha hydrogen atom. Often, relatively stable enol forms result from the tautomeric equilibrium if a hydrogen atom is attached in a position alpha to two carbonyl groups as in the case with ethyl acetoacetate:



The hydrocarbon 1,3-cyclopentadiene has two hydrogen atoms which are attached alpha to each of two conjugated carbon-carbon double bonds. One of the two hydrogen atoms may be displaced by the alkali metals to yield a salt and molecular hydrogen.¹ In tetrahydrofuran solution, sodium cyclopentadienide is rapidly formed by the attack of cyclopentadiene upon metallic sodium:



Stability is achieved by the cyclopentadienyl carbanion through resonance stabilization as each of the five carbon atoms is equivalent to the other four due to the distribution of the negative charge around the ring.

The acidity of cyclopentadiene is also demonstrated by its ability to attack Grignard reagents such as ethylmagnesium bromide to form magnesium cyclopentadienide bromide:



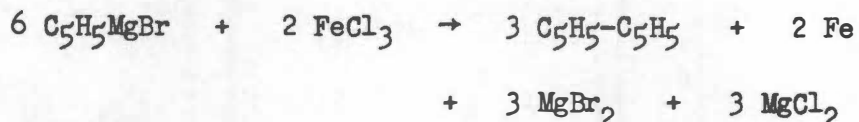
Magnesium cyclopentadienide can be obtained by sublimation of magnesium cyclopentadienide bromide at 200–230° C. and 10^{-4} mm.²

Wilkinson, Cotton, and Birmingham have made a study of the chemical reactions of sodium and magnesium cyclopentadienides in an attempt to obtain information about the nature of the C_5H_5 -metal bond.² Exchange reactions with halides of iron, cobalt, and nickel take place with ease. Strong complexing agents were found to remove the metal ion from the compounds. These compounds were found to be easily hydrolyzed by water as might be expected for the salt of a very weak acid. The authors concluded that the C_5H_5 -metal bond must be ionic if the metal is one of the alkali metals or magnesium. They proposed the nomenclature "metal cyclopentadienide" for such ionic compounds between metals and cyclopentadiene.

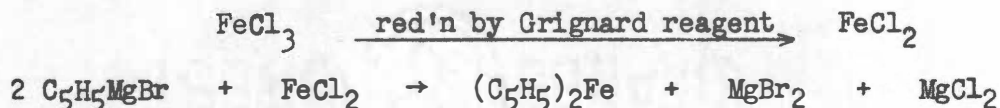
2. Ferrocene Structure

In contrast to the ionic salts formed between cyclopentadiene and the strongly-electronegative alkali metals and magnesium, compounds of an entirely different class between cyclopentadiene and the transition metals

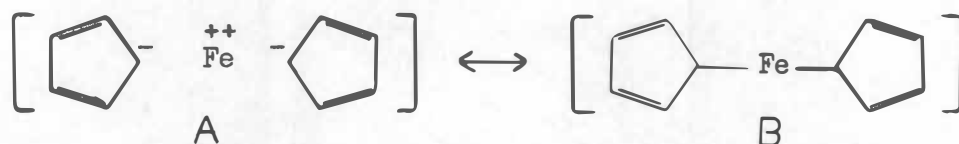
have been isolated and characterized. In an attempt to prepare an intermediate in a proposed synthesis of the hydrocarbon fulvalene, Kealy and Pauson treated cyclopentadienylmagnesium bromide with iron(III) chloride in ether.³ The reaction which was expected to occur is as follows:



A yellow solid was isolated from the organic layer which, upon elemental analysis, gave the empirical formula $\text{C}_{10}\text{H}_{10}\text{Fe}$. Cryoscopic measurements in benzene showed that the empirical formula was the correct one. The authors named the new compound "dicyclopentadienyliron" and concluded that the reaction must have taken place as follows:

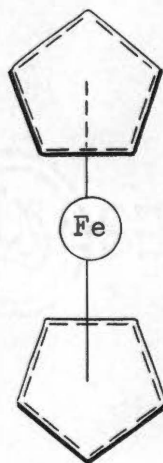


The compound, which was the first stable organoiron compound to be isolated, melted at $173\text{--}174^\circ$ and sublimed at 100° . It was found to be insoluble in and unattacked by water, strong sodium hydroxide solution, and concentrated hydrochloric acid solution. Such stability was wholly unexpected, and Kealy and Pauson attempted to account for this remarkable behavior by postulating that the cyclopentadienyl groups achieved a degree of aromaticity and, hence, stability through the acquisition of a negative charge. Resonance stabilization through the following hybrid scheme was thought to be in effect.



Twenty-five resonance hybrids may be depicted for the ionic structure, A.

Wilkinson, Rosenblum, Whiting, and Woodward recognized that the stability of the new compound could not be justified on the basis of partially-ionic carbon-iron-carbon bonding.⁴ They reasoned that, since the carbon atoms of each cyclopentadienyl ring are attached to a single hydrogen atom and possess equal unsaturation, the unit negative charge could be distributed uniformly over the cyclopentadienyl group with the iron atom being bonded equally and symmetrically to each of the ten carbon atoms. The resulting structure was termed a "molecular sandwich."



Considerable evidence which serves to substantiate the symmetrical molecular sandwich concept has been obtained from many sources. Engelmann carried out magnetic susceptibility studies on the compound and found the molecule to be diamagnetic.⁵ Diamagnetic behavior implies a spherical symmetry for the electronic charge distribution. Lippincott and Nelson

obtained the vibrational spectra for the dicyclopentadienyliron and also for the ruthenium analog.⁶ Only one carbon-hydrogen frequency was observed. More than one frequency would have been observed if the iron atom had been bound to only one carbon atom in each ring. Thus, all of the hydrogen atoms in each cyclopentadienyl group are equally positioned with respect to the iron atom, and each carbon-hydrogen bond has the same energy. In addition, a symmetric ring breathing mode of vibration was also found.

X-ray diffraction studies by several research groups have verified the existence of the "molecular sandwich" structure with the iron atom in a central position between the parallel planes of the cyclopentadienyl rings.^{7,8,9} Additional papers dealing with the proof of the structure are to be found in a comprehensive review of the subject compiled by Pauson.¹⁰

Obviously, the iron complex differs greatly in its chemical behavior and in its structure from the alkali metal cyclopentadienides. The need for an improved nomenclature system which would clearly delineate between the two distinct classes was emphasized by the large number of sandwich-type compounds of transition metals and cyclopentadiene which are being prepared. Also, the term "dicyclopentadienyl" is misleading because the bicyclic olefin dicyclopentadiene is a very stable compound which is formed rapidly from cyclopentadiene at room temperature by means of a Diels-Alder condensation of two molecules.¹¹ Wilkinson, Cotton, and Birmingham recognized the need for an improved nomenclature

system and recommended that the iron compound be named bis-(cyclopentadienyl)iron(II).² Analogs of the iron compound with other transition elements would be named in a similar manner. The name "metal cyclopentadienide" was to be reserved for the chemically-dissimilar ionic compounds. This system appears to be the accepted one in use today.

A somewhat more convenient system of nomenclature has come into general use as a consequence of the fact that bis-(cyclopentadienyl)-iron(II) has aromatic characteristics which are common to the aromatic organic compounds. For instance, little or no polyolefinic behavior is shown by the iron compound as is demonstrated by its failure to undergo the Diels-Alder reaction with maleic anhydride in boiling benzene.¹² On the other hand, bis-(cyclopentadienyl)iron(II) will participate in such reactions as the Friedel-Crafts acylation with acetyl chloride and anhydrous aluminum bromide. The name "ferrocene" is in common usage to denote the neutral bis-(cyclopentadienyl)iron(II) molecule. This molecule can be oxidized to give the bis-(cyclopentadienyl)iron(III) cation which is referred to as the "ferricinium" ion. An analogous neutral compound of the sandwich type with ruthenium would be called ruthenocene. For convenience and brevity, the ferrocene system of nomenclature will be used hereafter in the present work except for instances in which greater clarity is demanded.

3. General Methods of Preparation

The preparation and characterization of ferrocene have led to the preparation of bis-cyclopentadienyl metal compounds of many of the transition elements. These compounds have the same structure as ferrocene

but differ in their stability and reactions. Neutral compounds of the formula $(C_5H_5)_2M$ with ferrocene-type behavior have been prepared for the following transition elements: titanium,^{13,14} zirconium,¹⁴ vanadium,^{2,14} niobium,¹⁴ tantalum,¹⁴ chromium,^{2,15} molybdenum,¹⁵ tungsten,¹⁵ manganese,² iron,² cobalt,² nickel,² ruthenium,¹⁶ and mercury.¹⁷

In the course of the experimental work which led to the preparation of these compounds, several fairly general preparative methods emerged. With the understanding that limitations are imposed upon these general methods, the more successful ones are outlined as follows:

1. Cyclopentadienylmagnesium bromide with metal halides in ether, benzene-ether, or tetrahydrofuran solution.^{3,14,18}
2. Cyclopentadienylmagnesium bromide with metal acetylacetonate in toluene or benzene-ether solution.^{16,18,19}
3. Alkali metal cyclopentadienides with metal halides in tetrahydrofuran or ethylene glycol dimethyl ether.^{2,13,14,17}
4. Cyclopentadiene with metal or metal halides in amine solvent.^{20,21}
5. Alkali metal cyclopentadienides with metal thiocyanate in liquid ammonia.²²
6. Cyclopentadiene with metal carbonyls in vapor phase at elevated temperatures.^{15,19,23}

Method 3 has been the most widely employed of the six methods. The alkali metal cyclopentadienides are quite soluble and stable in dry tetrahydrofuran and in ethylene glycol dimethyl ether. Likewise, many transition metal halides such as iron(II) chloride, cobalt(II) chloride,

and others are appreciably soluble in these solvents. Methods 1 and 2 suffer from the disadvantage of having to prepare two Grignard reagents; cyclopentadienylmagnesium bromide is prepared from ethylmagnesium bromide. Method 2 is quite lengthy in comparison with the others in that the metal acetylacetonate must be prepared and purified. Many transition elements do not readily form chelate complexes with acetylacetone. Platinum is a notable example of this behavior.²⁴ Also, a large excess of Grignard reagent is required in tying up the acetylacetone in the final reaction.

Methods 5 and 6 have not been widely employed even though they were the first successful methods found for some of the elements. For the most part, their limitations are quite obvious. The reaction of cyclopentadiene with metal carbonyls has been known to yield compounds other than the neutral bis-cyclopentadienyl metal compound.¹⁵ Many of the metals do not form stable carbonyls. In many instances, the bis-cyclopentadienyl metal compound which would be formed through the carbonyl reaction is not stable at the temperatures which are employed. In the author's opinion, method 4 holds the greatest promise for future commercial preparation of the ferrocene-type compounds, particularly ferrocene. Some of the by-products of the final reactions are useful in early stages of the process and can be easily recycled.²¹

As mentioned above, many of the preparative schemes yield products other than the simple type $(C_5H_5)_2M$. For example, many bis-cyclopentadienyl metal carbonyls have been prepared and are of great interest. The present study will not be dealing with these derivatives of the ferrocene-type compounds, and further discussion of the numerous methods of synthesis

will not be attempted. The review by Pauson should be consulted for additional information.¹⁰

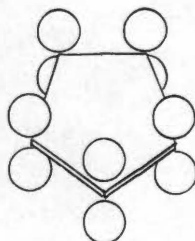
4. Electronic Configuration

After the pentagonal antiprism structure for the bis-cyclopentadienyl metal compounds had been confirmed experimentally, many attempts were made to unravel the problem of how the cyclopentadienyl groups are bound to the metal atoms. The earliest attempts to explain the bonding in ferrocene were based on the postulate that all of the pi electrons of the cyclopentadienyl groups are used in bonding these two groups to the central iron atom so that all of the available electronic orbitals of the iron are filled to produce the electronic configuration of the inert gas, krypton.^{4,9} The assumption of the krypton configuration was given as the reason for the great stability of ferrocene. This explanation was soon invalidated for two very good reasons. First, the observation was made that ferrocene would not be expected to participate in the aromatic reactions such as the Friedel-Crafts reaction if the pi electrons were involved in bonding with the iron atom.¹² Second, many stable bis-cyclopentadienyl metal compounds have been prepared from transition metals in which the achievement of the stable inert gas electronic configuration is impossible.¹³

The molecular orbital theory treatment of the problem has been the most useful. Dunitz and Orgel,^{7,25} Jaffe,²⁶ and Moffitt²⁷ have made significant contributions to the elucidation of the bonding in ferrocene and its analogs. The result of their efforts appears to be a relatively-correct, general picture of the bonding situation. For instance, the

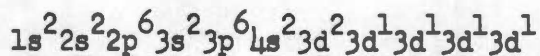
molecular orbital theory can account for the magnetic properties as well as the energy of the metal-cyclopentadienyl ring bonds. The theory also correctly predicted the existence of compounds with only one cyclopentadiene ring linked by means of the same type of bonding to a metal atom. Many examples of this structure are found with the cyclopentadienyl metal carbonyls. Free rotation of the rings relative to each other is allowed in the theory and is observed experimentally with disubstituted ferrocenes. The paper by Moffitt lends itself to use by those not well-trained in molecular orbital theory.

The essential postulates of the theory are hereby presented. Moffitt approached the problem by bringing two cyclopentadienyl radicals into proximity with an iron atom. Five $2p$ electrons in each ring are not engaged in bonding. They are assigned to π molecular orbitals which results in pairing of four of them. The one unpaired electron per ring remains unpaired, and its density is distributed uniformly throughout the cyclopentadienyl radical. The π electron density is pictured as follows:



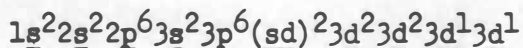
Before the approach of the two cyclopentadienyl radicals, the neutral iron atom has the following electronic configuration in somewhat

expanded form:



The five 3d orbitals of the metal, which are normally equivalent, are of three types depending upon their magnetic quantum numbers, m_l . Since the orbital quantum number for a d band is three, the following values are allowed for the magnetic quantum numbers: $m_l = 0, \pm 1, \pm 2$, respectively. The molecular orbital theory shows that only the pair of orbitals with $m_l = \pm 1$ has both the same transformation properties and approximately the same energy content as one of the available orbitals of each cyclopentadienyl ring. The combination of the matching orbitals produces strong bonding.

As the cyclopentadienyl radicals are brought into close proximity with the iron atom, the high pi electron density of the rings will cause repulsion and hybridization of one of the 3d orbitals and the 4s orbital to form two new sd orbitals, one bonding and the other antibonding. The iron atom now has the following electronic configuration before bonding:



Linear sd-hybrid bonding takes place between the unpaired electrons on each ring and the two available bonding 3d electrons of the iron atom. The resonance of the cyclopentadienyl ring is undisturbed. The net result is a single covalent bond from the metal atom to each ring as a whole, not to a particular carbon atom in each ring. Effects attributed to bonding by other orbitals are neglected in this treatment to a first approximation.

The molecular orbital theory when extended to other transition metals predicts that metals which have two singly-occupied d orbitals that can be used in bonding are capable of forming bis-cyclopentadienyl compounds having the pentagonal antiprism structure. Indeed, this prediction has been fulfilled in that some pi-bonded cyclopentadienyl compound has been prepared with essentially every transition metal.

5. Physical and Chemical Properties

The general behavior of the neutral bis-cyclopentadienyl metal compounds is rather typical of that of covalent compounds. They have a relatively high vapor pressure and may be sublimed. Ferrocene sublimes at 100° at atmospheric pressure and is stable up to 400° .¹⁸ The vapor pressures of ferrocene analogs have not been measured with accuracy and are usually less than that of ferrocene at a given temperature. Regardless, all may be sublimed under reduced pressure.

Most of the compounds decompose at their melting point. The great similarity in the physical properties of the compounds is demonstrated by their melting points. The neutral bis-cyclopentadienyl metal compounds in Period 4, which includes ferrocene, all melt at or within a few degrees of 173° . The Period 5 element compounds melt at approximately 196° , and those in Period 6 melt at $218-219^{\circ}$.¹⁰

The problem of air oxidation greatly complicates the manipulation of these compounds in the laboratory. Ferrocene is quite stable in air, but oxygen must be excluded from the system when the other compounds are present. Sublimation under high vacuum is one of the better means of purification in that oxidation during the process is reduced to a minimum.

The infrared spectra of the compounds point to their similarity and high symmetry. The high degree of symmetry of the molecules leads to simple absorption spectra in the infrared region.⁶ The standard heats of formation at 25° for ferrocene and nickelocene have been evaluated from the vapor phase vibrational spectra and are +33.8 kcal. mole⁻¹ for ferrocene and +62.8 kcal. mole⁻¹ for nickelocene after correcting for the heat of sublimation, 16.8 kcal. mole⁻¹.^{6,28} Ruthenocene has been estimated to be thermodynamically more stable than ferrocene, while cobaltocene was placed between ferrocene and nickelocene in stability.

Greater chemical reactivity is shown by the compounds with the longest carbon-metal distance. The energies of these bonds have been estimated for ferrocene and nickelocene by Dunitz and Orgel.²⁵ The bond in ferrocene was calculated to be more stable by approximately 120 kcal. mole⁻¹. The longer ring-metal distance in nickelocene as found by X-ray studies serves to substantiate this estimate.^{9,29} One or both of the cyclopentadienyl groups in nickelocene are sufficiently labile as to be displaced by carbon monoxide³⁰ and nitric oxide,^{31,32} whereas ferrocene is unattacked by them.

Wilkinson, Cotton, and Birmingham compared ferrocene and analogous compounds of cobalt, nickel, ruthenium, vanadium, chromium, and manganese with sodium, potassium, magnesium, and some rare earth cyclopentadienides from the standpoint of magnetic properties, mass spectra, infrared spectra, exchange reactions, hydrolytic behavior, olefinic character, and electrical conductance in liquid ammonia and tetrahydrofuran solutions.² This work was quite successful in establishing their relative stabilities for

the purpose of classifying the bis-cyclopentadienyl compounds according to the type of ring-metal atom bond. Their findings are briefly outlined.

As related earlier in the present work, the cyclopentadienyl rings were found to be bound to the metal atom by electrostatic forces in the cyclopentadienides of sodium, potassium, and magnesium and of the rare earths studied. Surprisingly, the bis-cyclopentadienyl compound of the transition element manganese was also found to be ionically bonded. The infrared spectrum of $(C_5H_5)_2Mn$ showed the presence of olefinic rings rather than cyclopentadienyl rings with no double bond character as found in ferrocene. Also, manganese cyclopentadienide was found to be instantly hydrolyzed in water. This completely unexpected behavior was attributed to the stability of the manganese(II) ion.

They showed that the neutral bis-cyclopentadienyl metal compounds of iron, cobalt, nickel, ruthenium, vanadium, and chromium possessed strong covalent ring-metal atom bonds and that an order of stability could be established through the exchange studies in organic solvents with ferrocene as the standard with maximum stability. No isotopic exchange between labeled iron(II) cation and unlabeled ferrocene in ethanol was observed. Manganese cyclopentadienide reacted instantly with iron(II) chloride to produce ferrocene and manganese(II) chloride as follows:



No exchange between iron(II) cation and cobaltocene or nickelocene was observed. The chromium compound did exchange up to 70 per cent in a reaction that involved the exchange of metal atoms in a covalent anti-prism structure as follows:

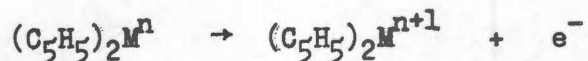


The transition elements studied are arranged in an approximate order of decreasing stability of their bis-cyclopentadienyl metal compound:



The authors concluded that, regardless of whether the bonding of the cyclopentadienyl groups to the metal atoms was ionic or covalent, the resulting structure was still of the pentagonal antiprism or "sandwich" type.

The oxidation potentials of many of the neutral and cationic bis-cyclopentadienyl metal compounds have been determined polarographically in water and in 90 per cent ethanol for the general reaction



where n may have the value of 0, 1, 2, or 3. For the most part, the behavior of these compounds closely parallels that of the corresponding metal ions or their complex ions.¹⁰ A trend was observed in going from compounds with metal atoms of low atomic weight to those with high atomic

weight. The higher molecular weight compounds were found to be more stable in their higher oxidation states.

B. Statement of the Problem

The neutral bis-cyclopentadienyl metal compounds ferrocene, cobaltocene, and nickelocene were prepared and their behavior studied in cyclohexane solution under hydrogen pressures up to 120 atmospheres. The conditions of temperature and hydrogen pressure under which these compounds would react with hydrogen were determined.

The possible uses of these bis-cyclopentadienyl metal compounds or metals derived therefrom as catalysts for the hydrogenation of unsaturated organic molecules were investigated. The following compounds were employed as hydrogen acceptors: benzene, nitrobenzene, cyclohexene, nitroethane, ethyl laurate, and acetone. Where appropriate, the kinetic equations which govern the rates of the reactions were determined and the reaction rate constants were evaluated. The temperature coefficients and, consequently, the apparent activation energies for the reactions were determined where feasible over suitable temperature ranges.

CHAPTER II

EXPERIMENTAL

A. Preparation of Bis-cyclopentadienyl Metal Compounds

1. Bis-(cyclopentadienyl)iron(II)

Ferrocene was prepared by the reaction of sodium cyclopentadienide with iron(II) chloride in tetrahydrofuran.² A 1-l. three-necked flask was equipped with a reflux condenser, mechanical stirrer, and separatory funnel. The apparatus was dried by passing dry nitrogen through the flask while it was being heated on a Glas-Col heating mantle. Eleven grams of sodium shavings (0.5 mole) was added to 400 ml. of dry tetrahydrofuran in the flask. The atmospheric oxygen was swept out with a stream of dry nitrogen.

With the reflux condenser cooled to -10° by a circulated water-methanol solution, 35 g. of dry cyclopentadiene was added dropwise with stirring over a ten-minute period. The reaction mixture was warmed to accelerate the reaction between the sodium and cyclopentadiene. The evolution of hydrogen ceased before the last trace of sodium had reacted and dissolved. Three milliliters of cyclopentadiene was added without effect upon the unreacted sodium. By this time, the solution had turned dark gray.

Anhydrous iron(II) chloride (0.25 mole) was added with stirring to the solution of sodium cyclopentadienide. An additional 100 ml. of tetrahydrofuran was added. The flask was heated on the Glas-Col heating mantle until the solution refluxed slowly. Refluxing with stirring was

continued for three hours. The solution was filtered while still warm through a Buchner funnel.

The filtered solution was added to a 1-l. three-necked flask which was supported in a Glas-Col heating mantle and equipped with a fine capillary tube extending to the bottom of the flask, a water-cooled cold finger, and a water-cooled condenser with a receiver flask. The entire system was vacuum-tight with the exception of the capillary tube which was used for admitting nitrogen. The tetrahydrofuran was removed by distillation under reduced pressure which was maintained by a water aspirator. Nitrogen was passed through the capillary tube to aid the distillation process.

After the removal of the solvent, the capillary tube was replaced by a solid rubber stopper, and the side condenser was replaced by a vacuum line which was attached to a Cenco Hyvac pump through a Dry Ice-methanol cold trap. The flask was evacuated and heated with a heating mantle. Approximately two-thirds of the ferrocene sublimed onto the cold finger. The ferrocene which remained on the flask walls was dissolved in a petroleum ether-diethyl ether solution. This solution was filtered and evaporated to dryness.

The crude ferrocene was collected, dissolved in petroleum ether, and recrystallized at -78° . The crystals were filtered from the cold solution and air-dried on the filter. They were then transferred to an all-glass sublimation tube and sublimed three times at 100° under a moderate vacuum. The light-orange crystals melted at $170-172^{\circ}$ in a sealed tube which was evacuated (reported $173-174^{\circ}$).³ Ferrocene is not subject to oxidation by atmospheric oxygen and was, therefore, stored under

air in screw-cap glass vials.

2. Bis-(cyclopentadienyl)cobalt(II)

Cobaltocene was prepared by the reaction of sodium cyclopentadienide with anhydrous cobalt(II) chloride in tetrahydrofuran.² Unlike ferrocene, cobaltocene is rapidly attacked by atmospheric oxygen. As a consequence of this behavior, a nitrogen atmosphere was maintained in all of the apparatus used in this preparation. Operations which required exposure of the solution or precipitates to atmospheric oxygen were carried out as rapidly as possible. In order to minimize the time required to change parts of the apparatus while in use, an all ground-glass joint system was constructed.

A 1-l. three-necked flask was equipped with a mechanical stirrer, reflux condenser, and a separatory funnel. After thoroughly drying the apparatus, 450 ml. of dry tetrahydrofuran was added. Twenty-three grams of sodium (1 mole) was reduced to shavings under tetrahydrofuran and added to the flask. The oxygen was swept out with dry nitrogen. Sixty-eight grams of dry cyclopentadiene (1 mole) was added batchwise with stirring to the sodium over a period of thirty minutes. The flask was cooled in an ice bath during this period in order to prevent an excessive loss of cyclopentadiene by vaporization. After stirring for one hour, the ice bath was removed, and the reaction mixture was heated gently to accelerate the formation of sodium cyclopentadienide.

After the last trace of sodium disappeared, the flask was cooled in a stream of tap water. Sixty-five grams of anhydrous cobalt(II) chloride (0.5 mole) was added with stirring. The solution was stirred

overnight at room temperature and under a nitrogen atmosphere. The tetrahydrofuran was removed by vacuum distillation following the transfer of the solution to a 1-l. Claisen flask. The condenser was cooled with circulated ice water.

After the solvent was removed, nitrogen was admitted to the evacuated flask. The cobaltocene was extracted from the solid material in the flask with petroleum ether. The solution was placed in a Dewar flask filled with Dry Ice to crystallize. The subliming carbon dioxide provided a protective cover over the solution against oxygen.

The crude cobaltocene crystals were filtered cold on a Buchner funnel and dried by pulling nitrogen through the funnel. The Buchner funnel was covered with an inverted Pyrex funnel through which the nitrogen was passed.

The crude material was transferred to the sublimation tube and sublimed in vacuo two times at 130-160°. The sublimation apparatus was flushed out three times with dry nitrogen prior to being heated to the sublimation temperature. After each sublimation the almost black crystals were rapidly scraped from the cold finger of the sublimation apparatus into a screw-cap glass vial which was immediately placed in an apparatus for evacuation and filling with nitrogen. The vial was closed in an atmosphere of nitrogen and stored in a refrigerator at 0°. The cobaltocene crystals were effectively protected by this procedure from atmospheric oxygen during storage. See Chapter II, Section E, for a description of this procedure and the apparatus used. Samples of cobaltocene, which were stored for periods of time greater than a month,

were resublimed before use.

The melting point was determined with samples in an evacuated capillary tube which was completely immersed in heavy mineral oil in a modified Thiele melting point apparatus. This method was required in these measurements to prevent atmospheric oxidation of the compound and to prevent the compound from subliming out of the tube. A 9-mm. Pyrex tube was drawn down to capillary size on one end and sealed on that end. A few crystals were added to the capillary section, and the large open end was attached to a vacuum pump for immediate evacuation. The evacuated capillary tube was closed above the crystals with a flame and pulled off from the larger tubing. Using this method, the cobaltocene melted at 170-173° with decomposition.

3. Bis-(cyclopentadienyl)nickel(II)

Nickelocene was prepared by the reaction of cyclopentadienylmagnesium bromide with nickel acetylacetonate in toluene.¹⁹ An all ground-glass joint apparatus was used for this preparation. A 1-l. three-necked flask was equipped with a reflux condenser, a mechanical stirrer with gas-tight bearings, and a separatory funnel. A bubble tube was attached to the reflux condenser in order to detect gas evolution.

Ten grams of thoroughly-dried Grignard-grade magnesium turnings and 350 ml. of sodium-dried diethyl ether were added to the dry flask. Nitrogen was passed over the ether for fifteen minutes to sweep out the oxygen. With the reflux condenser cooled with water at 0°, 55 g. of sodium-dried ethyl bromide was added over a forty-minute period. The

formation of ethylmagnesium bromide started immediately. The ether was allowed to reflux for thirty minutes after the addition of ethyl bromide was completed.

Dry toluene (450 ml.) was added to the flask, and the ether was distilled off through a distilling head which replaced the reflux condenser. Forty-five minutes were required to remove most of the ether during which time the temperature rose to 92° . The system was again flushed out with nitrogen and cooled in an ice bath. The distilling head and condenser were replaced by the reflux condenser, and the apparatus was made gas-tight. Thirty-five grams of cyclopentadiene was added dropwise to the ethylmagnesium bromide solution.

The evolution of ethane, which indicated that the reaction of cyclopentadiene with ethylmagnesium bromide was taking place, started after the contents of the flask were warmed on a heating mantle. The evolution of ethane could not be detected after one hour thus signifying the completion of the formation of cyclopentadienylmagnesium bromide. The reaction mixture was cooled in an ice bath.

A solution of 16 g. of nickel acetylacetonate in 350 ml. of toluene was added dropwise to the cold cyclopentadienylmagnesium bromide solution. The toluene solution of the nickel complex had been previously dried by distillation to remove any toluene-water azeotrope. The final reaction in which the nickelocene was formed was completed in three hours by stirring at $30-35^{\circ}$.

The purification of nickelocene was carried out as rapidly as possible in order to prevent excessive exposure of the complex to

atmospheric oxygen. Regardless, a considerable amount of the compound was lost by oxidation during purification. The toluene solution was poured on a cracked ice-ammonium chloride mixture to decompose any excess cyclopentadienylmagnesium bromide. The ammonium chloride-magnesium bromide solution was then extracted several times with 1 l. of diethyl ether in 200-ml. portions. The ether-toluene extract was then extracted several times with 700-800 ml. portions of water in order to remove the light-yellow precipitate that remained in the organic layer. This precipitate was undoubtedly the oxidation product of the nickelocene.

After filtration, the solution was evaporated to near dryness in a Claisen flask with the aid of a water aspirator. The process was accelerated by passing a stream of nitrogen through the solution by means of a fine capillary tube which extended to the bottom of the flask. Care was taken to prevent overheating the crystals which began to appear around the sides of the flask as dryness was approached. The nickelocene was dissolved in a minimum of petroleum ether, and the solution was filtered immediately. The solution was placed in a Dewar flask filled with Dry Ice to crystallize overnight. Again, the carbon dioxide formed a protective layer over the surface of the solution.

The dark-green needles of nickelocene were rapidly filtered from the cold solution and added to the vacuum sublimation apparatus. After evacuation for two hours with a Cenco Hyvac pump which was protected by a Dry Ice-methanol cold trap, the apparatus was closed to the pump, and the crystals were sublimed at 100° . The crystals were rapidly scraped from the cold finger into a screw-cap glass vial which was evacuated and

filled with nitrogen. The compound was stored under nitrogen in the refrigerator at 0°. No decomposition could be observed in unopened vials after six months. Nickelocene was observed to be more resistant to oxidation by atmospheric oxygen than was cobaltocene.

The melting point was measured in an evacuated Pyrex capillary tube in the same manner as described for cobaltocene, m.p. 169-173° with decomposition (reported 171-173° with decomposition).¹⁹

B. Preparation of Compounds to be Hydrogenated

1. Benzene

LaPine thiophene-free benzene was fractionally distilled in a five-foot glass helix-packed column at 5:1 reflux ratio. The fraction which was retained had a 0.1° boiling range and was stored over sodium wire in brown screw-cap bottles, b.p. 79.3°/740-743 mm., n_D^{20} 1.5010 (reported b.p. 80.05-80.15°/760 mm., n_D^{20} 1.5011).³⁵

2. Cyclohexene

This olefin was prepared by the dehydration of cyclohexanol.³⁴ A 1-l. round-bottomed flask was mounted in a Glas-Col heating mantle and attached to a small reflux condenser. A distilling head with a thermometer well was placed at the top of the reflux condenser. A take-off condenser from the distilling head to an ice-cooled receiver flask completed the apparatus. Water at 76-78° was circulated through the reflux condenser, and tap water was employed to cool the take-off condenser.

In each dehydration reaction, 600-700 ml. of Eastman white label cyclohexanol was added to the flask. Twenty milliliters of concentrated

sulfuric acid was added, and the solution was heated until it boiled gently. The reflux condenser permitted the cyclohexene (b.p. $83.2^{\circ}/760$ mm.) and water which were formed to distil into the receiver, but the unreacted cyclohexanol (b.p. $160.8^{\circ}/760$ mm.) was returned to the reaction flask. The acidic alcohol solution was refluxed until approximately 80 per cent of the cyclohexanol had been dehydrated. Attempts to carry the reaction farther resulted in the formation of much decomposed material in the reaction flask.

The cyclohexene and water from two such reactions were combined, and excess sodium chloride was added to the water layer to salt out the olefin. The 1 l. of cyclohexene which was obtained was mixed with 1 l. of drum-grade methanol, and the solution was added to the pot of an 8-ft. Vigreux fractionation column. The methanol-cyclohexene azeotrope was collected at a 4:1 reflux ratio, b.p. $55.6^{\circ}/760$ mm.³⁵ The above procedure was employed to effect a separation of the cyclohexene from any cyclohexanol which was carried into the receiver during the reaction by entrainment.

The azeotropic distillate, which had a volume of 1400 ml., was cooled overnight to 0° in a refrigerator. In order to remove the methanol, the cold solution was washed five times with 400-ml. portions of distilled water which was also at 0° . The cyclohexene was dried by shaking periodically for several hours with 1 lb. of anhydrous magnesium sulfate. The filtered olefin was fractionally distilled through an 11-ft. Vigreux column at a 6:1 reflux ratio. A trace of hydroquinone was added to suppress polymerization, b.p. $82.3-82.4^{\circ}/736-739$ mm., n_D^{20} 1.4463

(reported b.p. $83.2^{\circ}/760$ mm., n_D^{20} 1.4467).³³ The olefin was stored in brown screw-cap bottles.

3. Nitrobenzene

Two liters of Eastman white label nitrobenzene was added to the pot of a 13-ft. glass helix-packed fractionation column for fractional distillation under reduced pressure. The pressure was controlled with a flutter valve manostat. After properly heading the column, approximately 1.5 l. was collected at a reflux ratio of 8:1, b.p. 93.4 – $93.8^{\circ}/16$ – 17 mm., n_D^{20} 1.5524 (reported b.p. 94.2 – $95.4^{\circ}/16$ – 17 mm.).³³

4. Nitroethane

One kilogram of Eastman white label nitroethane was fractionally distilled through a 13-ft. glass helix-packed fractionation column at a 25:1 reflux ratio, b.p. 112.9 – $113.2^{\circ}/741$ – 746 mm., n_D^{20} 1.3911 (reported $114.0^{\circ}/760$ mm.,³⁶ n_D^{20} 1.3910³⁷). The compound was stored in a brown screw-cap bottle.

5. Acetone

Three pounds of Baker and Adamson reagent acetone was shaken with 0.1 g. of potassium permanganate and a few pellets of sodium hydroxide. The solution was added to the pot of a 13-ft. glass helix-packed fractionation column where it was boiled under total reflux for ten hours. An additional 0.3 g. of potassium permanganate was added, and fractional distillation at a 10:1 reflux ratio was started after heading the column.

The distillate was shaken periodically over a six-hour period with 0.5 lb. of 8-mesh Drierite and then passed through a 22-mm. diameter column which was packed with 0.5 lb. of 8-mesh Drierite. The acetone was filtered through a fine-pore fritted-glass funnel and stored in two brown screw-cap bottles, b.p. 54.0-54.1°/740-743.5 mm., n_D^{20} 1.3592 (reported b.p. 56.1-56.2°/760 mm., n_D^{20} 1.35911).³³

6. Ethyl Laurate

Ethyl laurate was prepared by the sulfuric acid-catalyzed esterification of lauric acid (n-dodecanoic acid) in ethanol.³⁸ Eastman white label lauric acid (2 moles) was dissolved in 1 l. of absolute ethanol in a 2-l. three-necked flask. Twenty milliliters of concentrated sulfuric acid was added, and the solution was boiled for nineteen hours under total reflux. Mechanical stirring was required during this period to prevent the solution from bumping.

A 20-in. Vigreux column was attached to the flask. Five hundred ml. of benzene was added, and the water-ethanol-benzene ternary azeotrope was removed by fractional distillation.³⁵ The distillation was stopped as the ethyl laurate solution started to darken. The ester was washed three times in a separatory funnel with 1-l. portions of distilled water in order to remove the sulfuric acid, dried with anhydrous magnesium sulfate, and filtered.

The ethyl laurate was purified by fractional distillation through an 11-ft. Vigreux column under reduced pressure at a 4:1 reflux ratio, b.p. 180.5-181.2°/42 mm., n_D^{20} 1.4294 (reported b.p. 180.4°/42 mm.).³⁸

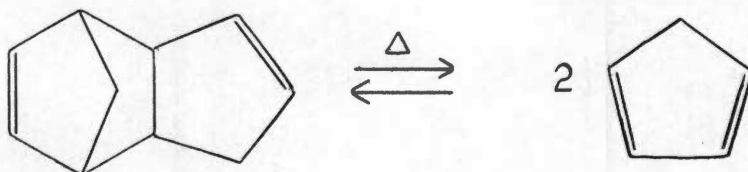
C. Preparation of Solvents, Intermediates, and
Miscellaneous Compounds

1. Cyclohexane

Matheson, Coleman, and Bell c.p. cyclohexane was passed through a 22-mm. diameter column which was packed with 12 cm. of 4A Molecular Sieves in 1/16-in. pellet form (Linde Air Products Co.) and 30 cm. of 100-200 mesh activated Silica Gel (Davison Chemical Co.). A flow-rate of 1.2 ml. per minute was employed. Water was removed by the Molecular Sieves, and aromatic compounds such as benzene were adsorbed by the Silica Gel. The cyclohexane was stored in brown screw-cap bottles and used without further purification, n_D^{20} 1.4252 (reported n_D^{20} 1.4263).³³

2. Cyclopentadiene

Dicyclopentadiene, which is a dimer of cyclopentadiene, can be broken into two molecules of cyclopentadiene at the boiling temperature of the dimer (170°) or above by means of a simple thermal cracking reaction:



This method was used to prepare limited quantities of cyclopentadiene as needed because the problem of dimerization complicates the storing of the compound. Cyclopentadiene will dimerize at 10° at the rate of 1 per cent per hour and at -20° at the rate of 0.05 per cent per hour.^{11,39}

Storage must, therefore, be carried out at low temperatures in order to prevent the accumulation of appreciable quantities of dicyclopentadiene. The cracking of dicyclopentadiene was carried out by slowly dropping the dimer into hot mineral oil and condensing the cyclopentadiene in a cold receiver flask.

A 2-l. three-necked flask was fitted with a mechanical stirrer with gas-tight bearings, a 125-ml. separatory funnel, and a 20-in. Vigreux column with a total take-off head and a thermometer well. The Vigreux tube was constructed from 19-mm. Pyrex tubing. A 200-mm. water-cooled condenser was attached to the head of the column and extended down into a receiver flask which was supported in a Dry Ice-methanol bath in a Dewar flask.

Seven hundred milliliters of Nujol (heavy mineral oil) was added to the flask with 0.2 g. of hydroquinone which tends to suppress peroxide and polymer formation. The oxygen in the flask was flushed out with nitrogen. Two hundred milliliters of dry dicyclopentadiene, which was kindly supplied by the Enjay Company, Inc., Elizabeth, New Jersey, was admitted at the rate of 7-10 ml. per minute to the rapidly-stirred mineral oil which was maintained at 250° by means of a Glas-Col heating mantle.

The cyclopentadiene, which rapidly evolved as the dimer made contact with the hot oil, was efficiently separated from the uncracked dimer by the 20-in. Vigreux column. A similar 14-in. column was found not to function as well. Cyclopentadiene boils at $41.5^{\circ}/760$ mm. whereas dicyclopentadiene has a much higher boiling point, $170^{\circ}/760$ mm.³⁹ The

dicyclopentadiene was returned to the hot oil for cracking while the monomer passed through the Vigreux tube, condensed in the water-cooled condenser, and collected in the receiver which was maintained at -78° . Undoubtedly, some dicyclopentadiene was carried over into the receiver by entrainment with the cyclopentadiene.

The yield of cyclopentadiene was estimated to be 70-80 per cent. The compound was stored at -78° in the tightly-stoppered receiver flask in a Dewar flask filled with Dry Ice and methanol. A trace of hydroquinone was added to suppress peroxide formation. The olefin was normally used within two to three days following the cracking operation. The cyclopentadiene was dried by swirling with Drierite before it was used in any of the reactions which were carried out under anhydrous conditions.

3. Tetrahydrofuran

Du Pont technical tetrahydrofuran was fractionally distilled through an 8-ft. Vigreux column at a 5:1 reflux ratio, b.p. $64.5-65.0^{\circ}/743-745$ mm. Iron wire was added to suppress peroxide formation.

An adsorption column was constructed for the further purification of the tetrahydrofuran. The column was formed from a 4-ft. length of 25-mm. Pyrex tubing with a 15-mm. coarse-pore fritted-glass funnel and a stopcock sealed on the lower end. A syphon tube to the impure solvent bottle was attached to the top of the column by means of a $34/45$ ground-glass joint. The column was packed to a height of 11 in. with 100-200 mesh Silica Gel (Davison Chemical Co.) and to an additional 37 in. with 13X Molecular Sieves in 1/16-in. pellet form (Linde Air Products Co.).

The distilled tetrahydrofuran was passed through the column at the rate of 1 ml. per minute and stored in brown screw-cap bottles. No hydrogen was evolved when the solvent was treated with freshly-cut sodium.

4. Toluene

Toluene was used as a solvent only in the preparation of the bis-cyclopentadienyl metal compounds and various intermediates and was not required to be of high purity. Drum grade toluene was fractionally distilled through an 8-ft. Vigreux column at a 6:1 reflux ratio. The fraction which was retained for solvent use had a 0.4 degree boiling range and was stored in brown screw-cap bottles over sodium wire.

5. Lauryl Alcohol

One hundred grams of Eastman technical lauryl alcohol (dodecanol-1) was fractionally distilled at reduced pressure through an 11-ft. Vigreux column at a 5:1 reflux ratio, b.p. 150-151°/18-19 mm., n_D^{25} 1.4400.

6. Nickel(II) Acetylacetonate

Two methods were employed to prepare the chelate compound between divalent nickel and acetylacetone (2,4-pentanedione). The first method, which was devised by Gach, involved the reaction of one mole of freshly-precipitated nickel(II) hydroxide with two moles of acetylacetone.⁴⁰

Nickel(II) hydroxide was prepared by two methods. The hydroxide was precipitated from solutions of Baker and Adamson reagent nickel(II) nitrate by (1) passing ammonia into the solution until the blue $\text{Ni}(\text{NH}_3)_6^{\text{II}}$ ion started to form, and (2) by adding sodium hydroxide

solution. The precipitated nickel(II) hydroxide was washed with acidified distilled water and dried at 110° .

Nine grams of dry nickel hydroxide, $\text{Ni}(\text{OH})_2 \cdot \frac{1}{4} \text{H}_2\text{O}$, was refluxed for forty minutes with 22 ml. of distilled Eastman practical acetylacetone in 250 ml. of toluene. The water which formed in the reaction was removed by azeotropic distillation of the binary water-toluene azeotrope, b.p. $84.1^{\circ}/760 \text{ mm.}$ ³⁵ The saturated toluene solution of nickel acetylacetonate was diluted with diethyl ether and allowed to stand in the refrigerator for crystallization. The blue-green crystals were filtered, washed with ether, and dried at 110° . A 50 per cent yield based on nickel hydroxide was obtained.

A second method was devised in order to eliminate the problem of preparing nickel hydroxide which is difficult to wash free from alkali and to dry. This procedure entailed refluxing readily available nickel(II) carbonate with acetylacetone in toluene solution to give the following reaction:



Nickel(II) carbonate is insoluble in toluene whereas the acetylacetonate chelate is soluble.

Thirty grams of Baker and Adamson reagent nickel(II) carbonate was refluxed for five hours with 65 ml. of distilled acetylacetone in 500 ml. of drum toluene. The solution volume was then reduced to 350 ml. by distilling part of the toluene. The solution was diluted with diethyl ether and allowed to stand in a refrigerator at 0° for crystallization.

The crystals were filtered, washed with ether, and dried at 110° . Nickel acetylacetonate was found to sublime at $170-180^{\circ}$ in vacuo. The success of this new synthesis was confirmed by a carbon-hydrogen analysis.*
Calculated for $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2$: C, 46.75; H, 5.49. Found: C, 46.75; H, 5.31.

7. Anhydrous Iron(II) Chloride

Approximately 50 g. of Baker and Adamson reagent iron(II) chloride tetrahydrate was pulverized and added to a 500-ml. round-bottomed flask which was mounted in a Glas-Col heating mantle and attached to a Cenco Hyvac pump through a Dry Ice-methanol cold trap. After flushing out the system with nitrogen, the salt was maintained at $200-250^{\circ}$ in vacuo for eight hours. The product was stored in a tightly-closed screw-cap bottle.

8. Anhydrous Cobalt(II) Chloride

One hundred nineteen grams of Baker and Adamson reagent cobalt(II) chloride hexahydrate was pulverized and added to the same apparatus as used in the dehydration of iron(II) chloride. The salt was maintained at approximately 300° or slightly below for seven hours under vacuum. The progress of the dehydration was followed by observing the accompanying change in the color of the salt from pink to blue.

*The analyses were made by the Weiler and Strauss Microanalytical Laboratory, Oxford, England.

D. Cylinder Gases

1. Hydrogen

Hydrogen was obtained in 2000-psi. cylinders from the National Cylinder Gas Company and was used without further purification.

2. Nitrogen

Nitrogen was obtained from the National Cylinder Gas Company. When dry nitrogen was required, the gas was passed through a 22-mm. diameter column which was packed with 0.5 lb. of 4-mesh indicating Drierite.

3. Carbon Dioxide

A cylinder of carbon dioxide was obtained from the Pure Carbonic Company.

E. Procedure for Handling Cobaltocene and Nickelocene

Both nickelocene and cobaltocene are susceptible to oxidation by atmospheric oxygen, and, for this reason, they must be stored in an inert atmosphere. If possible, they should be handled only in an inert atmosphere. Experience has shown that exposure to air for periods of time less than thirty seconds does not produce detectable deterioration of the compounds. As a result of this finding, the transfer of nickelocene or cobaltocene from the storage containers to the reaction vessels was made quickly in air. Except in a few cases, the crystals were added to a liquid in the reaction vessel. The liquid served to prevent contact of

the compounds with oxygen until the reaction vessel could be swept out with hydrogen.

The general method which was employed for handling these compounds is hereby given. The nitrogen-filled glass storage vial was removed from the refrigerator, allowed to warm to room temperature for at least one hour, and weighed. The desired amount of crystals was rapidly transferred with a spatula from the vial to the reaction vessel. The vial was immediately closed and reweighed in order to obtain the weight of compound which was removed.

The glass vial was then slipped into a loop of pipe-stem cleaner which fitted snugly around the vial. A length of copper wire was attached to the loop so as to form a handle or bail. The cap of the vial was loosened one-half turn, and the entire assembly was lowered into a tube which was constructed from a Pyrex 45/50 ground-glass joint. The inner joint was pulled down to a round end, and the top outer joint was joined to a length of 10-mm. Pyrex by means of a taper seal. The vacuum-tight vessel was attached through a three-way "T" stopcock to a nitrogen tank and to a Cenco Hyvac pump.

The system was alternately evacuated for ten minutes with the pump and filled to 15 psi. with nitrogen. This cycle was repeated three times. After the final filling with nitrogen, the joint was disengaged, and the vial was lifted to the top of the tube where its cap was instantly tightened, thus leaving it filled with nitrogen. The vial was returned to the refrigerator for storage.

The reaction vessel to which the bis-cyclopentadienyl metal compound was added was closed and swept out with hydrogen during the evacuation of the glass vial.

F. Sublimation Apparatus

An all-glass vacuum sublimation apparatus was constructed from a Pyrex 45/50 ground-glass joint (See Figure 1). A 125-ml. Pyrex flask which served as the crude sample container was sealed onto the inside joint which comprised the bottom of the apparatus. A cold finger, which was constructed of 17-mm. Pyrex tubing, extended through a ring seal in the outside joint into the lower half of the apparatus. When the apparatus was separated following a sublimation, the crystals on the cold finger were exposed for easy removal. The vacuum line was attached to a vacuum stopcock which was sealed to the upper section of the apparatus. The entire assembly was annealed for two hours at 560° in an annealing oven.

Apiezon "T" stopcock grease was found to be the most satisfactory lubricant for the large 45/50 joint. This grease has the proper viscosity and low vapor pressure for use up to 110°. Since the liquid level of the mineral oil bath which was used to heat the sublimation apparatus came only to within 2 in. of the joint, the joint itself was never heated above 50-70°. A Teflon sleeve, which was obtained from the Fischer and Porter Company, was tried as a possible means of sealing this joint. The joint was not sufficiently vacuum-tight when the sleeve was used to permit sublimation of materials which were attacked by oxygen.

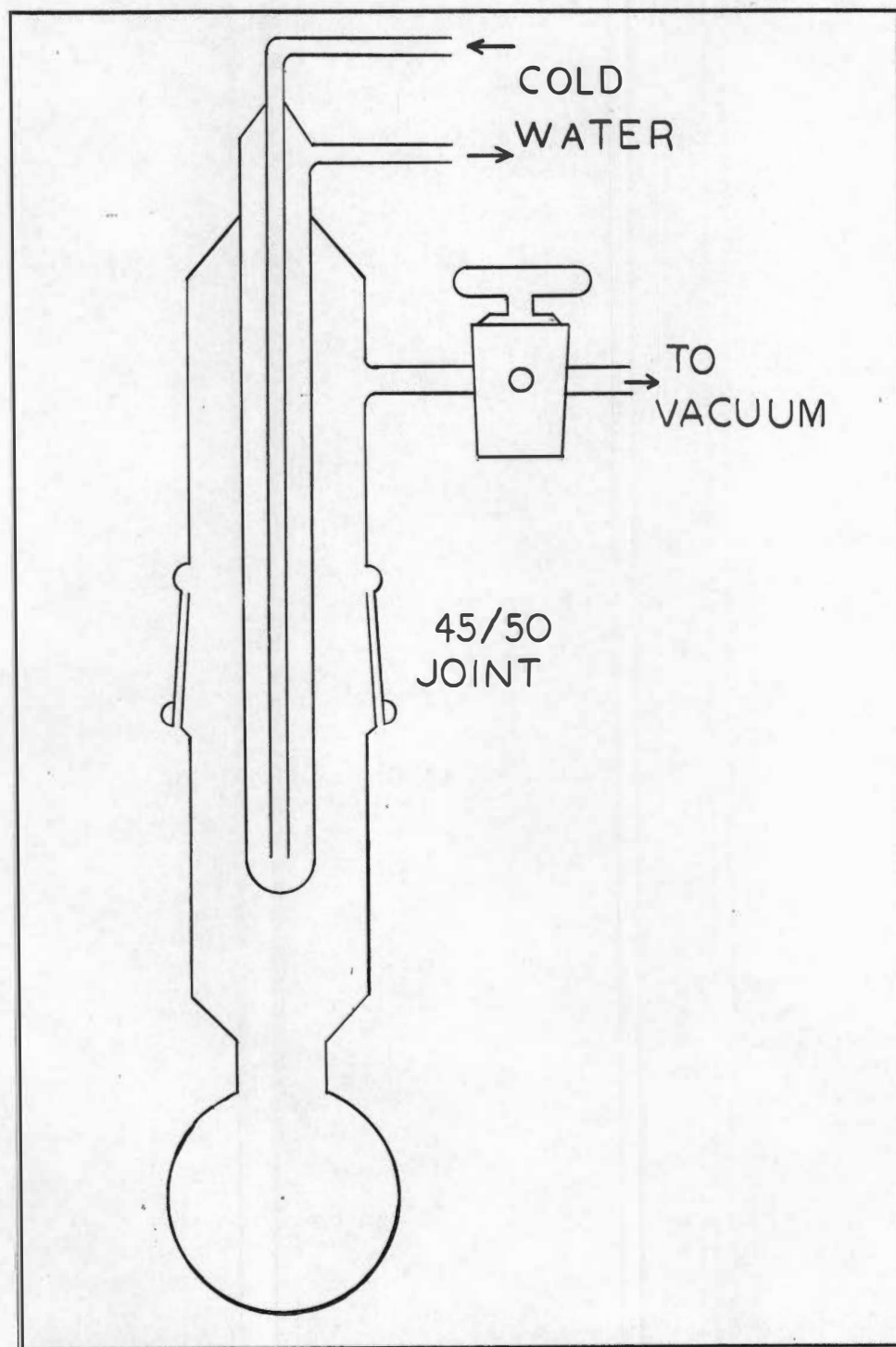


FIGURE 1. VACUUM SUBLIMATION TUBE

However, the sublimation of stable materials under a moderate vacuum might be carried out successfully with this type of seal present in the system. The great advantage in using the Teflon sleeve is the complete absence of contamination of the sublimed product by stopcock grease.

The sublimation apparatus was most successful in the sublimation of the bis-cyclopentadienyl metal compounds in that it was completely vacuum-tight, and compounds underwent no oxidation while being sublimed in this system.

G. Hydrogenation Apparatus

1. Steel Reaction Vessel

A steel reaction vessel or "bomb" which had an internal volume of 52.9 ml. was employed for studying the reaction of hydrogen with the bis-cyclopentadienyl metal compounds and for carrying out the hydrogenation of unsaturated compounds (See Figure 2). The reaction vessel was custom-made by the American Instrument Company and had been previously cold-tested to 15,000 psi. by them. The bomb was closed by means of a copper gasket mounted on the bomb head. Six Allen-head thrust bolts, which were greased with graphite, held the head and gasket against the gasket seat on the bomb proper to make the pressure seal. A 3-in. section of pressure tubing was joined to the head of the bomb for the attachment of pressure gages.

The reaction vessel was used both with and without glass liners. In the event no liner was used, a stem of pressure tubing, which extended from the center of the head into the bomb with the end bent toward the

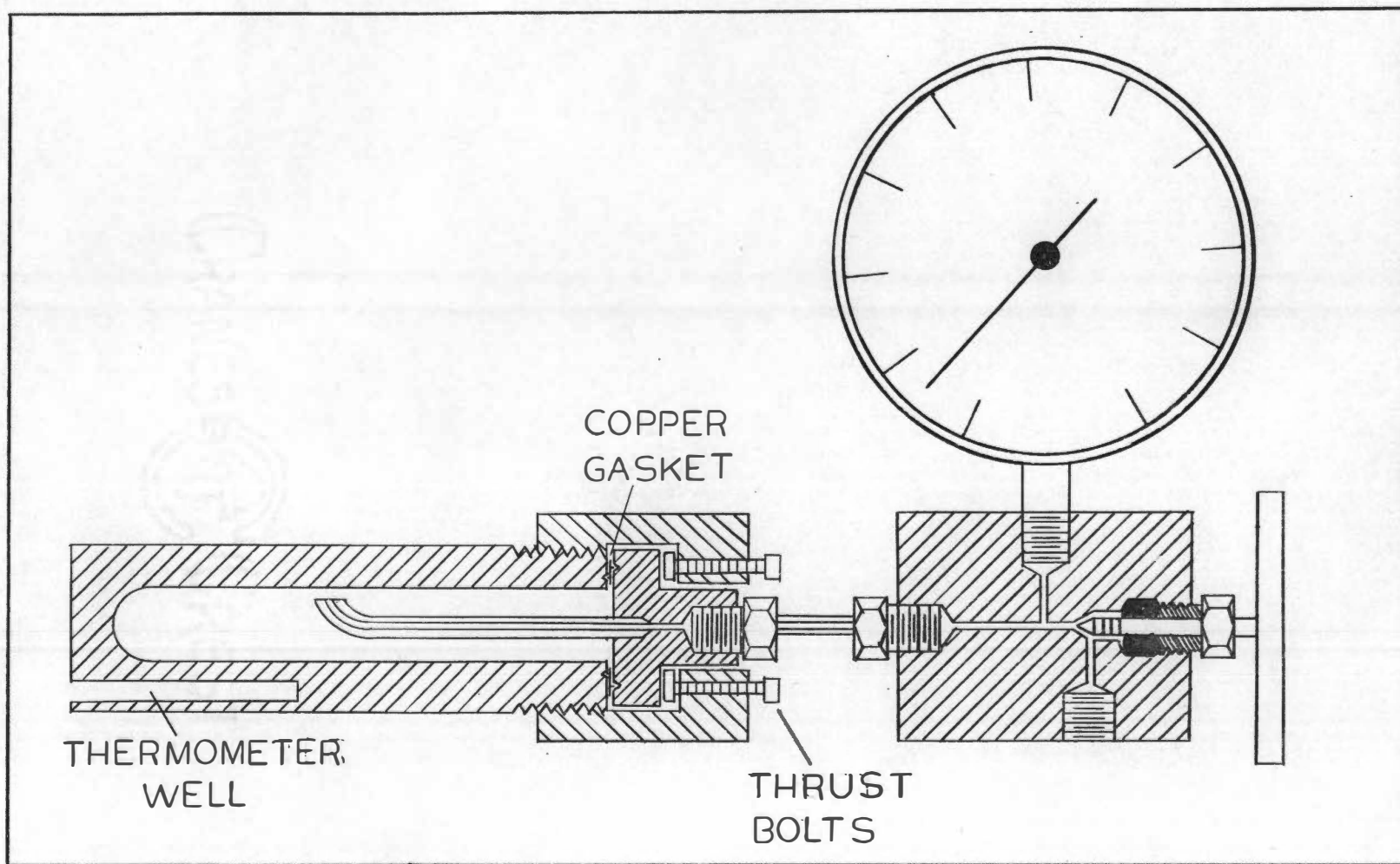


FIGURE 2. STEEL REACTION VESSEL AND GAGE

wall of the vessel, was attached to prevent liquids from flowing into the head of the bomb. This section of tubing decreased the free volume of the bomb by 2.5 ml.

2. Temperature Measurement

The temperature of the reaction vessel was obtained by means of an iron-constantan thermocouple which was inserted in a 3-in. thermocouple well in the back of the bomb. A length of pipe-stem cleaner was wrapped around the thermocouple over a 3-in. section up to within 1 in. of the hot junction in order to secure the wire in the thermocouple well and to prevent fraying of the insulation as the bomb was rocked on the shaker. The potential difference was measured by a Leeds and Northrup portable potentiometer which was sensitive to 0.01 mv. A correction was instrumentally added to the millivolt readings to extend the cold junction from room temperature to a hypothetical 0°.

The thermocouple was not calibrated. Instead, the values of electromotive force as a function of temperature as obtained by Roeser and Wensel of the National Bureau of Standards for the iron-constantan thermocouple system were plotted and used to convert the observed electromotive force to temperature.⁴¹ This procedure was justified because of (1) the limited precision and accuracy of the potentiometer, and (2) the existence of temperature gradients within the reaction vessel. At best, the temperature was measured to within $\pm 0.2^\circ$ when the bomb was at a constant temperature. The error due to the temperature gradients was undoubtedly larger in the measurements which were taken as the bomb was being heated or cooled.

3. Pressure Measurements

The Bourdon-type gage was used exclusively for measuring the total pressure within the reaction vessel. The following gages were employed:

- (1) Laboratory Test Gauge, range 0-1000 psig., gage vol. 13.6 ml.
- (2) Ashcroft Duragauge, range 0-1000 psig., gage vol. 24.4 ml.
- (3) Ashcroft Duragauge, range 0-2000 psig., gage vol. 11.8 ml.
- (4) U. S. Gauge Co. Supergauge, range 0-5000 psig., gage vol. 11 ml.

Each gage was attached to a needle valve block which in turn was attached to the head of the reaction vessel through pressure tubing. With the exception of the 0-5000 psig. gage, the gages were calibrated on a dead-weight tester which was used through the courtesy of the Department of Mechanical Engineering, University of Tennessee, Knoxville. The tester was manufactured by the Amthor Testing Instrument Company and had a pressure range of 0-1000 psi. Pressure tables were constructed permitting the rapid conversion of gage readings to psi. absolute.

The volume of the gas space in each calibrated gage was determined in the following manner. The reaction vessel outlet on the needle valve block was closed with a blank plug, and the gage was filled to approximately two-thirds of its full pressure range with hydrogen and sealed off by closing the needle valve. The gage was then attached to a mercury-filled gas buret through a second needle valve which was added as a precautionary measure against accidentally releasing hydrogen into the gas buret too fast.

Small amounts of hydrogen were released from the gage volume into the gas buret where the volume released was determined at atmospheric pressure. From Boyle's Law considerations:

$$P_a v = -v_g \Delta P_g$$

or

$$v_g = -\frac{P_a v}{\Delta P_g}$$

where v is the volume of gas measured at atmospheric pressure, P_a . v_g is the volume occupied by the gas in the gage. ΔP_g is the change in gage pressure upon releasing the sample of gas. In the determination of v_g , a value of 13.6 ml. was obtained with an average deviation of ± 0.13 ml.

A second method was used in which the gas was admitted from the gage being calibrated into a second gage whose volume was known. The unknown volume was calculated from the pressure changes upon releasing hydrogen from one gage into another and from the known volume of the second gage.

4. Heating and Shaking Mechanism

The reaction vessel, when in use, was mounted in an electric heater whose heat output was controlled by a Powerstat voltage control. The input voltage to the Powerstat was stabilized at 115 volts by a transformer which was manufactured by the National Transformer Corporation. A band of 2-in. woven asbestos tape was placed around the entrance to the heater in order to prevent cool air from circulating between the heater and the bomb. The bomb was secured by means of a bolt through the back plate of the heater.

The heater was mounted on a rocking mechanism which tilted the bomb through a 90° angle (45° on each side of horizontal) at the rate of 46-47 cycles per minute. The same constant rocking rate was used with all of the studies.

At a given heater voltage, the ultimate equilibrium temperature which the bomb obtained depended upon (1) the room temperature, and (2) whether or not the bomb was being rocked. Likewise, the heating rate at a given voltage was found to be a function of these two variables. A plot of the equilibrium bomb temperature as a function of the heater voltage is given in Figure 3 for an average room temperature with the bomb in motion.

5. Glass Liners

Pyrex glass liners were used to hold the solutions of the bis-cyclopentadienyl metal complexes during many of the hydrogenation reactions. The glass liner allows one to withdraw the reaction mixture from the bomb for a visual observation of the solution and, particularly, of any solid material that deposited. Frequently, a metal which is formed by the reduction of a salt of the metal in solution will deposit as a mirror upon the sides of the vessel in which reduction takes place. The mirror formation on the sides of the bomb could not be observed. Glass liners also reduced the possibility that reactions were catalyzed on the iron surface of the bomb walls. The liners were ineffective in stopping the vapor of the compound from making contact with the bomb walls.

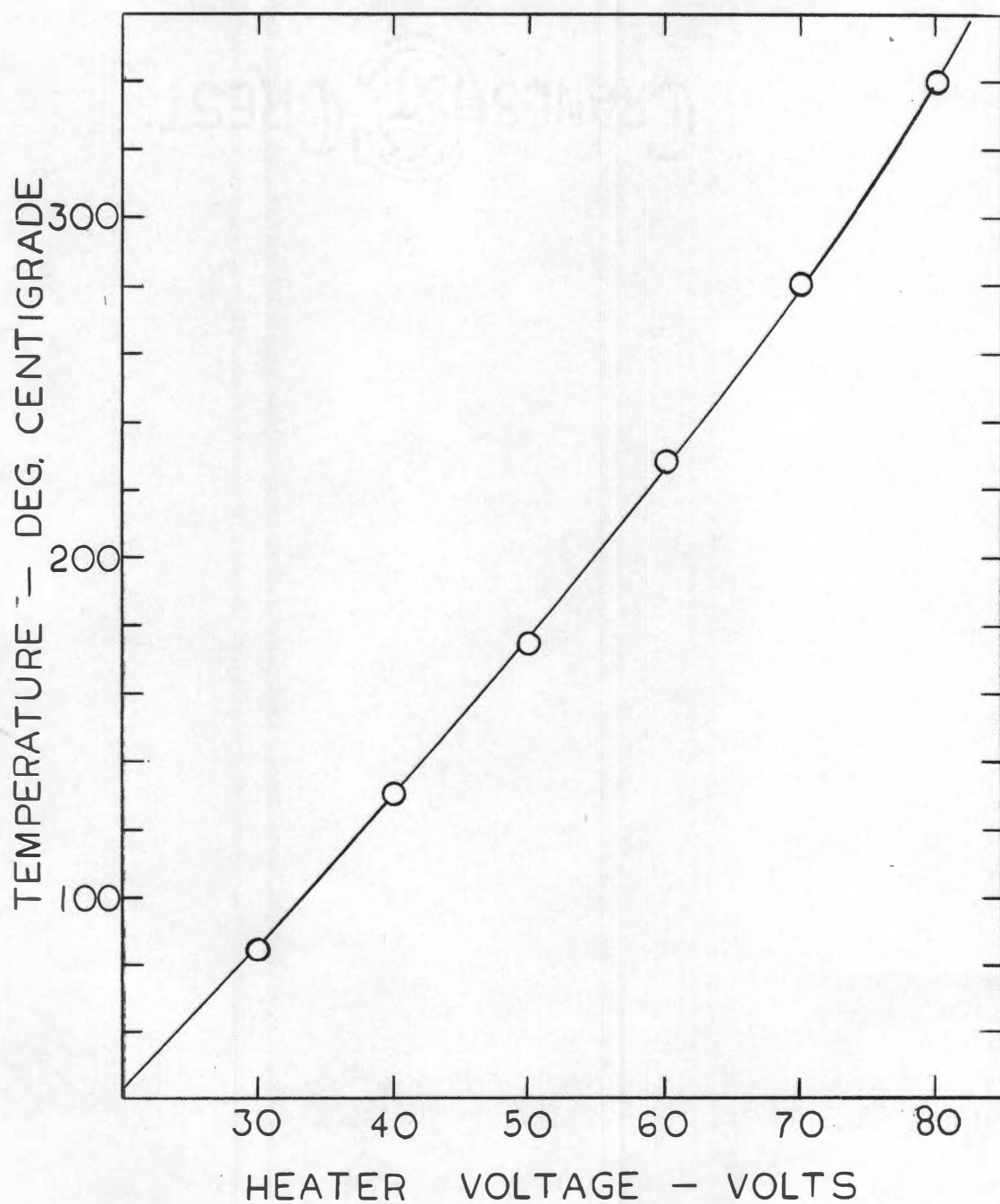


Figure 3. Equilibrium bomb temperature as a function of the heater voltage.

Two general types of liners were constructed (See Figure 4). Both were made of 20-mm. Pyrex tubing with a pinhole blown in the side 3 in. from the bottom to admit hydrogen. The most commonly-used liner had a 14/20 ground-glass joint sealed to the top which served as a cap. The outer half of the joint was pulled down to a test-tube end as close as possible to the ground end in order to conserve space in the bomb. The inner half of the joint was blacked with a soft lead pencil in order to prevent the cap from sticking. The graphite served as a lubricant and did not contaminate the solutions used in the liner. The volume of the glass in the liner was determined by weighing the liner and calculating its volume from the known density of Pyrex glass, 2.23 g./cm.³.

A second type of liner which eliminated the ground-glass joint was used with many of the reactions. While this liner had the advantages of greater capacity and no ground-glass joint, it had many disadvantages. The solutions could not be recovered from used liners, and a new liner had to be prepared for each reaction.

A 6-8 in. section of 12-mm. Pyrex tubing was sealed to a 10-in. length of 20-mm. tubing. The 20-mm. tubing was pulled down into a test-tube end 6 in. from the taper seal. A pinhole was blown in the center of the 20-mm. section. A large rubber stopper was bored to fit the 20-mm. tubing rather snugly. A hole, which was large enough to accommodate 5-mm. tubing, was drilled in the center of the side of the stopper. The stopper was slipped onto the liner such that the side hole was positioned directly over the pinhole. A short section of 5-mm. tubing with an attached rubber blowtube was attached to the side hole

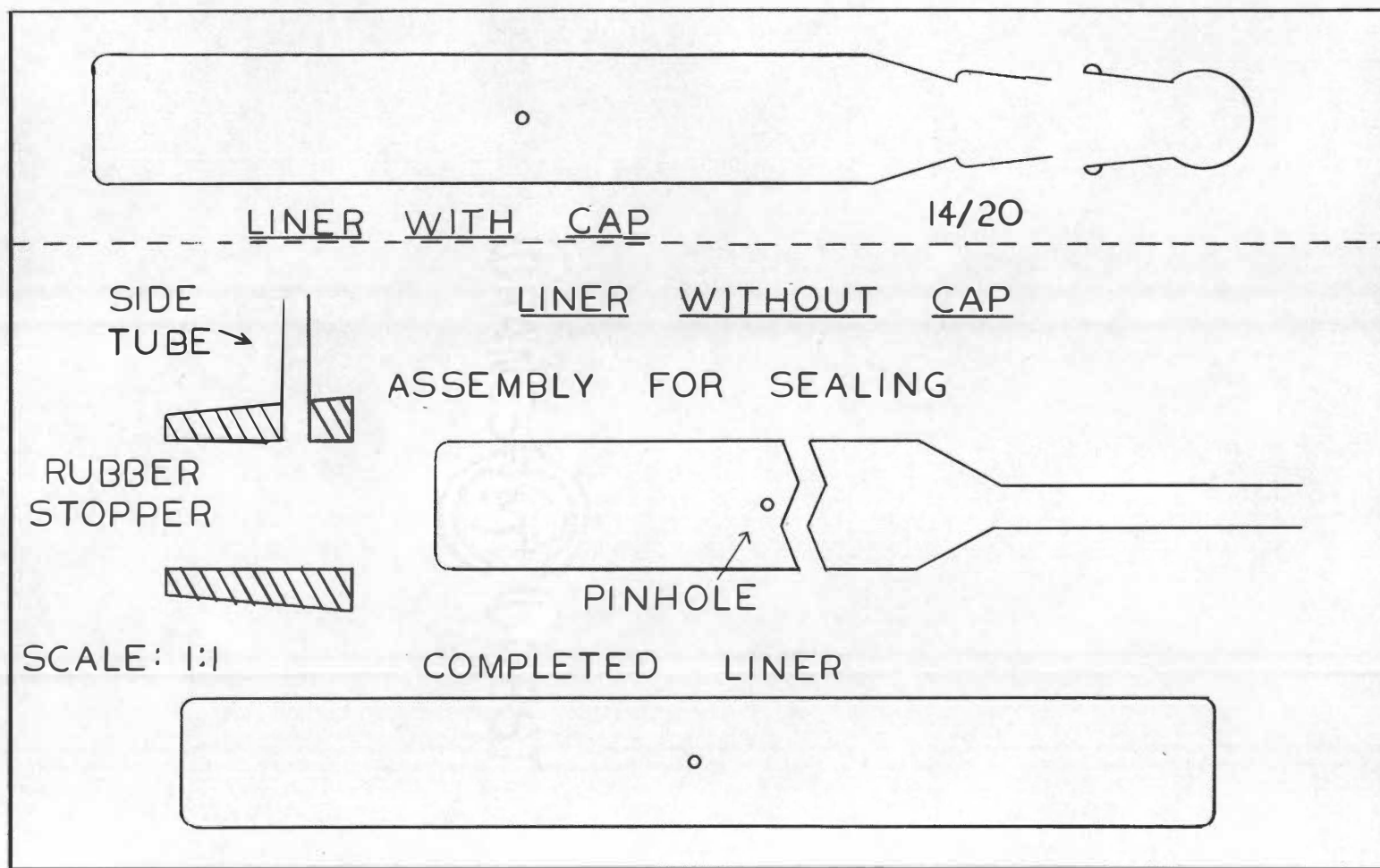


FIGURE 4. GLASS LINERS FOR REACTION VESSEL

of the stopper.

The solution which was to be hydrogenated was added to the liner which had its lower end cooled to -78° in a Dry Ice-methanol bath in order to reduce the solution vapor pressure. The liner was then closed at the taper seal by means of a hand torch and the blow tube which was attached to the pin hole. The volume of the glass in the liner was determined from the weight of the entire assembly minus the weight of glass which was pulled off in sealing the liner.

H. Hydrogenation Procedures and Calculations

1. Charging Reaction Vessel

The steel reaction vessel was thoroughly cleaned before the start of each reaction. First, the inside of the bomb was scoured with a roll of carborundum paper which was held against the inside wall of the bomb by means of a screwdriver as the bomb was rotated on a lathe. This treatment was found to be necessary for the removal of all traces of catalytically-active material which was deposited by previous reactions. Such scouring was not required following reactions which were carried out in glass liners. Second, the bomb was thoroughly scrubbed with a Nylon brush with soap and water in order to remove particles which were dislodged by the treatment on the lathe. Finally, the vessel was rinsed in a stream of distilled water and then methanol. The methanol was removed by evacuating the bomb with a water aspirator.

If no liner was to be used, 10 ml. of solvent or hydrogen acceptor was added to the bomb. If a glass liner was employed, 5-8 ml. was added

to the liner which was sealed and placed in the bomb. The bis-cyclopentadienyl metal compounds were added directly to the solvent or hydrogen acceptor* in the bomb or liner. In general, sufficient compound was added so that approximately 0.1 g. of the parent metal was present. The compounds were found to be completely soluble in the solvents which were employed at the ratio of solute to solvent which was used.

The head of the bomb, which was carefully cleaned, was set in place, and the cap was screwed down to within one-half turn of the head thrust ring. The six head bolts were gradually tightened in a 1-4-2-5-3-6 order. An appropriate gage was attached, and the system was flushed out three times with hydrogen by filling to 1000 psig. and releasing the gas. The bomb was then filled with sufficient hydrogen to give the desired pressure when the bomb reached the reaction temperature.

Little trouble was experienced as a result of the bomb leaking through the head gasket or high pressure tubing connections. Most leaks were detected by observing the drop in pressure as the bomb stood at room temperature. A very small leak produced a sizeable pressure drop rather quickly because the hydrogen volume in the vessel was small. The complete immersion of the bomb and needle valve block in water as a means of detecting leaks was avoided if possible because of the attendant rusting of the equipment. A detergent-water solution was found to be useful for locating leaks around joints in the pressure tubing.

*The term "solvent" will be used henceforth in this section to refer to either solvent, hydrogen acceptor, or both as a solution.

The bomb-gage assembly was secured in the heater mount, and the thermocouple was inserted in the thermocouple well. The rocker was started in order to dissolve the bis-cyclopentadienyl metal compound in the solvent.

2. Pressure-Temperature Studies

The preliminary studies with each bis-cyclopentadienyl metal compound-hydrogen acceptor system were involved with determining the temperature range over which hydrogen absorption would take place. This determination was made by comparing the pressure-temperature curves of the system in question with and without the bis-cyclopentadienyl metal compound being present. The bomb was heated slowly through a temperature interval at a fixed voltage to obtain the total pressure as a function of the temperature for a charge of solvent or hydrogen acceptor and hydrogen.

A charge of bis-cyclopentadienyl metal compound was then added to the system, and again the total bomb pressure was measured as a function of the temperature. Care was taken to use the same initial hydrogen pressure in both determinations. A comparison of plots of pressure as a function of temperature for both series of measurements revealed the temperature at which the absorption of hydrogen proceeded at a measurable rate. The magnitude of the rate of hydrogen absorption was estimated by comparing pressure-time plots of data which were taken with and without the bis-cyclopentadienyl metal compound being present. In the latter method, the rate of heating over the temperature range in question must be the same in each set of data.

Several limitations exist in this type of determination. If the rate of hydrogen absorption is so small that the dP/dt due to hydrogen absorption is much smaller than the dP/dt due to heating, the hydrogen absorption may not be detected. A slow rate of heating and a large temperature coefficient for the hydrogen absorption reaction helps reduce this limitation. A comparison of the initial and final hydrogen pressures at room temperature was also helpful in determining if hydrogen absorption took place.

The pressure-temperature-time data were most useful in establishing temperature intervals which were suitable for apparent activation energy determinations for those reactions whose kinetics were determined.

3. Constant Temperature Studies

These studies were conducted for the purpose of determining the mathematical expressions which govern the rate of hydrogen absorption and, hence, the kinetics of the reactions. The bomb was charged as described previously, and the initial hydrogen pressure was established such that the total pressure did not exceed four-fifths of the full-scale reading of the pressure gage when the bomb was heated to the desired reaction temperature.

The bomb was heated rapidly without shaking to within 10° of the reaction temperature on a heater voltage setting of 90-120 v. The voltage was then immediately reduced to the equilibrium voltage setting for the desired temperature (See Figure 3). The bomb was started rocking after the temperature had become constant. The pressure was recorded as a function of the shaking time. Pressure readings were

taken with the bomb stationary with an accompanying 5 per cent error in the shaking rate (46-47 cycles per minute).

Some hydrogen absorption before the shaking was started was often observed. This phenomenon is not surprising because hydrogen diffusion through the solvent to the catalyst is rapid at the high hydrogen pressures that were used. Also, a small but rapid drop in temperature was observed immediately after the shaking had started due to a cooling action by air as the bomb was rocking. After one to two minutes the temperature readings leveled off and became constant.

In order to determine the kinetic expression for the reaction of hydrogen molecules with acceptor molecules on the surface of the reduced metal from the bis-cyclopentadienyl metal compound, the rate of absorption of hydrogen molecules from the gaseous phase by reaction with the acceptor was calculated from the change in total pressure with time, dP/dt . The simplifying assumption was made that the hydrogen and solvent molecules obey the Ideal Gas Law in the vapor phase in spite of much experimental evidence that deviations from this Law are to be expected at high pressures and temperatures. However, in the two-phase system which is being treated here, so many compensating variables existed that the assumption proved to be a useful one.

Hydrogen in the system occupied a volume v_b at the temperature T_b in the reaction vessel and a volume v_g at a gage temperature T_g in the pressure gage. In most of the reactions which were conducted, the vapor pressure of the solvent or hydrogen acceptor, p , was significant in comparison with the hydrogen pressure. The assumptions were made that

(1) the partial pressure of the solvent molecules in the vapor phase in the bomb was identical with the saturation vapor pressure of the solvent, p , at that temperature, and (2) no solvent molecules diffused into the gage volume. Thus, the pressure of hydrogen in the gage was just the total pressure of the system, P . In the bomb proper, the hydrogen pressure was the total pressure minus the vapor pressure of the solvent, or $P - p$.

An expression for the total number of moles of hydrogen present in the system, n , was obtained by means of an Ideal Gas Law expression for the moles of hydrogen present in the bomb and in the gage:

$$n = \frac{P v_g}{R T_g} + \frac{(P-p) v_b}{R T_b} \quad (1)$$

Upon differentiating this expression with respect to time, t , a differential equation was obtained which related the rate of absorption of hydrogen, dn/dt , to the rate of change of the total pressure, dP/dt .

$$\frac{dn}{dt} = \left[\frac{v_g}{R T_g} + \frac{v_b}{R T_b} \right] \frac{dP}{dt} \quad (2)$$

The vapor phase volume in the bomb, v_b , was obtained by subtraction of the volume of liquid phase at room temperature and the volume of glass in the liner or hydrogen entrance tube from the volume of the empty bomb. The solvent expands as the bomb is heated, but the error made in assuming that the vapor phase volume does not change was reduced by the vaporization of the solvent. The gage temperature, T_g , was assumed to be room temperature or slightly above by a few degrees.

The use of Equation 2 in evaluating the kinetic expressions for the rates of reaction will be treated as each bis-cyclopentadienyl metal compound is discussed in Chapter 3.

4. Variable Temperature Studies

The "Variable Temperature Method" of determining apparent activation energies from a single reaction instead of a series of rate constant determinations at several fixed temperatures was first outlined by Kirslis.⁴² This method has been of great value in the present work because it afforded a method of determining apparent activation energies in reactions where constant temperature data at several temperatures would have been almost worthless. Many variables which normally are present in a series of constant temperature rate constant determinations such as uniformity of catalyst sample and external catalyst poisons are either eliminated entirely or else held constant when this method is used.

A rather brief, generalized treatment of the Variable Temperature Method is given in the present work. An appropriate temperature interval is chosen over which the apparent activation energy, E_a , is to be determined. A heater voltage is determined which will heat the reaction vessel through the desired temperature range at a reproducible rate such that sufficient time would be spent by the bomb in going through the interval for a measurable reaction to take place. Normally, a 20-40° temperature range was chosen. While the rate of heating, dT/dt , need only be reproducible in the temperature range, a desirable condition is one in which the rate is a constant through the temperature range since corrections for small deviations can be made easily.

If a charge of catalyst, hydrogen, and hydrogen acceptor is heated in a reaction vessel at constant volume, then, at any given bomb temperature, T_b , the net or observed rate of change of the bomb pressure may be expressed in terms of two other derivatives as follows:

$$\left(\frac{dP}{dt}\right)_{\text{net}} = \left(\frac{dP}{dt}\right)_{\text{heating}} + \left(\frac{dP}{dt}\right)_{\text{reaction}} \quad (3)$$

The quantity $(dP/dt)_{\text{reaction}}$ is the derivative from which the reaction rate, dn/dt , was calculated (Equation 2). $(dP/dt)_{\text{net}}$ can be obtained in several ways from data which give the total pressure as a function of the reaction time, t , and the temperature, T_b . The method used in the present work was to obtain $(dP/dt)_{\text{net}}$ by means of a straightedge from an accurate plot of P as a function of t at each desired temperature. The derivative $(dP/dt)_{\text{heating}}$ is more difficult to evaluate.

$(dP/dt)_{\text{heating}}$ is, for the most part, an empirically-determined quantity which is a function of the rate of heating, the bomb pressure and temperature, the vapor pressure of the solvent, and the solubility of hydrogen in the liquid phase. Many second-order effects such as the change in the volume of the liquid phase upon heating are also operative. The variables can be consolidated empirically into two variables, the temperature and pressure, by holding such variables as the rate of heating and the amount of hydrogen acceptor present constant at a given temperature. The problem finally emerges as one of evaluating $(dP/dt)_{\text{heating}}$ as a function of pressure at several temperatures.

$$\left(\frac{dP}{dt}\right)_{\text{heating}} = f(P) \text{ at constant temperature} \quad (4)$$

An evaluation of $f(P)$ can be made from several blank determinations by heating the bomb through the desired temperature range under exactly the same conditions as are to be used in the variable temperature reaction with the exception that no catalytic materials are added. Thus, $\left(\frac{dP}{dt}\right)_{\text{reaction}} = 0$. Several determinations of $f(P)$ are made with the initial hydrogen pressure being varied so that the pressure dependency of $(dP/dt)_{\text{heating}}$ at each temperature can be evaluated. The determination of $(dP/dt)_{\text{heating}}$ is discussed in detail for each reaction for which the apparent activation energy was determined.

The calculation of the reaction rate, dn/dt , at each temperature, T_b , considered within the temperature range was made by means of the following:

$$\frac{dn}{dt} = \left[\frac{v_g}{R T_g} + \frac{v_b}{R T_b} \right] \left[\left(\frac{dP}{dt} \right)_{\text{net}} - \left(\frac{dP}{dt} \right)_{\text{heating}} \right] \quad (5)$$

Equation 5 is not used in this form because the specific reaction rate constant, k , rather than dn/dt , is required for the calculation of activation energies. Therefore, dn/dt must be related mathematically to the rate constant, k , by means of the constant temperature studies before a calculation of E_a is made. The calculation of the apparent activation energy of a reaction over the specified temperature range was made using the Arrhenius expression for the temperature coefficient of a reaction:

$$k = A \exp (-E_a/RT) \quad (6)$$

A plot was constructed of $\log_{10} k$ as a function of the reciprocal of the absolute temperature, $(T)^{-1}$. The slope of the resulting straight line was $-E_a/2.303 R$ from which E_a was calculated in units of kcal.mole^{-1} .

CHAPTER III

EXPERIMENTAL RESULTS

A. Bis-(cyclopentadienyl)iron(II)

1. Reaction with Hydrogen

No experimental evidence was obtained which showed that hydrogen would reduce ferrocene to iron and other products in cyclohexane solution at temperatures up to 180° and hydrogen pressures of the order of 2000 psi. Reaction with hydrogen did not take place in cyclohexane even in the presence of platinum added in the form of platinum(IV) oxide. A maximum hydrogen pressure of approximately 1900 psi. was reached at 243° in the latter experiment. The failure of the hydrogen reduction of ferrocene in the presence of platinum is most surprising in view of the aromatic character of ferrocene and of the high activity of platinum toward catalyzing the hydrogenation of aromatic compounds such as benzene.

Some difficulty was experienced in carrying out studies with ferrocene at temperatures above its melting point ($170-173^{\circ}$). The vapor pressure of liquid ferrocene was sufficiently high for it to sublime into the cooler parts of the bomb and thereby cause clogging of the pressure tubing. The use of glass liners for the bomb partially alleviated the difficulty.

2. Studies with Unsaturated Compounds

A series of experiments was performed to determine if ferrocene was capable of functioning as a homogeneous catalyst for the hydrogenation of certain unsaturated compounds. The combined results of the experiments, which are described below, indicate that ferrocene is not capable of activating molecular hydrogen under the experimental conditions studied.

a. Benzene. An attempt was made to hydrogenate benzene at 150° using a charge of 0.0724 g. of ferrocene in 10 ml. of benzene in a glass liner. No hydrogen absorption was observed after shaking for ten hours under a hydrogen pressure of 880 psi. The ferrocene-benzene solution was unaltered by the treatment. The bomb walls were found to be active in catalyzing the hydrogenation of benzene at temperatures above 170°, and, for this reason, no attempt was made to study ferrocene and benzene at higher temperatures. The conclusion was drawn that molecular hydrogen is not activated by ferrocene for the hydrogenation of benzene at temperatures between 25° and 150° and hydrogen at pressures of 600-800 psi.

b. Acetone. Acetone was found to be resistant to hydrogenation in the presence of ferrocene at temperatures below 180° and hydrogen pressures below 800 psi. Ferrocene was also found to be stable under these conditions in acetone solution.

c. Nitrobenzene. The nitro group was not hydrogenated at 150° in the presence of dissolved ferrocene under a hydrogen pressure of 900 psi. after a shaking time of twenty-four hours. The benzene ring also was not hydrogenated during this treatment. The solution of ferrocene in nitrobenzene was apparently unaltered by the treatment.

d. Cyclohexene. A charge of 5 ml. of cyclohexene and 0.14 g. of ferrocene in 5 ml. of cyclohexane was placed in a glass liner, and temperature-pressure measurements were made up to 180° with a maximum hydrogen pressure of approximately 800 psi. No hydrogen absorption was observed below 170° , and very slow absorption was observed at 180° and attributed to the hydrogenation of cyclohexene on the bomb walls. Similar activity by the bomb walls was observed in the case of benzene at 180° . The ferrocene-cyclohexene solution was unchanged after the reaction. No deposition of iron on the liner walls occurred.

Cyclohexene and ferrocene were observed to undergo reaction in the presence of atmospheric oxygen to form a dark brown resinous solid of unknown composition. The reaction occurred at the liquid phase-air interface. A control experiment with cyclohexene alone showed that ferrocene must be present for reaction to take place. No solid compound between cyclohexene and ferrocene formed during the hydrogenation studies.

e. Ethyl laurate. A charge of 0.05 g. of ferrocene in 5 ml. of ethyl laurate was maintained at $290-302^{\circ}$ under a hydrogen pressure of 3000 psig. for six hours. An almost undetectable amount of hydrogen was absorbed, and the ferrocene underwent reaction with the ethyl laurate or its decomposition products to form a dull yellow solid of unknown composition. The ferrocene color was completely absent from the treated solution. No metallic iron was deposited, and the ethyl laurate was somewhat discolored and had a bad odor.

The results of this experiment indicate that ferrocene does not function as a homogeneous catalyst in the hydrogenolysis of ethyl

laurate. The ferrocene itself is evidently reactive toward the ethyl laurate at elevated temperatures.

B. Bis-(cyclopentadienyl)cobalt(II)

1. Reaction with Hydrogen

Cobaltocene was found to react slowly with hydrogen in cyclohexane solution to produce cobalt metal and cyclopentane as follows:



The reaction was almost nondetectable at 150° under a hydrogen pressure of approximately 800 psi. At 170° the destructive hydrogenation of cobaltocene according to the above equation appears to be autocatalytic with an induction period being required. The induction period was clearly indicated in the constant temperature studies with benzene.

The cobalt was deposited in two distinct forms in the glass reaction liner. A cobalt mirror covered a small fraction of the wall area in the segment of the liner which made contact with the cyclohexane solution. In addition to the mirror of cobalt, the metal was also found in a highly-divided particle form.

The number of moles of hydrogen which were consumed in the destructive hydrogenation of cobaltocene plus the deposit of metallic cobalt are substantial experimental evidence that the course of the reaction is as given in the above equation. On the basis of this reaction, the experimental yields which were calculated from the hydrogen consumption were 90-110 per cent of the theoretical value for those reactions which were

performed above 170°.

The reaction of hydrogen with cobaltocene was carried out in the presence of 2 mg. of platinum(IV) oxide. The platinum oxide did not lower the minimum reaction temperature which was required for the reduction under the hydrogen pressures which were used. Apparently platinum, which would be formed from the oxide under the experimental conditions used, does not function as a catalyst for the destructive hydrogenation of cobaltocene.

2. Constant Temperature Hydrogenation of Benzene

With the information available as to the conditions of temperature and hydrogen pressure which were required for the destructive hydrogenation of cobaltocene in cyclohexane, a study was made to ascertain (1) if the same reaction would occur in solution with a hydrogen acceptor, benzene, and (2) if the benzene would be hydrogenated to cyclohexane on the cobalt metal which might be produced. Reactions were carried out at approximately 170° with 0.13-0.15 g. of cobaltocene dissolved in 10 ml. of benzene. The course of the reactions was followed by observing the absorption of hydrogen as calculated from the hydrogen pressure decrease.

The results of these experiments indicate that the cobaltocene was destructively hydrogenated in benzene to form finely-divided metallic cobalt which, in turn, was active in catalyzing the hydrogenation of benzene to cyclohexane (See Figure 5). An induction period was observed before the absorption of hydrogen began.

An experiment was performed to show that the hydrogenation of benzene proceeded by heterogeneous catalytic hydrogen reduction on the

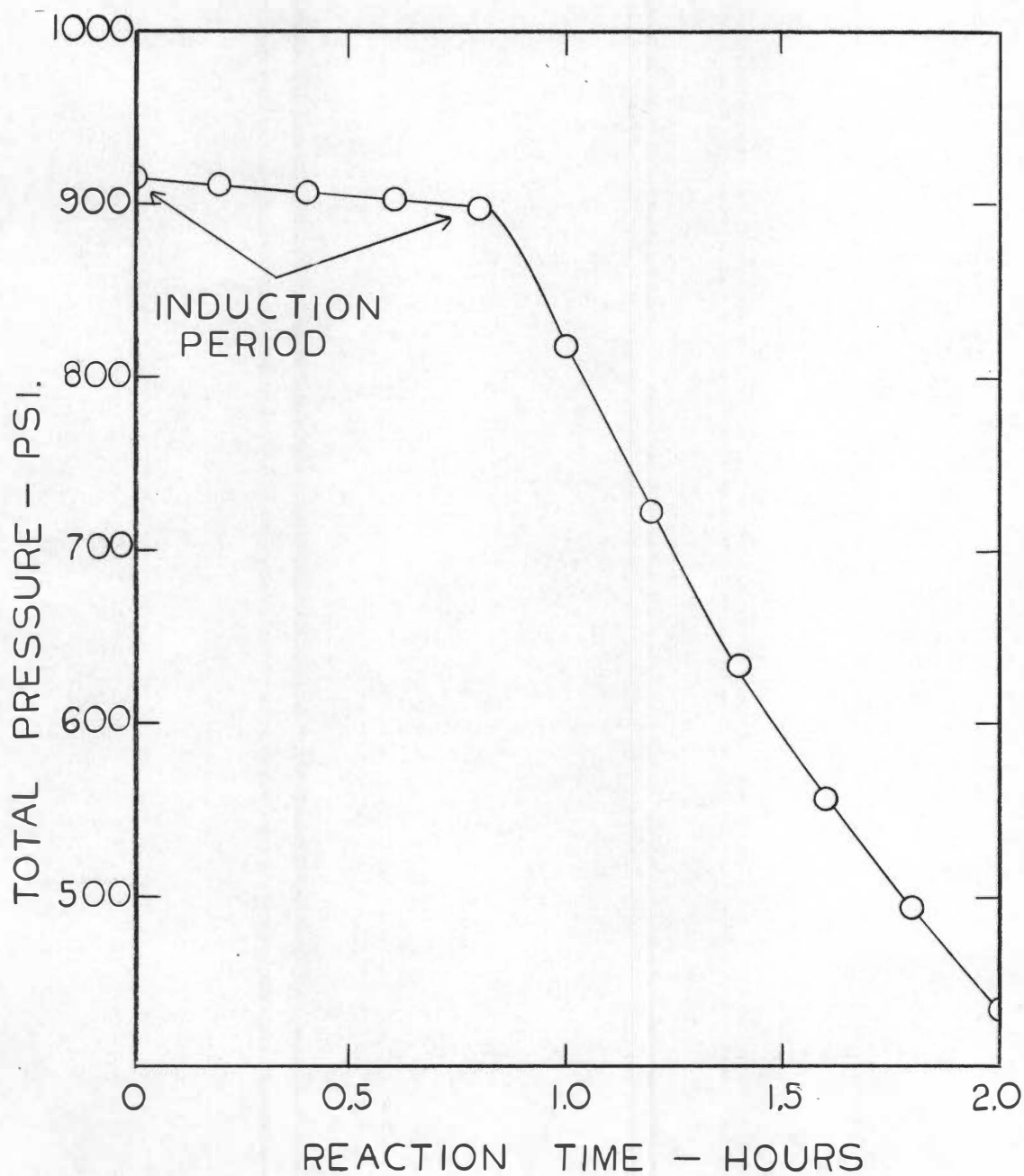


Figure 5. The total pressure as a function of the reaction time for the hydrogenation of benzene on cobalt at 168.6°. Cobalt added as cobaltocene.

surface of the metallic cobalt rather than by some homogeneous mechanism which involved cobaltocene. The metallic cobalt, which had been stored under methanol following the two preceding hydrogenation reactions, was pipetted under methanol into the hydrogenation bomb. The alcohol was evaporated under reduced pressure, and 10 ml. of benzene was added to the evacuated bomb through an evacuation-filling apparatus which is described by Smith and Fuzek.⁴³ The benzene was hydrogenated to cyclohexane at 150° on the prereduced cobalt with hydrogen at pressures as low as 375 psi.

The kinetic expression for the rate of hydrogenation of benzene on the surface of the metallic cobalt was determined. Plots of the logarithm of the hydrogen pressure* as a function of the reaction time were found to be linear for each of the three constant temperature reactions (See Figure 6). Such mathematical behavior can be accounted for if the kinetics are first order in hydrogen pressure and zero order in benzene concentration. The fundamental kinetic expression is postulated to be

$$-\frac{dn}{dt} = k w P_H \quad (1)$$

where n is the number of moles of hydrogen in the vapor phase in the bomb; t is the reaction time; w is the weight of catalytic material present; and P_H is the hydrogen pressure in the bomb proper. k is the

*A plot of benzene vapor pressure as a function of temperature was used to obtain the vapor pressure of benzene for the correction of the total pressure to the hydrogen partial pressure, P_H .⁴⁴

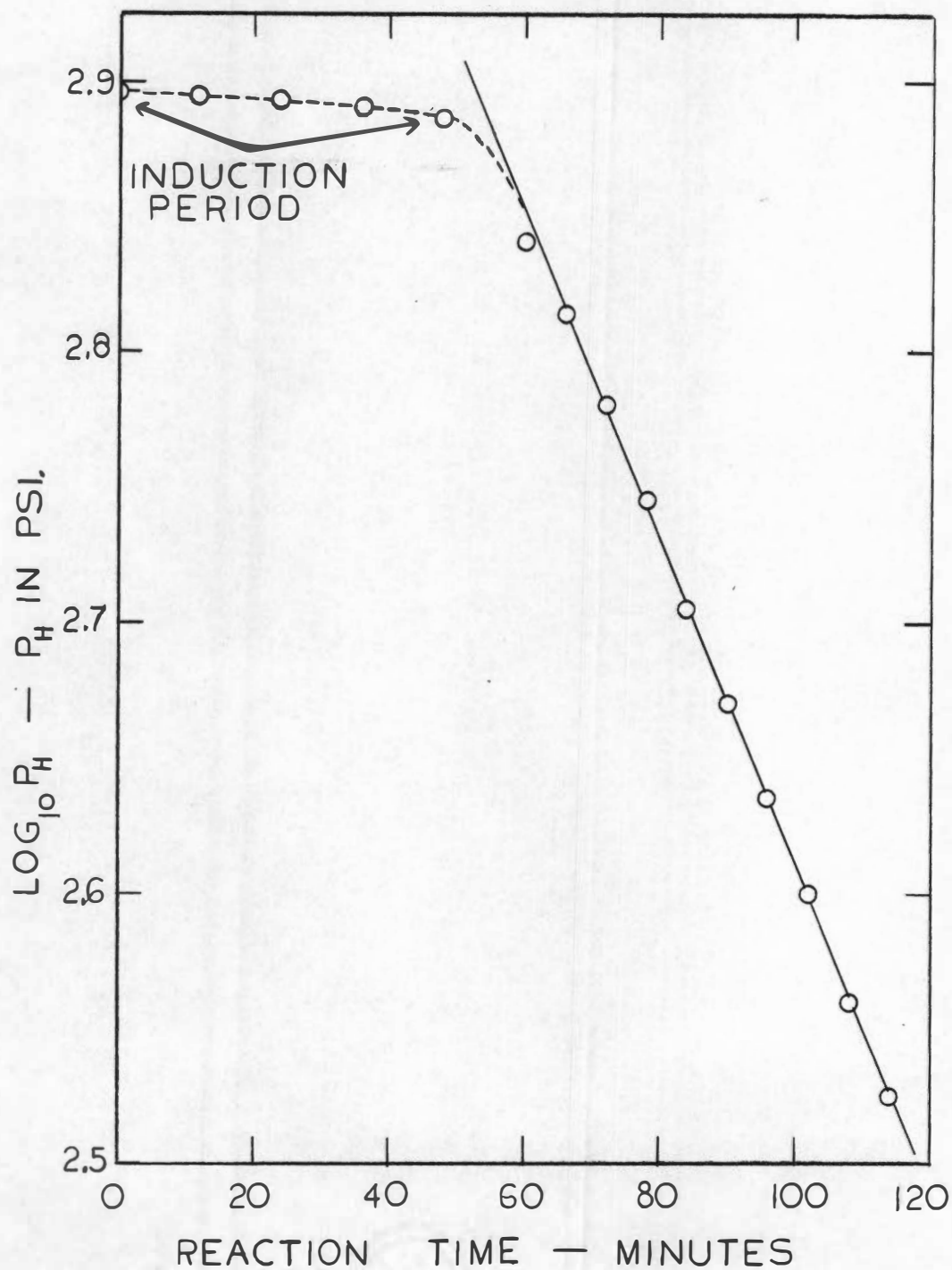


Figure 6. The logarithm of the hydrogen pressure as a function of the reaction time for the hydrogenation of benzene on cobalt at 168.6°. Cobalt added as cobalt-ocene.

specific reaction rate constant which is given in the units moles of hydrogen/(min., g. cobalt, psi. of hydrogen). While equation 1 was found to be valid up to the point of 50 per cent conversion of benzene to cyclohexane in the hydrogen pressure range between 300 and 900 psi., the gradual transition of the kinetic expression at low benzene concentrations and higher or lower hydrogen pressures is not precluded.

The rates of reaction of heterogeneous catalytic reactions are determined by the concentration of the reactants and also by the amount of catalyst present, w . The product kw , or k' , was found to be a linear function of the catalyst weight, w , for catalyst weights up to 0.25 g. for the hydrogenation of benzene over Raney nickel in the same apparatus as used in the present work.⁴⁵ Hence, in using less than 0.1 g. of less-active cobalt, the rate of reaction in the present study should also be a linear function of the catalyst weight as is given in equation 1.*

The rate constant, k , is a true measure of the catalytic activity of the catalytic metallic cobalt at the temperature for which k was measured. The calculation of k is hereby outlined. In Chapter II, Section H, an expression was derived for the rate of change in the number of moles of hydrogen present in the bomb as a function of the rate of change in the total pressure at constant temperature with the final

*This assumption is valid because the same kinetics are found for the Raney nickel and the cobalt-catalyzed hydrogenation of benzene. In addition, the reaction rates are much less than those in the case of the hydrogenation of benzene on Raney nickel such that the rate of diffusion of benzene to the surface of the catalyst is much faster than the rate of reaction.

resulting equation as follows:

$$\frac{dn}{dt} = \left[\frac{v_g}{R T_g} + \frac{v_b}{R T_b} \right] \frac{dP}{dt} \quad (2)$$

Equations 1 and 2 are equated to give the following equation:

$$- \left[\frac{v_g}{R T_g} + \frac{v_b}{R T_b} \right] \frac{dP}{dt} = k w P_H \quad (3)$$

Let the quantity within the brackets be denoted as the constant, A.

$$- A \frac{dP}{dt} = k w P_H \quad (4)$$

Within the bomb proper, the total pressure, P, was composed of the hydrogen partial pressure, P_H , and the saturation vapor pressure of benzene, p, which was constant at constant temperature.*

$$P = P_H + p \quad (5)$$

Equation 5 is differentiated with respect to time at constant temperature, T_b , to give equation 6.

$$\frac{dP}{dt} = \frac{dP_H}{dt} \quad (6)$$

Upon substituting for dP/dt in equation 4 and rearranging the resulting expression, we have

$$k = - \frac{A}{w} \cdot \frac{d \ln P_H}{dt} \quad (7)$$

*The vapor pressure of the liquid phase is not appreciably altered by the hydrogenation of part of the benzene to cyclohexane.

Equation 7 shows that a plot of $\ln P_H^*$ as a function of time should be linear with a slope $-k\omega/A$. k was calculated by means of equation 8 which is obtained from equation 7 by substitution for the constant, A . $d\ln P_H/dt$ was evaluated by drawing the best straight line through a plot of $\log P_H$ as a function of the time and calculating $d\ln P_H/dt$ from the slope of the line (See Figure 6).

$$k = -\frac{1}{R\omega} \left[\frac{v_g}{T_g} + \frac{v_b}{T_b} \right] \frac{d\ln P_H}{dt} \quad (8)$$

The values for the reaction rate constants as calculated from equation 8 are tabulated in Table I.

3. Variable Temperature Hydrogenation of Benzene

The reaction rate constants for the hydrogenation of benzene on metallic cobalt were determined at five-degree intervals in the temperature range between 135° and 170°. These measurements were made by the Variable Temperature Method with some minor modifications being made to the original method as discussed by Kirslis.⁴² The apparent activation energy, E_a , was calculated over the same temperature range from the rate constants.

a. Calculations. In Chapter II, Section H, the basic principles of the Variable Temperature Method were discussed, and an equation was derived from which the rate of hydrogen absorption, dn/dt , could be calculated at a given bomb temperature, T_b , as the bomb was being

*The prefix "ln" is used to denote the natural logarithm of a quantity to the base "e", whereas "Log" is used to denote the common logarithm of a quantity to the base 10.

TABLE I

RATE CONSTANTS FOR THE HYDROGENATION OF BENZENE ON COBALT PRODUCED
UNDER REACTION CONDITIONS BY HYDROGEN REDUCTION OF
BIS-(CYCLOPENTADIENYL)COBALT(II)

Reaction Number	Vol. Benzene, ml.	Wt. Cobalt Added as (C ₅ H ₅) ₂ Co, g.	Reaction Temperature	k x 10 ⁻⁶ moles H ₂ / (min., psi. H ₂ , g. Co)
1	10	0.0471	168.6°	33.6
2	10	0.0431	170.1°	49.1
3	10	0.1171	149.8° ^a	87.5
4	10	0.0302 ^b	149.4°	26.1

^aIn order to prereduce the cobaltocene, the charged bomb was rocked at 170° until 50 psi. of hydrogen was absorbed. The temperature was lowered to 150°, and the reaction was continued at the lower temperature.

^bCobalt from previous reductions of cobaltocene was added instead of cobaltocene.

heated through a given temperature interval. The equation is as follows:

$$\frac{dn}{dt} = \frac{1}{R} \left[\frac{v_g}{T_g} + \frac{v_b}{T_b} \right] \left[\left(\frac{dP}{dt} \right)_{\text{net}} - \left(\frac{dP}{dt} \right)_{\text{heating}} \right] \quad (9)$$

The kinetic expression for the hydrogenation of benzene on cobalt at temperature, T_b , within the specified temperature range was determined through the constant temperature studies. The expression for dn/dt as given in equation 1 is substituted in equation 9, and the resulting equation is solved for the reaction rate constant, k , to give:

$$k = - \frac{1}{R w P_H} \left[\frac{v_g}{T_g} + \frac{v_b}{T_b} \right] \left[\left(\frac{dP}{dt} \right)_{\text{net}} - \left(\frac{dP}{dt} \right)_{\text{heating}} \right] \quad (10)$$

All of the quantities except the heating correction term, $(dP/dt)_{\text{heating}}$, are readily calculated at any bomb temperature.

The heating correction term was calculated from pressure-temperature-time data obtained from blank runs which were carried out in an identical manner as the rate constant determinations except that no catalytic materials were present. From plots of the total bomb pressure, P , and the bomb temperature, T_b , as functions of the time, t , values of $(dP/dt)_{\text{blank}}$ were calculated at specified temperatures within the 135-170° interval. The slopes were determined with the aid of a straight-edge. The derivatives $(dP/dt)_{\text{blank}}$ would be identical with the heating correction terms $(dP/dt)_{\text{heating}}$ if the total bomb pressure, P , were the same in both the blank and reaction determinations at a given temperature. This condition was never realized experimentally except by chance. The

term $(dP/dt)_{\text{blank}}$ can be corrected to give $(dP/dt)_{\text{heating}}$.

From Ideal Gas Law considerations (See Appendix I), the following relation can be derived:

$$\left(\frac{dP}{dt}\right)_{\text{heating}} = P_{\text{reaction}} \left[\frac{1}{P} \frac{dP}{dt} \right]_{\text{blank}} \quad (11)$$

Equation 11 is valid at a specified temperature, T_b , only if dT/dt during the reaction experiment is the same as that of the blank run. Equation 12 was used in calculating the rate constants, k :

$$k = - \frac{1}{R w P_H} \left[\frac{v_g}{T_g} + \frac{v_b}{T_b} \right] \left[\left(\frac{dP}{dt}\right)_{\text{net}} - P \left(\frac{1}{P} \frac{dP}{dt}\right)_{\text{blank}} \right] \quad (12)$$

The experimental procedure which was strictly adhered to in this study is outlined below:

1. Ten milliliters of benzene was used without a glass liner.
The pressure range which was investigated was 700-800 psi.
The pressure was measured by the 0-1000 psi. Laboratory Test Gauge.
2. The bomb was heated to 92.5° (5.00 mv. on iron-constantan thermocouple) on 80 v. heater voltage. At exactly 92.5° the heater voltage was reduced immediately to 55 v.
3. Pressure-temperature-time readings were taken as the bomb was heated through the temperature range $110-175^\circ$.

A tabulation of the quantity $\left[\frac{1}{P} \frac{dP}{dt} \right]_{\text{blank}}$ is given in Table II. The average values were used in all of the rate constant calculations.

TABLE II

HEATING CORRECTION TERMS FOR THE VARIABLE TEMPERATURE DETERMINATION
OF THE RATE CONSTANTS FOR THE HYDROGENATION OF BENZENE ON
COBALT FROM BIS-(CYCLOPENTADIENYL)COBALT(II)

Bomb Temperature, Degrees Centigrade	$\left[\frac{1}{P} \frac{dP}{dt} \right]_{\text{blank}} \times 10^3, \text{ min.}^{-1}$		
	Determination Number		Average
	1	2	
135	3.035	3.305	3.170
140	2.827	2.908	2.868
145	2.442	2.643	2.543
150	2.255	2.432	2.343
155	1.978	2.225	2.102
160	1.775	2.007	1.892
165	1.597	1.768	1.683
170	1.442	1.332	1.387

b. Results. Two experimental determinations of the reaction rate constants were made, and the rate constants are recorded in Table III. Experiment 1 was performed using metallic cobalt catalyst which had been prepared by reducing bis-(cyclopentadienyl)cobalt(II) in cyclohexane with hydrogen at 1700 psi. and at 170°. The finely-divided cobalt was washed three times with methanol by centrifugation and decantation and stored under methanol until used. The cobalt was added to the hydrogenation bomb under methanol which was then removed by evacuating the vessel with a water aspirator. Ten milliliters of benzene was added to the evacuated bomb.

Cobaltocene was added directly to the benzene in the reaction vessel in experiment 2. Because of the resistance of cobaltocene toward hydrogen reduction at temperatures below 170°, the cobaltocene was pre-reduced in situ at 170°. The bomb was then cooled to room temperature, and additional hydrogen was added before continuing with the determination of the rate constants. Care was taken to hold the bomb at 170° sufficiently long for all of the cobaltocene to be reduced.

The apparent activation energy, E_a , for the hydrogenation of benzene on the cobalt catalysts produced from cobaltocene was determined from the Arrhenius equation which is given below in logarithmic form:

$$\text{Log } k = \text{Log } A - \frac{E_a}{2.303 R T} \quad (13)$$

Plots were made of Log k as a function of $(T^\circ K)^{-1}$, and the values of E_a were calculated from the slopes of the resulting straight lines (See Figure 7). The calculated values of the apparent activation energies

TABLE III

THE RATE CONSTANTS FOR THE HYDROGENATION OF BENZENE ON COBALT FROM BIS-(CYCLOPENTADIENYL)COBALT(II) IN THE TEMPERATURE RANGE 135-170°

Reaction Temperature, Degrees Centigrade	Reaction Rate Constant, $k \times 10^6$, moles H_2 /(min., psi. H_2 , g. Co) Determination Number	
	1 ^a	2 ^b
135	2.47	7.44
140	4.02	8.63
145	4.39	10.73
150	---- ^c	14.17
155	8.32	19.43
160	11.71	25.92
165	14.87	33.36
170	17.72	42.00

^aMetallic cobalt was prepared by hydrogen reduction of cobaltocene in cyclohexane prior to its use. The weight of cobalt used in the rate constant determination was 0.0445 g.

^bCobaltocene was added directly to the benzene and reduced by hydrogen at 170° prior to the hydrogenation reaction. The weight of reduced cobalt present was 0.0532 g.

^cThe shape of the pressure versus time curve at 150° made an accurate determination of the slope impossible.

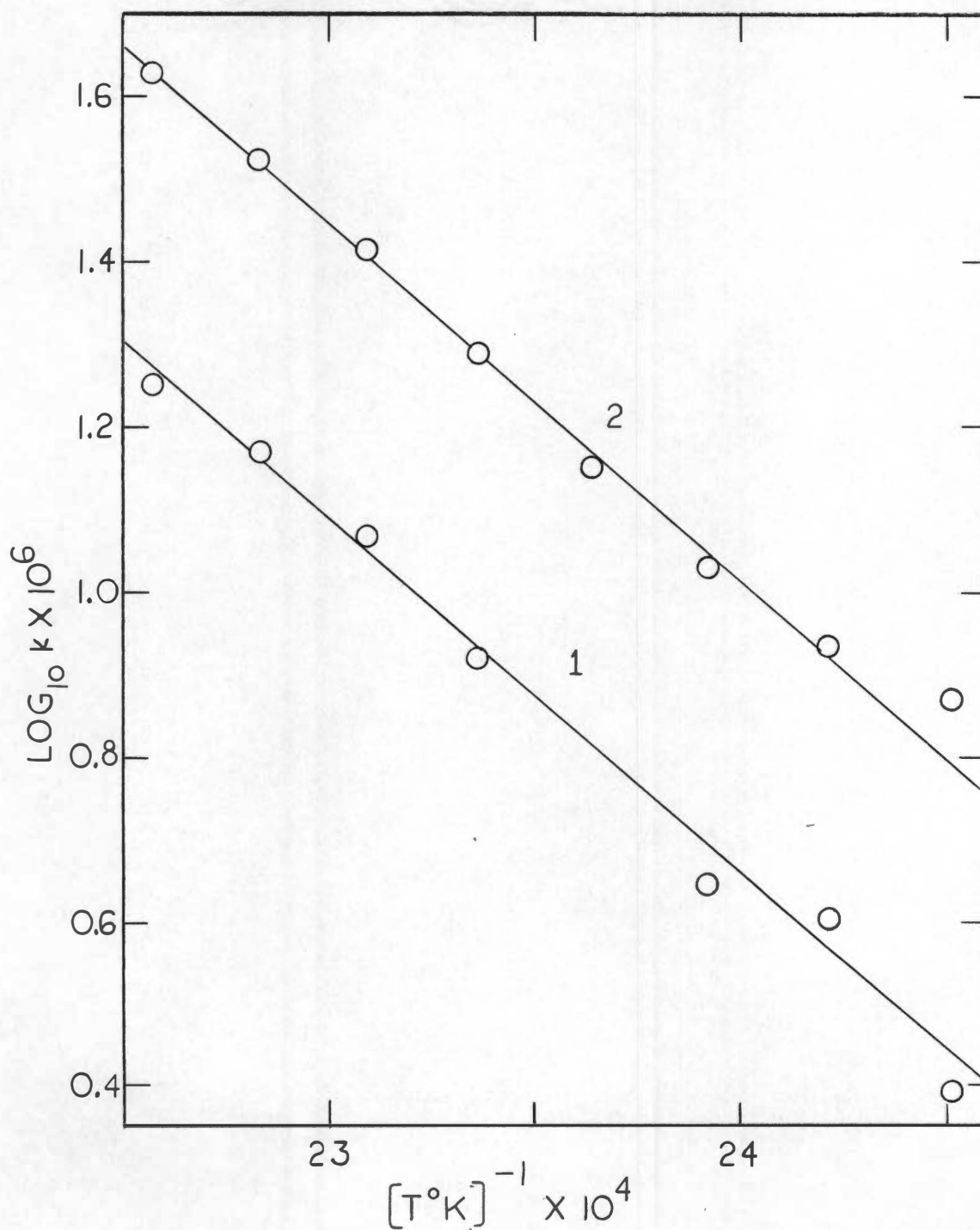


Figure 7. The logarithm of the reaction rate constant as a function of the reciprocal of the absolute temperature for the hydrogenation of benzene on cobalt. Curve 1: cobalt added as metallic cobalt. Curve 2: cobalt added as cobaltocene.

are tabulated in Table IV.

4. Hydrogenolysis* of Ethyl Laurate

The catalytic hydrogenolysis of esters of fatty acids to long-chain alcohols has become an important industrial process. The reaction of ethyl laurate with hydrogen proceeds very smoothly at 250° on a copper chromite catalyst under hydrogen at 2500 psi. to give high yields of dodecanol-1 (lauryl alcohol) according to the following equation:



The present study was initiated to determine the behavior of ethyl laurate in the presence of bis-(cyclopentadienyl)cobalt(II) under hydrogen at pressures up to 2500 psi. and at temperatures up to 325°.

a. Temperature-pressure studies. The reaction vessel pressure was determined as a function of the temperature for a charge of 10 ml. of ethyl laurate and hydrogen at an initial pressure of 1500 psig. No glass liner was used, and the bomb pressure was obtained with the uncalibrated Supergauge. Several heating curves were obtained by varying the heater voltage. Approximately the same pressure was obtained at a given temperature regardless of the heater voltage. A heater voltage of 80 v. was finally selected as being the most suitable for this study. Decomposition of the ethyl laurate was observed at temperatures above 350° during the calibration experiments. A plot of the bomb pressure, P,

*The term "hydrogenolysis" applies to the cleavage of a bond in an organic molecule with the simultaneous addition of a hydrogen atom to each fragment.

TABLE IV

THE APPARENT ACTIVATION ENERGY FOR THE HYDROGENATION OF BENZENE IN
THE TEMPERATURE RANGE 135-170° ON METALLIC COBALT PREPARED BY
HYDROGEN REDUCTION OF BIS-(CYCLOPENTADIENYL)COBALT(II)

Determination Number ^a	Apparent Activation Energy, Ea, kcal. mole ⁻¹
1	19.91
2	19.79

*The same determination designation is used in Table III and
Figure 7.

as a function of the bomb temperature, T_b , is given in Figure 8. The pressure was essentially a linear function of the temperature between 200° and 325°.

A similar temperature-pressure determination was made with a charge of 10 ml. of ethyl laurate, 0.558 g. of cobaltocene (equivalent to 0.174 g. of cobalt), and hydrogen at an initial pressure of 1500 psig. The bomb was heated on 80 v. as in the calibration experiment. A plot of bomb pressure as a function of the bomb temperature for this charge is given in Figure 9. By comparing the plots in Figures 8 and 9, the temperatures at which hydrogen absorption occurred were determined.

A rapid uptake of hydrogen was observed at 200° followed by much slower hydrogen absorption as the bomb was heated to 325°. The first absorption of hydrogen is attributed to the destructive reduction of cobaltocene to form metallic cobalt and cyclopentane. The second stage of hydrogen absorption, which was quite slow in comparison with the first, is thought to be a reaction between ethyl laurate and hydrogen presumably upon the surface of the metallic cobalt. A clear, colorless liquid was removed from the reaction vessel. The cobalt was present in a finely-divided particle form. The above reaction was repeated with the same results.

b. Constant temperature studies. The effect of slowly reducing the cobaltocene in ethyl laurate at 170° upon the catalytic activity of the cobalt was studied. Since cobaltocene melts at 170-173° with decomposition, slow reduction at 170° would be expected to give a cleaner reaction than the rapid reaction at 200° after some possible decomposition

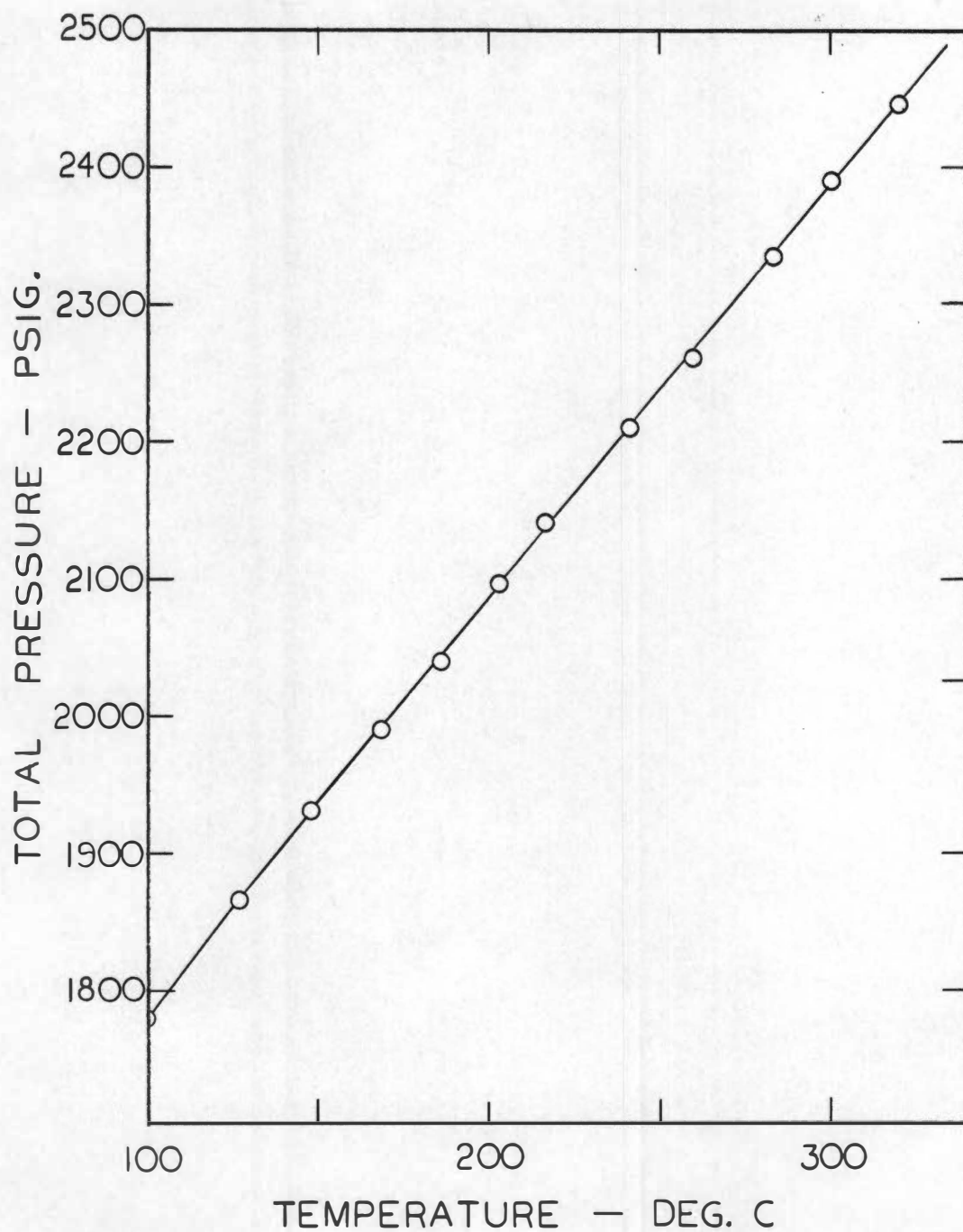


Figure 8. The total pressure as a function of the bomb temperature for a charge of hydrogen and 10 ml. of ethyl laurate. Heater voltage 80 v.

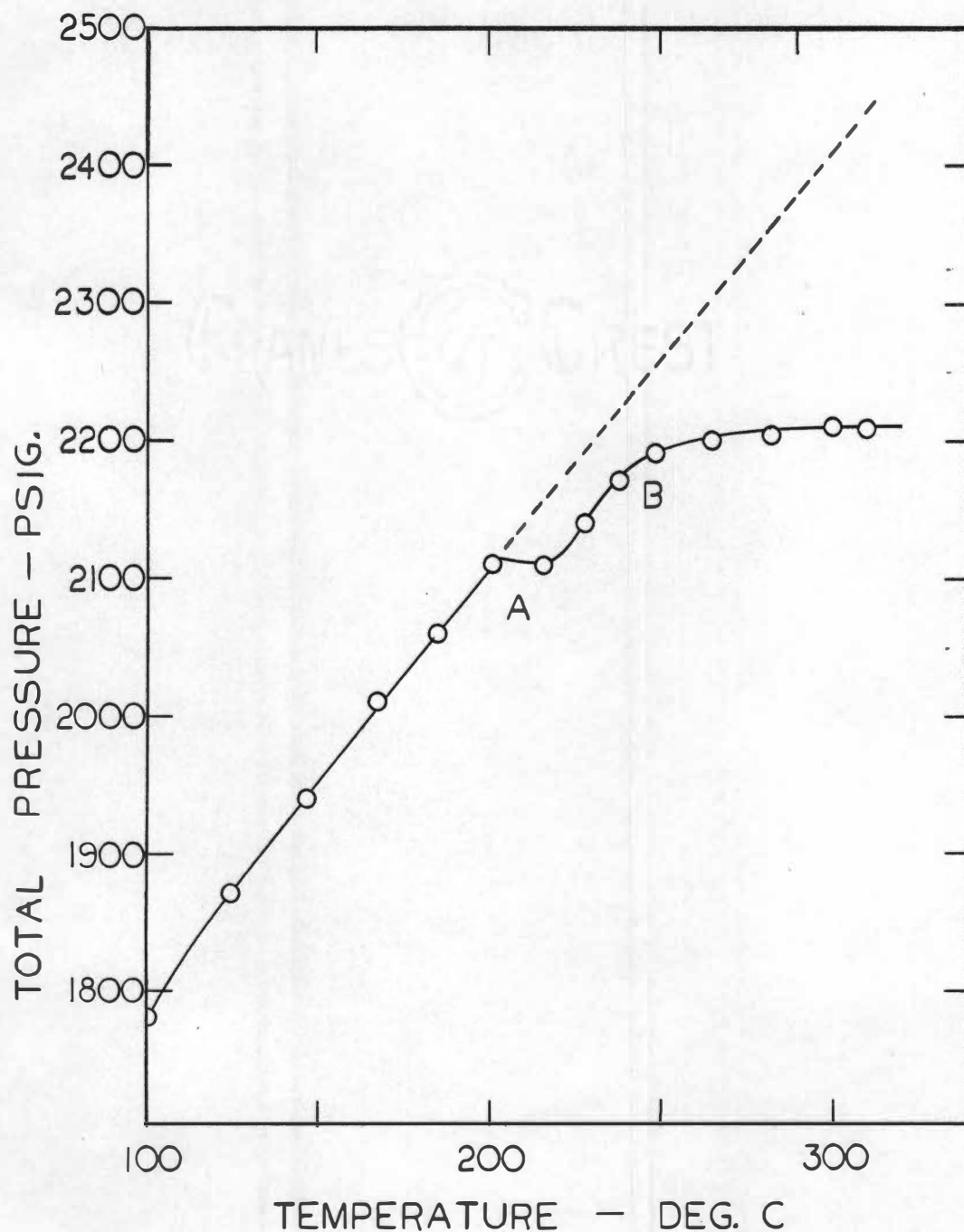


Figure 9. Total pressure as a function of the bomb temperature for the hydrogenolysis of ethyl laurate on cobalt from cobaltocene. Bomb charge: 10 ml. of ethyl laurate and 0.29 g. of cobaltocene. Heater voltage 80 v. Point A: reduction of cobaltocene. Point B: start of hydrogenolysis of ethyl laurate.

of the cobaltocene had occurred. An experiment was performed in which 0.19 g. of cobaltocene in 10 ml. of ethyl laurate was reduced by hydrogen at 2000 psig. for four hours at 170° . Thereafter, the bomb was rapidly heated to 315° . A temperature of $315-329^{\circ}$ was maintained for eighteen hours while the bomb was rocking. A drop in hydrogen pressure of only 30 psig. was observed indicating very slow reaction. The liquid phase was colored reddish-brown and had some suspended solid material in it. Unlike the reaction products in previous reactions, the liquid had an obnoxious odor. The conclusion was reached that a more active cobalt catalyst was obtained by reduction near 200° rather than at 170° .

The hydrogenolysis of ethyl laurate was attempted using metallic cobalt from previous hydrogenolysis reactions as the catalyst. The cobalt had been washed in methanol following its initial use and stored under the alcohol. The cobalt was added to the bomb under methanol which was then removed by evacuating the bomb with a water aspirator. Ten milliliters of ethyl laurate was added to the evacuated bomb. The catalyst weight was 0.0432 g. No hydrogen absorption was observed after shaking for ninety minutes at $251-254^{\circ}$ at a hydrogen pressure of 2230 psig. and after shaking for five hours at 301° at a hydrogen pressure of 2360-2370 psig. No direct proof was thereby obtained that the metallic cobalt was the catalyst in the hydrogenolysis reactions. Evidently, the cobalt produced by reduction of cobaltocene in ethyl laurate was active until exposed to atmospheric oxygen.

e. Identification of reaction products. Many products are known to result from the hydrogenolysis of ethyl laurate. The product which is

obtained seems to be determined largely by the particular catalyst which is used rather than by the reaction conditions. Thus, the identification of the reaction products was deemed necessary.

A positive identification of dodecanol-1 in the reaction products was never accomplished. The preparation of pure derivatives of dodecanol-1 such as the phenylurethan and the 3,5-dinitrobenzoate is quite difficult. Dodecanol-1 reacts with the reagents much slower than does ethanol which would also be present. Indeed, these derivatives of dodecanol-1 are rather difficult to prepare with the pure alcohol. Regardless, an attempt was made to prepare derivatives of dodecanol-1 with phenylisocyanate and 3,5-dinitrobenzoyl chloride.

In order to saponify unreacted ester, 7 ml. of reaction products from a single hydrogenolysis reaction was refluxed for one hour in 40 ml. of 95 per cent ethanol with 2 g. of sodium hydroxide. After cooling, a white solid solution formed. The formation of the solid solution was thought to be due to the presence of sodium laurate which was formed in the saponification reaction. The solid solution was dissolved in 95 per cent ethanol and added to 1 l. of distilled water. The solution was made acid with hydrochloric acid.

Approximately 7 ml. of an oil separated and was removed by means of a separatory funnel. Fifty milliliters of benzene was added to the organic layer in the pot of a 30-in. Vigreux column. Fractional distillation was conducted in order to remove the water-ethanol-benzene binary and ternary azeotropes. The high-boiling oil was not distilled.

The preparation of lauryl 3,5-dinitrobenzoate was attempted with 2.5 ml. of the oil.⁴⁶ Light-yellow crystals were obtained and

recrystallized from a 1:1 water-ethanol solution. The compound melted at 39-40° whereas the 3,5-dinitrobenzoate was reported to melt at 60°. Recrystallization failed to improve the melting point. The ethyl 3,5-dinitrobenzoate was reported to melt at 91-92°. Conclusive results were not obtained.

Attempts to prepare the phenylurethan derivative of dodecanol-1 resulted in the formation of white crystals which melted at 239-240° whereas the derivative with dodecanol-1 is reported to melt at 74°. ⁴⁶ The compound which was obtained was undoubtedly sym-diphenylurea (m.p. 240°) which is formed in the hydrolysis of the reagent phenylisocyanate. ⁴⁷ The work on the preparation of derivatives of dodecanol-1 was abandoned at this point in favor of a different approach to the problem. The identification of the reaction products was sought through measurement of physical constants such as the boiling point and the refractive index.

The reaction products from the hydrogenolysis of 10 ml. of ethyl laurate were fractionally distilled through a 2-ft. Vigreux column at 13-15 mm.* with three fractions being collected. The head temperature was determined with an iron-constantan thermocouple placed in the thermocouple well which was packed with zinc filings. The system was evacuated with a Cenco Hyvac pump, and the pressure was regulated by a flutter-valve manostat. The pressure was measured by a mercury manometer. The distillation data are tabulated in Table V.

*The pressure within the fractionating column may have been higher than the recorded pressure because of a clogged stopcock between the column and the vacuum pump.

TABLE V

THE FRACTIONAL DISTILLATION OF THE REACTION PRODUCTS OF THE
HYDROGENOLYSIS OF TEN MILLILITERS OF ETHYL LAURATE
ON METALLIC COBALT PRODUCED FROM
BIS-(CYCLOPENTADIENYL)COBALT(II)

Fraction Number	Head Temperature, deg. C./13-15 mm. ^a	Volume Collected, ml.
1	92.4°	1.0
2	139.3°	0.5
3	145.7-147-5°	2.0

^aThe column pressure may have been higher by 10-20 mm. The pressure given is the minimum possible pressure.

The boiling point of each fraction was measured at atmospheric pressure by the micro method of Siwoloboff.⁴⁸ A liquid sample was drawn up to a height of approximately 4 mm. in a commercial melting point capillary tube by first heating the end of the tube in the flame of a match and then submerging the open end in the liquid until the proper size sample was obtained. The sample was shaken into the closed end of the capillary tube, and a 5-mm. section of a smaller capillary tube with a closed end was shaken down into the liquid in the larger tube in an inverted position. The boiling point of the sample was determined as follows. The assembly was heated a few degrees above the sample boiling point in an aluminum melting point block. Air was driven out of the inverted inner capillary tube in this process. The melting point block was allowed to cool very slowly with the boiling point being taken as the liquid phase just started to enter the inverted tube.

The refractive index of each fraction was determined at 20.0° with a Bausch and Lomb Abbe Refractometer. The refractometer was maintained at the correct temperature by water which was circulated through the water jackets of the prisms. The boiling points and refractive indices of the three fractions are tabulated in Table VI with the same constants for probable reaction products dodecanol-1, n-undecane, and n-dodecane for comparison.*

The data indicate that n-undecane and ethyl laurate comprise the greater portion of the fractionally distilled reaction mixture. Support

*Dodecanol-1, n-undecane, and n-dodecane are the most common products of the hydrogenolysis of ethyl laurate.

TABLE VI

THE REFRACTIVE INDICES AND BOILING POINTS OF CONSTANT BOILING FRACTIONS
FROM FRACTIONAL DISTILLATION OF THE REACTION PRODUCTS FROM
HYDROGENOLYSIS OF ETHYL LAURATE ON COBALT IN COMPARISON
WITH THE CONSTANTS FOR CERTAIN POSSIBLE PRODUCTS

Fraction Number or Compound	Boiling Point deg. C./mm. Hg	Refractive Index, n_D^{20}
1	199-201°/732.2	1.4242
2	239°/740.5	1.4287
3	264.5°/732.2	1.4317
<u>n</u> -undecane ⁴⁹	193°/740	1.4190 ⁴⁹
<u>n</u> -dodecane ⁴⁴	212°/740	1.4217 ⁴⁹
dodecanol-1 ⁴⁴	258.1°/740	1.4400(n_D^{25}) ^a
ethyl laurate ⁵⁰	269°/760	1.4294 ^b

^aDodecanol-1 is a solid at 20° (m.p. 24°).⁵⁰

^bSee Preparation of Ethyl Laurate, p. 27.

was given this conclusion by gas chromatographic studies with fraction 1.* The elution times for the sample were compared with those for Eastman practical n-dodecane using a Celite-packed column at 150°. A high-boiling hydrocarbon oil was employed as the eluant. The study showed conclusively that n-dodecane was not present and that fraction 1 was composed of a principal component (92-95 per cent) which boiled below n-dodecane by 10-20°. Three lesser components were also observed. One of these boiled higher than n-dodecane, while the other two boiled below the main component.

The refractive index for fraction 3 would indicate that some dodecanol-1 might be present in that fraction. The boiling point of this fraction was found to be close to the boiling point of ethyl laurate so that the per cent dodecanol-1 would most likely be less than 10-20 per cent if present at all.

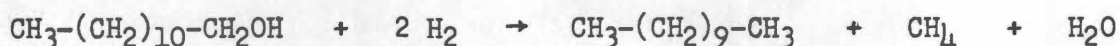
d. Conclusions. The conclusions reached in the cobaltocene-ethyl laurate study are (1) cobaltocene will react with hydrogen in ethyl laurate at or above 170° to produce cobalt metal and possibly cyclopentane; (2) ethyl laurate will undergo hydrogenolysis on the surface of the metallic cobalt above 250° with a hydrogen pressure of 2000 psig.; and (3) the end product of the hydrogenolysis reaction appears to be n-undecane.

*Thanks are due Dr. Edgar L. McDaniel, Jr., of the Tennessee Eastman Company, Kingsport, Tennessee, for making these determinations.

5. Hydrogenolysis of Dodecanol-1

The uncertainty in identifying the products obtained in the hydrogenolysis of ethyl laurate on cobalt from cobaltocene prompted an investigation of the behavior of dodecanol-1 under the conditions which led to the hydrogenolysis of ethyl laurate. The goal of this study was to ascertain whether or not dodecanol-1 would be stable under these conditions. If dodecanol-1 proved to be reactive, then a reason would be obtained which would explain the apparent absence of this compound in the products from the hydrogenolysis of ethyl laurate.

a. Hydrogenolysis results. A determination of the stability of dodecanol-1 at approximately 320° was made with hydrogen pressures in the range 2000-2500 psig. being employed. Ten milliliters of dodecanol-1 was held at 315-330° for forty hours under a hydrogen pressure of approximately 2300 psig. No liner was used in the bomb. Hydrogen was absorbed in an amount corresponding to 20 per cent reaction of the alcohol to give n-undecane, methane, and water as follows:



Either dodecanol-1 is thermodynamically unstable under the conditions of temperature and hydrogen pressure employed, or the walls of the reaction vessel were catalytically active. Also, the above reaction is merely a probable one, and no identification of the products was made. In view of the long reaction time, the dodecanol-1 was judged to be sufficiently stable for the effect of added cobaltocene to be determined.

A charge of 10 ml. of dodecanol-1 and 0.408 g. of cobaltocene was placed in the reaction vessel, heated rapidly to 170°, and held at that temperature for one hour. During this period the cobaltocene was reduced to cobalt under a hydrogen pressure of 2000 psig. The bomb was then heated with shaking over a two-hour period to 325°. A temperature of 324-326° was maintained for an additional ten hours. The hydrogen absorption revealed 60 per cent reaction of dodecanol-1 calculated on the basis of the formation of n-undecane.

In comparison with the blank reaction, the cobalt-catalyzed reaction was five to ten times as fast. These two experiments showed conclusively that dodecanol-1 is not stable under hydrogenolysis conditions, and that it would be removed by reaction with hydrogen if formed during the hydrogenolysis of ethyl laurate.

b. Identification of products. The reaction products in the liquid phase were divided into two clear, colorless phases. The ratio of volumes of the light or upper phase to the lower phase was 9:1. The upper phase was drawn off and added to the pot of a 1-ft. Vigreux column which was wrapped with Pyrex glass wool. The column had a diameter of 10 mm. Fractional distillation was conducted at a pressure of 742 mm., and five fractions were obtained. Table VII contains a tabulation of the boiling points and refractive indices of the collected fractions and of possible products.

The principal component of the reaction mixture was determined to be n-undecane whose boiling point and refractive index compare favorably with those obtained for fractions 2, 3, and 4. The presence of n-dodecane

TABLE VII

THE BOILING POINTS AND REFRACTIVE INDICES OF CONSTANT BOILING FRACTIONS
FROM THE FRACTIONAL DISTILLATION OF REACTION PRODUCTS FROM THE
HYDROGENOLYSIS OF DODECANOL-1 ON COBALT IN COMPARISON WITH
CONSTANTS FOR POSSIBLE REACTION PRODUCTS

Fraction Number or Compound	Volume Collected ml.	Boiling Point, deg. C./mm. Hg	Refractive Index	
			n_D^{20}	n_D^{25}
1	1.0	up to 191°/742	1.4133	1.4110
2	1.5	191-194°/742	1.4170	1.4150
3	2.0	194-196°/742	1.4177	1.4158
4	2.3	196-202°/742	1.4183	1.4160
5	1.3	202-210°/742	1.4192	1.4172
<u>n</u> -decane ⁴⁹		174°/760	1.4120	
<u>n</u> -undecane ⁴⁹		195.8°/760	1.4190	
<u>n</u> -dodecane ⁴⁹		216.3°/760	1.4217	
dodecanol-1 ⁴⁴		258.1°/740		1.4400

in fraction 5 is not ruled out. The low boiling point of n-decane eliminates this compound from consideration as a possible product except in trace amounts.

An analysis of the lower phase of the reaction products was not made as it apparently was unreacted dodecanol-1, water and components from the upper phase.

6. Hydrogenation of Acetone

A charge of 10 ml. of acetone and 0.05 g. of cobaltocene was added to the bomb, and the total pressure was determined as a function of the temperature from 25° to 180° (See Figure 10). An initial hydrogen pressure of 500 psi. was employed. No hydrogen absorption occurred during the measurements, and the cobaltocene was not decomposed by this treatment which held the solution between 170° and 180° for approximately thirteen minutes.

Because of the possibility of an induction period being required before the start of the hydrogenation reaction, an experiment was performed in which an acetone solution of cobaltocene was shaken at 170° under a total pressure of 810 psi. (before the start of the hydrogen absorption process). An induction period of approximately one hour followed by slow hydrogen absorption was observed (See Figure 11). The rate of hydrogen absorption was roughly linear with the shaking time, and a value of 0.566×10^{-4} moles H_2 min.⁻¹ was calculated for the rate of the reaction.

The solution after the reaction was yellow and did not have the characteristic odor of isopropanol. A rather distinctive fruit-like

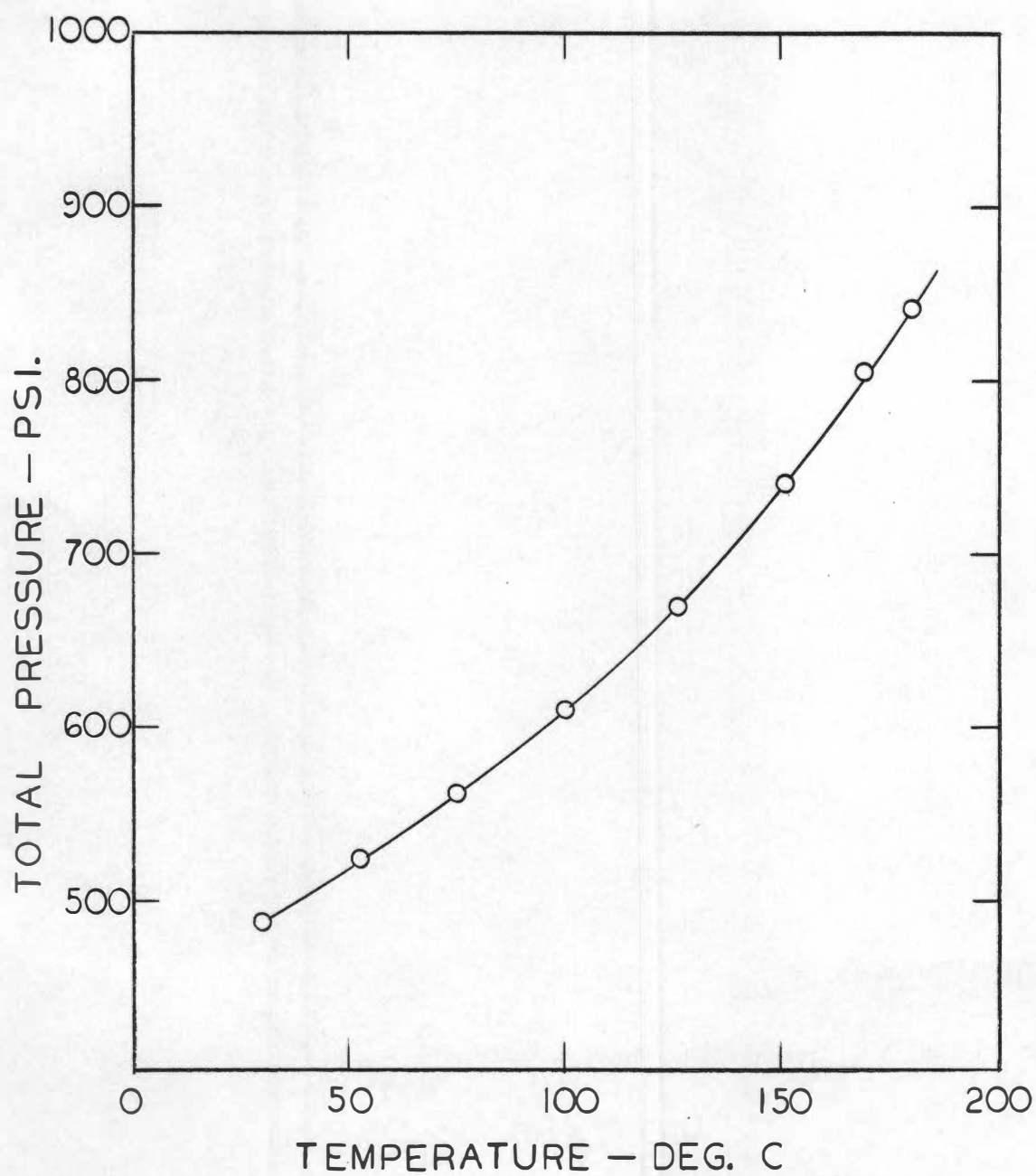


Figure 10. The total pressure as a function of the bomb temperature for a charge of hydrogen, acetone, and cobaltocene.

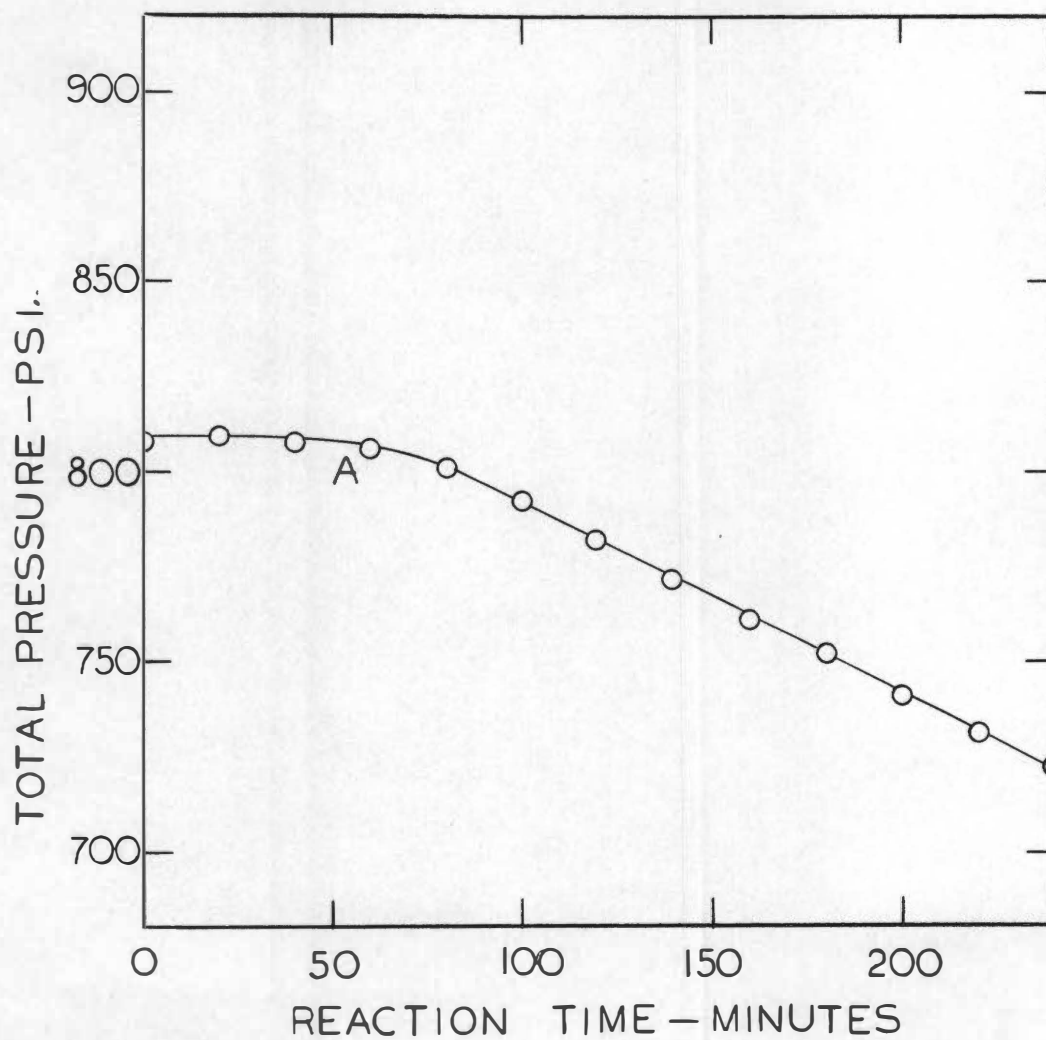


Figure 11. The total pressure as a function of the reaction time for the hydrogenation of acetone on cobalt at 170° . Cobalt added as cobaltocene. Point A: end of induction period.

odor, which was suggestive of esters, was apparent above that of the unreacted acetone. An identification of the reaction products was not made as some pyrolysis of the acetone had occurred as evidenced by tarry products. While some isopropanol was probably formed, the presence of other compounds was indicated by the odor of the products.

The cobaltocene did not undergo destructive hydrogenation to metallic cobalt and cyclopentane to the extent observed in benzene solution. Only a few particles of metallic cobalt could be withdrawn with a magnet from the solid material which formed during the reaction. Approximately 90-95 per cent of the cobalt remained in the form of a highly-dispersed blue solid which settled very slowly in the acetone solution.

Suitable explanations for the observed phenomena have not been obtained. Apparently some chemical action between cobaltocene and acetone occurred; otherwise the complete destructive hydrogenation reaction of the cobaltocene should have taken place. The blue solid material, whose formation undoubtedly prevented or at least hindered the formation of cobalt, could be a reaction product of acetone and cobaltocene or of a pyrolysis product of acetone involving cobalt or cobaltocene. The slow absorption of hydrogen can be accounted for on the basis of the reaction of hydrogen and acetone on the surface of the small particles of metallic cobalt to form isopropanol.

7. Hydrogenation of Nitrobenzene and Nitroethane

No success was achieved in reducing nitroethane and nitrobenzene using cobaltocene as a source of catalytic cobalt. No hydrogen absorption

was observed at temperatures below 170° , the minimum temperature at which the destructive hydrogenation of cobaltocene was found to occur. Thus, the possibility of the homogeneous activation of molecular hydrogen by dissolved cobaltocene molecules is ruled out. Evidently, metallic cobalt must be present for hydrogen absorption to take place.

While very slow absorption of hydrogen was observed above 170° , the pyrolysis of both nitro compounds was also very rapid at the elevated temperatures and high hydrogen pressures. Only decomposed tar-like products were obtained. While the possibility exists that nitro compounds could be reduced by hydrogen on metallic cobalt which had been previously prepared from cobaltocene, no experimental work was done on this approach because it was beyond the scope of the present problem.

8. Reaction with Cyclohexene

A study of the behavior of cobaltocene and cyclohexene under hydrogen could not be conducted because a fast, complete reaction involving cobaltocene and cyclohexene was found to occur at room temperature in cyclohexane solution. The cobaltocene was removed from solution in the form of a dark brown precipitate of unknown composition. The results obtained in the study on the hydrogenation of benzene definitely show that cyclohexene would be hydrogenated to cyclohexane on cobalt produced from cobaltocene as cyclohexene is usually a short-lived intermediate in the hydrogenation of benzene.

C. Bis-(cyclopentadienyl)nickel(II)

1. Reaction with Hydrogen

a. Solid state studies. Solid nickelocene was heated to its melting point (170-173°) under hydrogen at a maximum pressure of 1290 psi. A nickel mirror was deposited over a small portion of the glass liner near the sample. Most of the nickelocene decomposed to form a brown, resinous mass. No hydrogen absorption was observed. The mirror deposit suggests that the thermal decomposition of nickelocene molecules took place on the glass liner walls with the deposit of nickel atoms and the release of cyclopentadienyl radicals from the molecule.

b. Solution studies. A study was made of the reaction of hydrogen with nickelocene in cyclohexane solution. Nickelocene was found to react with hydrogen at pressures of the order of 800-1000 psi. At 80°, two hours was required for the complete reaction of 0.15 g. of nickelocene with hydrogen. The reaction was followed by the uptake of hydrogen determined by the lowering of the bomb pressure. At 50°, the reaction was too slow to be easily measured.

A rapid reduction of nickelocene in cyclohexane was observed in the temperature range 110-125° as the reaction vessel was being heated at the rate of 2 deg. min.⁻¹ (See Figure 12). At this temperature range, the reaction was too fast to be measured.

In all of the experiments, metallic nickel was deposited in the glass liners. Usually, a fairly uniform nickel mirror covered the portion of the walls of the glass liner only in the regions which made contact with the cyclohexane solution before the start of shaking. This

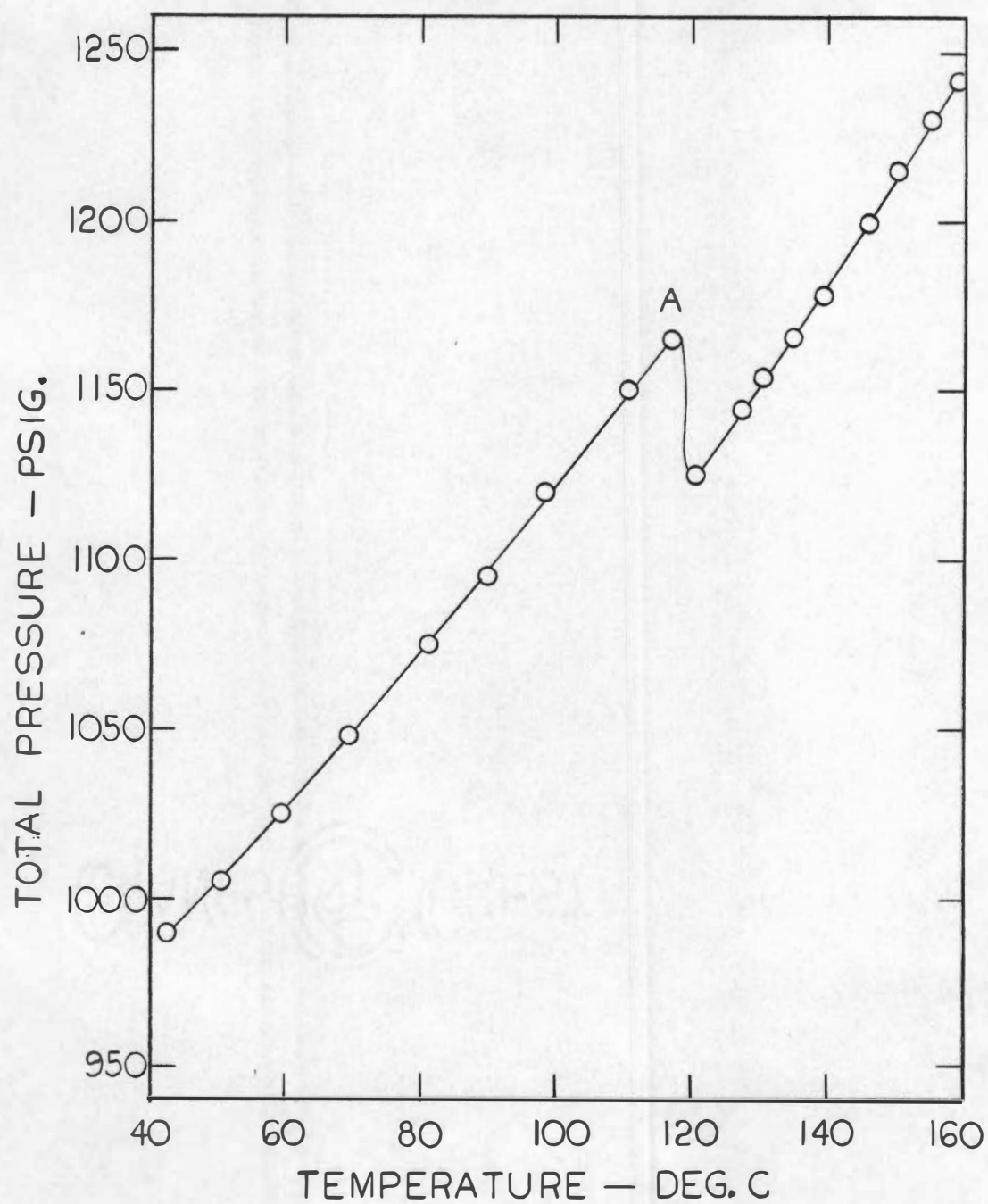


Figure 12. The total pressure as a function of the bomb temperature for a charge of hydrogen, cyclohexane, and nickelocene. Heater voltage 60 v. Point A: Start of hydrogen reduction of nickelocene.

behavior suggests that the deposition of the nickel mirror proceeded by thermal decomposition of nickelocene on the glass walls without action by hydrogen which, in the absence of shaking, would have had to diffuse through the solution to the liner walls. The presence of finely-divided nickel was observed in every experiment regardless of whether or not the mirror was formed.

Several experiments were performed to determine if the cyclopentadienyl radical was hydrogenated to cyclopentane in the destructive hydrogenation of nickelocene. The moles of hydrogen which were absorbed per mole of nickelocene were calculated from the hydrogen pressure decrease in a series of reductions of nickelocene in the bomb. The initial and final hydrogen pressures were measured at room temperature before and after the reaction. The maximum accuracy is obtained by this procedure. A tabulation of the reaction conditions and the results is given in Table VIII.

The destructive hydrogenation of nickelocene was found to require 4.94 ± 0.60 moles of hydrogen to reduce one mole of nickelocene. Apparently five moles of hydrogen are consumed per mole of nickelocene. This finding is compatible with the formation of cyclopentane as follows:



Table VIII shows that approximately the same results were obtained when the reaction was carried out in a glass liner as when no liner was used. The effects of added copper(II) oxide and iron wire were determined. Less hydrogen was absorbed when the copper (II) oxide was present,

TABLE VIII

THE REACTION OF HYDROGEN WITH BIS-(CYCLOPENTADIENYL)NICKEL(II)
IN CYCLOHEXANE SOLUTION

Determination Number	Reaction Temperature, deg. C.	Reaction Hydrogen Pressure, psi.	Moles of Hydrogen Absorbed per Mole of Nickelocene ^a
1	115-120 ^e	1100	4.48
2	78	1100	5.80
3 ^b	80	880-858	3.63
4 ^d	70-80	885-890	5.16
5 ^c	80	882-857	5.08
6 ^d	115-118 ^e	890-847	5.48

^aApproximately 0.1-0.3 g. of nickelocene was dissolved in 10 ml. of cyclohexane and added to the bomb.

^bA trace of copper(II) oxide (5 mg.) was added.

^cThree meters of iron wire was added.

^dGlass liners were used in all of the measurements except 4 and 6.

^eThe bomb was heated at a rate of 2 deg. min.⁻¹. All of the other reactions (2, 3, 4, and 5) were carried out at constant temperature by shaking for at least five hours.

whereas the iron wire did not influence the course of the reaction.

These foreign materials were added in an attempt to reduce or prevent the formation of the nickel mirror in preference to the finely-divided nickel. Nickel mirrors were formed in the presence of these additives.

No attempts were made to carry out the reduction of nickelocene in the presence of an active hydrogenation catalyst such as platinum or rhodium.

2. Hydrogenation of Benzene

The reaction of hydrogen with nickelocene proceeded in benzene solution under conditions identical with those required for the reaction in cyclohexane. No hydrogenation of benzene was observed in the presence of dissolved nickelocene. After the nickelocene was converted to metallic nickel and cyclopentane through reaction with hydrogen, the hydrogenation of benzene to cyclohexane proceeded at a measurable rate at temperatures above 80° with the reaction being catalyzed by the metallic nickel (See Figure 13). A series of constant temperature and variable temperature measurements was made in order to determine the kinetics of the hydrogenation of benzene upon metallic nickel produced by the destructive hydrogenation of nickelocene in situ.

a. Constant temperature measurements. A reaction was carried out at 56° with 0.32 g. of nickelocene dissolved in 10 ml. of benzene. After a forty-five minute induction period, slow hydrogen uptake was observed over an eight-day period during which time approximately 2 ml. of benzene was hydrogenated to cyclohexane. The hydrogen pressure dropped from 1075 psi. to 330 psi. as a result of the absorption of hydrogen by the

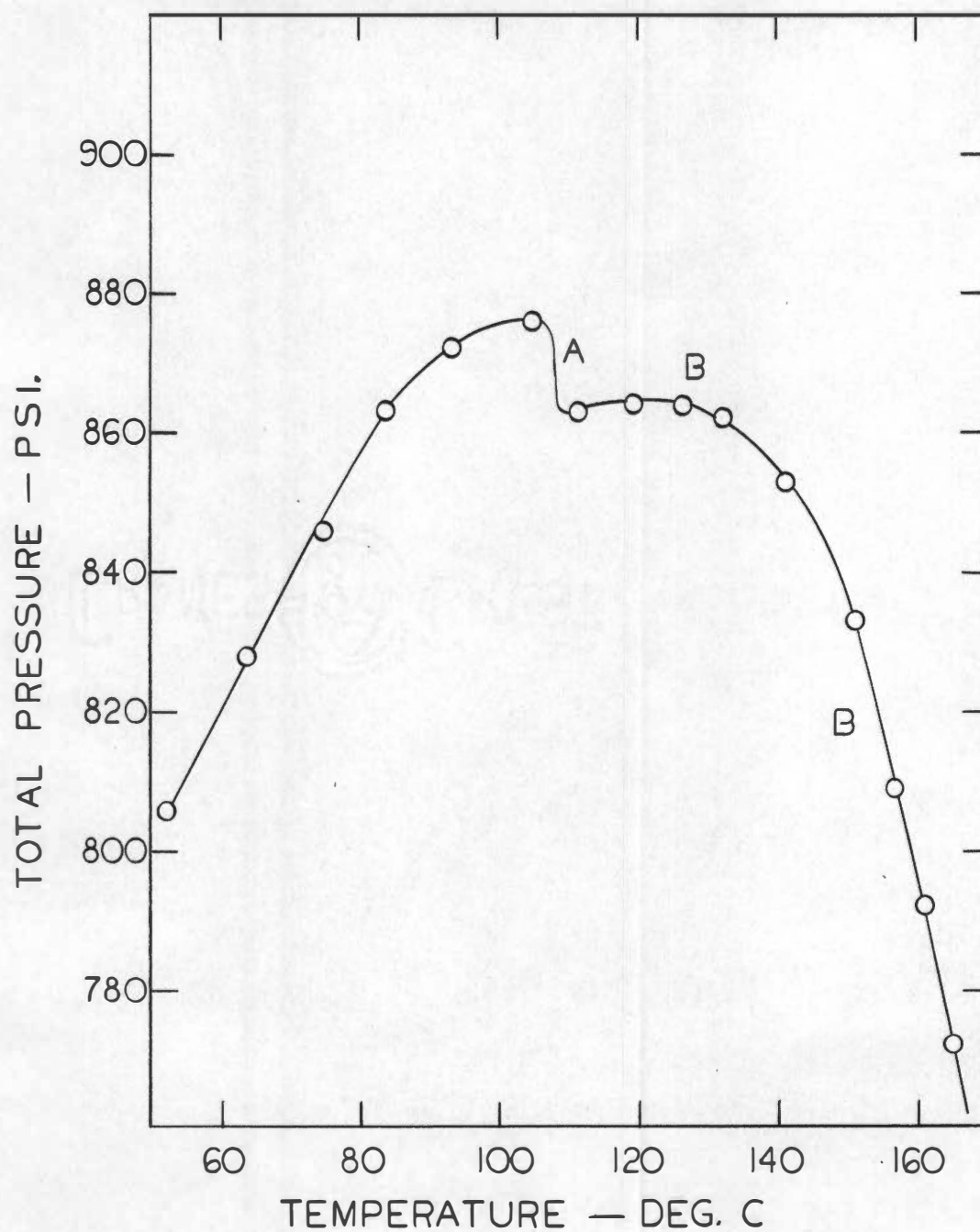


Figure 13. The total pressure as a function of the bomb temperature for the hydrogenation of benzene on nickel. Nickel added as nickelocene. Heater voltage 80 v. Point A: reduction of nickelocene. Point B: hydrogenation of benzene.

reaction. A good kinetic expression could not be derived from the data obtained in this experiment. The experiment did show that the finely-divided metallic nickel was catalytically active at 56° .

The hydrogenation of benzene at 152.5° on the nickel produced from 0.32 g. of nickelocene dissolved in 10 ml. of benzene was studied in order to obtain the kinetic expression for the reaction. The destructive hydrogenation of nickelocene took place immediately at the onset of shaking. Thereafter, the benzene was hydrogenated to cyclohexane on the surface of the nickel which was produced in the initial reaction. A plot of the logarithm of the hydrogen pressure, P_H , as a function of the time, t , yielded a linear curve (See Figure 14).

The reaction was indicated by the linear plot in Figure 14 to be first order in hydrogen pressure and zero order in benzene and cyclohexane concentrations up to 30 per cent reaction. The fundamental kinetic expression was postulated to be

$$-\frac{dn}{dt} = k w P_H$$

where n is the moles of hydrogen present; P_H is the hydrogen pressure which is obtained from the total pressure, P , by subtracting the benzene vapor pressure, p ; w is the weight of metallic nickel present as calculated from the weight of nickelocene that was added; t is the reaction time; and k is the reaction rate constant. Previous discussions (pp. 65-67) have shown that k can be related to the change in hydrogen pressure with time as follows:

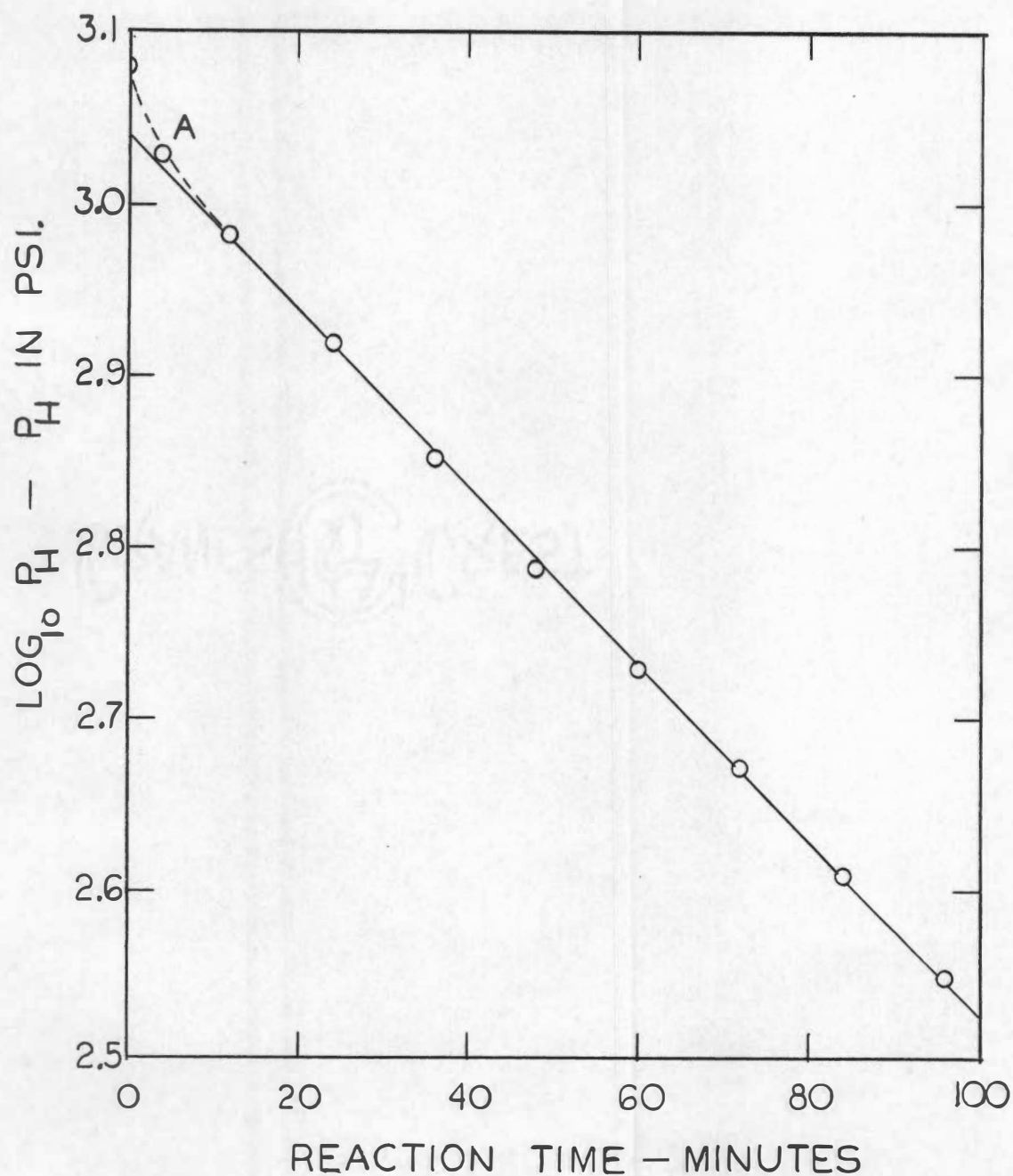


Figure 14. The logarithm of the hydrogen pressure as a function of the reaction time for the hydrogenation of benzene at 152.5° on nickel. Nickel added as nickelocene. Point A: reduction of nickelocene.

$$k = - \frac{1}{R w} \left[\frac{v_g}{T_g} + \frac{v_b}{T_b} \right] \frac{d \ln P_H}{dt}$$

The value of k at 152.5° , which was determined from the slope of the plot of $\log P_H$ as a function of the time. (See Figure 14), with the aid of the above equation, was 11.17×10^{-6} moles H_2 /(min., psi. H_2 , g. Ni).

The measurement of the reaction rate constant, k , at several temperatures was not carried out because variations in the catalytic activity per unit weight of nickel would prevent the use of the values of k thus obtained in the calculation of apparent activation energies. Variables such as reaction temperature and hydrogen pressure at the time of the reduction of the nickelocene play a significant role in determining the specific activity of the nickel which is produced.

b. Apparent activation energy determination. The reaction rate constants were determined for the hydrogenation of benzene on the nickel produced from nickelocene by hydrogen reduction in the benzene solution. Measurements were made at five-degree intervals over the temperature range $125-165^\circ$ using the Variable Temperature Method with approximately the same mathematical and experimental approach as outlined in the discussion on cobaltocene (See pp. 69-70).⁴²

The following experimental procedure was used in obtaining the heating correction terms from a blank determination and also the term $(dP/dt)_{net}$ in the actual rate constant determinations.

1. Ten milliliters of benzene was added to the bomb without a glass liner. The bomb pressure was measured with the 0-1000 psi. Ashcroft Duragauge.

2. The bomb was heated from room temperature on a heater voltage of 55 v.

3. Time-temperature-pressure readings were taken as the bomb was heated through the temperature range 110-170°.

4. The derivatives dP/dt were obtained with a straightedge from plots of the total pressure as a function of the time at the desired temperature. A tabulation of the heating correction terms, $\left[\frac{1}{P} \frac{dP}{dt}\right]_{\text{blank}}$, is given in Table IX. The average values were used in all of the rate constant determinations in this series with benzene and nickel.

Three reactions were carried out with the reaction rate constants being calculated by means of the Variable Temperature Method. The rate constants are tabulated in Table X. In conducting reactions 1 and 2, the nickel was added to the bomb as nickelocene; whereas in reaction 3, nickel which had been prepared as hydrogen reduction of nickelocene in cyclohexane was added under methanol. Fair agreement was obtained in the case of rate constants in experiments 1 and 2. A 10-20 per cent deviation from the average was observed. The rate constants calculated in experiment 3 were about one-half as large as those in experiments 1 and 2. This decrease in activity may be attributed to possible exposure of the metallic nickel to oxygen dissolved in the methanol which was used as a cover for the nickel during storage.

The apparent activation energy, E_a , was determined from the slope of a plot of $\log k \times 10^6$ as a function of the reciprocal of the absolute temperature (See Figure 15) with the differentiated form of the Arrhenius

TABLE IX

HEATING CORRECTION TERMS FOR THE VARIABLE TEMPERATURE DETERMINATION
OF THE RATE CONSTANTS FOR THE HYDROGENATION OF BENZENE
IN THE TEMPERATURE RANGE 120-165°

Bomb Temperature, Degrees Centigrade	$\left[\frac{1}{P} \frac{dP}{dt} \right]_{\text{blank}} \times 10^3, \text{ min.}^{-1}$		
	Determination Number		Average
	1	2	
120	2.810	2.933	2.872
125	2.665	2.838	2.752
130	2.525	2.683	2.605
135	2.348	2.495	2.422
140	2.210	2.274	2.242
145	2.002	2.068	2.035
150	1.578	1.718	1.648
155	1.147	1.513	1.330
160	0.923	1.385	1.147
165	0.737	1.275	1.007

TABLE X

REACTION RATE CONSTANTS FOR THE HYDROGENATION OF BENZENE IN THE
TEMPERATURE RANGE 125-165° ON NICKEL FROM
BIS-(CYCLOPENTADIENYL)NICKEL(II)

Reaction Temperature, Degrees Centigrade	Reaction Rate Constant, $k \times 10^6$, moles H_2 /(min., psi. H_2 , g. Ni)		
	Determination Number		
	1	2	3 ^a
125	13.88	11.18	6.86
130	15.40	12.63	8.22
135	17.57	14.94	8.67
140	20.06	15.11	10.22
145	24.66	18.71	11.42
150	27.08	20.92	12.20
155	30.03	23.79	14.65
160	33.77	27.22	17.21
165	38.30	31.19	19.15

^a Metallic nickel rather than nickelocene was added to the bomb.
The nickel was prepared by reduction of nickelocene in cyclohexane.

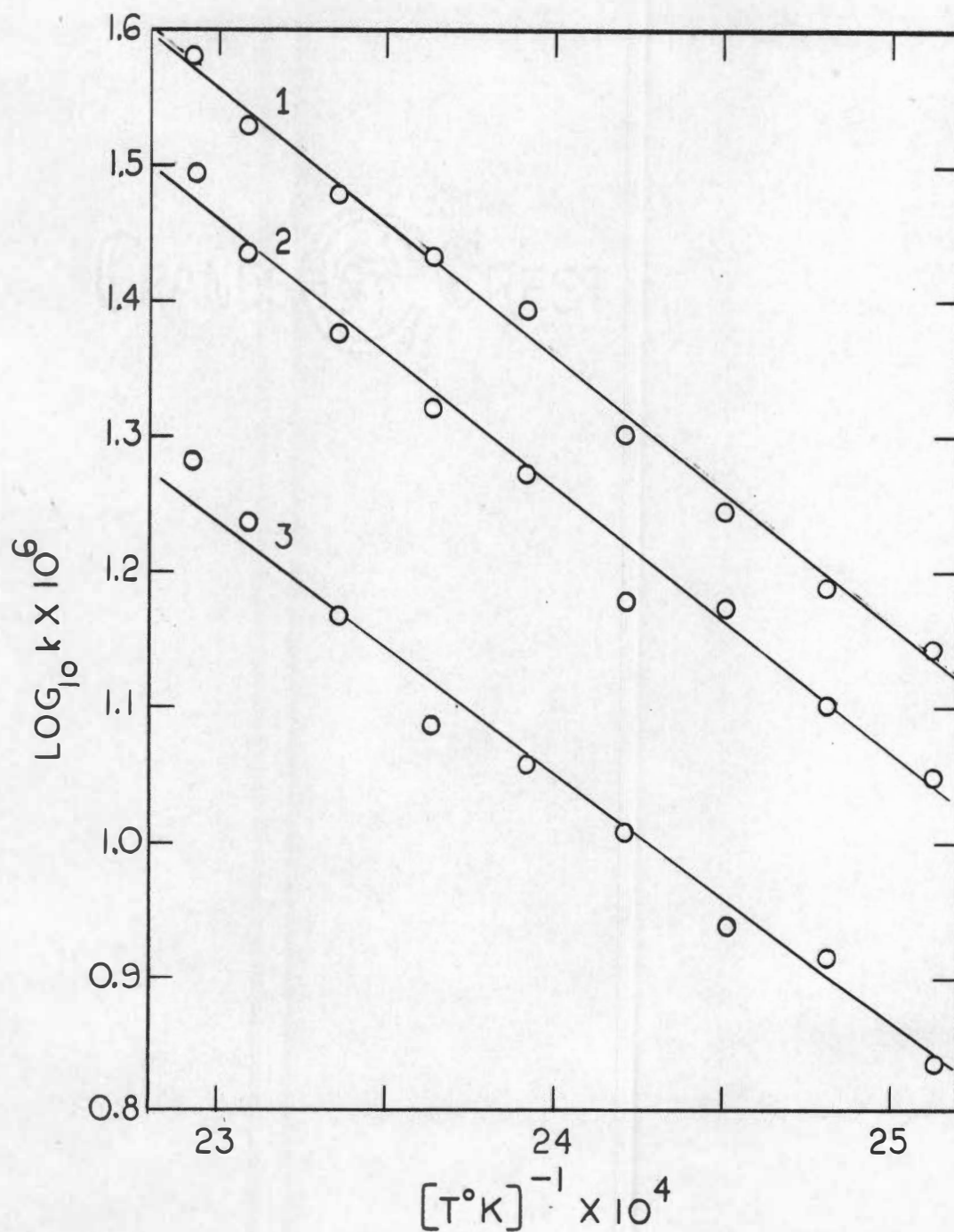


Figure 15. The logarithm of the reaction rate constant for the hydrogenation of benzene on nickel as a function of the reciprocal of the absolute temperature. Curves 1 and 2: nickel added as nickelocene. Curve 3: nickel added as metallic nickel.

equation:

$$E_a = - 2.303 R \frac{d \log k}{dT^{-1}}$$

Excellent agreement was obtained for the three values of the apparent activation energy (See Table XI). An average value of 8.78 ± 0.02 kcal. mole⁻¹ was obtained for E_a .

3. Hydrogenation of Acetone

The behavior of hydrogen and nickelocene dissolved in acetone was observed by means of heating curves in which the total bomb pressure was plotted as a function of the bomb temperature (See Figure 16). Nickelocene was destructively hydrogenated at 110-120° in acetone solution with hydrogen at a partial pressure of 560-580 psi. Metallic nickel was one product, and cyclopentane was probably formed in the reaction. Upon raising the bomb temperature to within the range 130-180°, the hydrogenation of acetone to isopropanol occurred. The nickel was removed from the bomb in the form of aggregates of small particles. The acetone-isopropanol solution was colorless.

a. Constant temperature measurements. The kinetic expression for the hydrogenation of acetone on nickel from nickelocene was determined by means of constant temperature studies at 170°. A charge of 0.143 g. of nickelocene in 10 ml. of acetone was placed in the bomb under an initial hydrogen pressure of 596 psi. The bomb was heated rapidly with shaking to 170° at which temperature the bomb pressure was measured as a function of the time.

TABLE XI

THE APPARENT ACTIVATION ENERGY FOR THE HYDROGENATION OF BENZENE
IN THE TEMPERATURE RANGE 125-165° ON METALLIC NICKEL FROM
BIS-(CYCLOPENTADIENYL)NICKEL(II)

Determination Number ^a	Apparent Activation Energy, E_a , kcal. mole ⁻¹
1	8.81
2	8.74
3	8.78

^aThe determination designation corresponds with that in Table X and Figure 15.

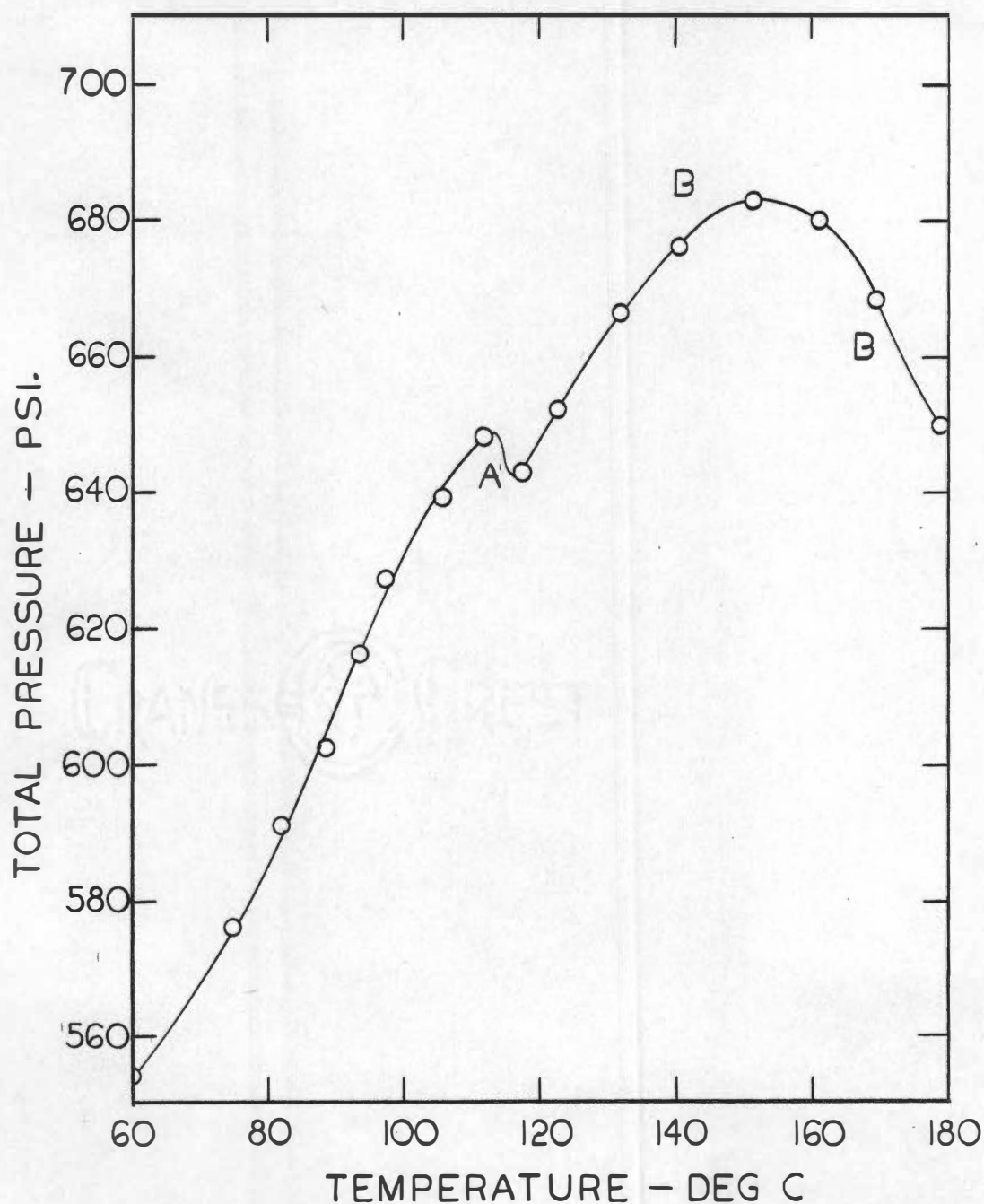


Figure 16. The total pressure as a function of the bomb temperature for the hydrogenation of acetone on nickel from nickelocene. Bomb charge: 10 ml. of acetone and 0.09 g. of nickelocene. Point A: reduction of nickelocene. Point B: hydrogenation of acetone.

Plots of the logarithms of the total pressure, P , and of the hydrogen partial pressure, P_H , as a function of the time are given in Figure 17.* The logarithm of the hydrogen partial pressure was found to be a linear function of the reaction time. The rate of reaction, dn/dt , is thereby indicated to be proportional to the hydrogen pressure, P_H . Also, the reaction rate must be independent of the concentration of acetone whose mole fraction in the liquid phase decreased from 1.0 to 0.6 during the reaction.

The following equation is proposed as the correct kinetic expression for the reaction rate:

$$-\frac{dn}{dt} = k w P_H$$

where n is the moles of hydrogen present; t is the reaction time; w is the weight of nickel present; P_H is the hydrogen partial pressure; and k is the reaction rate constant. Previous discussions (p. 52) have shown that dn/dt can be related to dP_H/dt to give the following equation for the rate constant:

$$k = -\frac{1}{R w} \left[\frac{v_g}{T_g} + \frac{v_g}{T_b} \right] \frac{d \ln P_H}{dt}$$

The above equation shows that, at constant temperature, a plot of $\log P_H$ as a function of the time should be linear. This was found to be true

*The hydrogen partial pressure was obtained by subtracting the saturation vapor pressure of acetone at 170° (240 psi.⁴⁴) from the total pressure. Figure 17 illustrates quite well the effect of correcting the total pressure for the liquid phase vapor pressure upon the kinetic measurements.

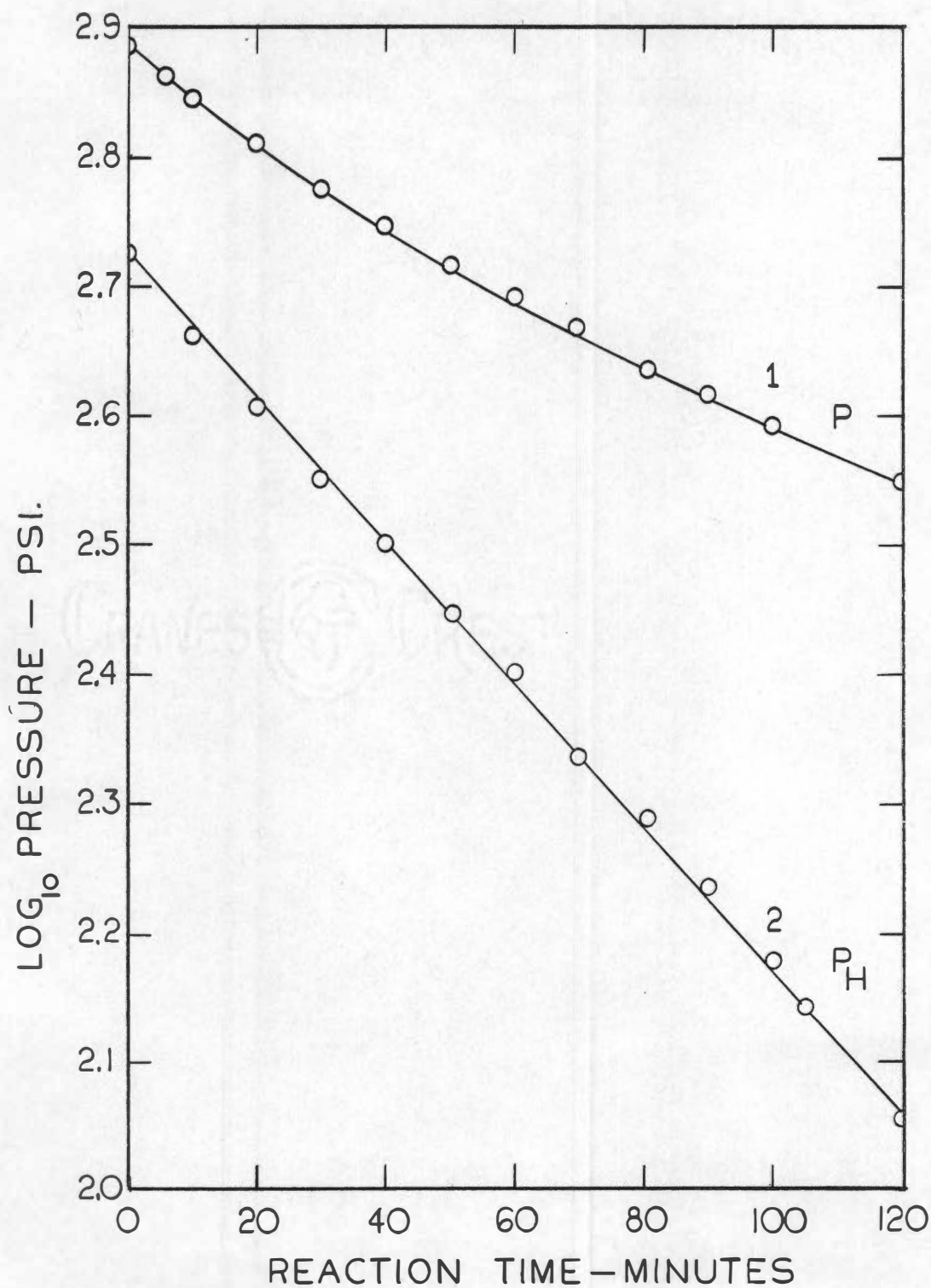


Figure 17. The logarithm of the total pressure and of the partial pressure of hydrogen as functions of the reaction time for the hydrogenation of acetone on nickel at 170° . Nickel added as nickelocene. Curve 1: total pressure, P . Curve 2: hydrogen pressure, P_H .

experimentally. A value of 3.125×10^{-3} moles H_2 /(min., psi.. H_2 , g. Ni) was calculated for k at 170°.

Again, the experimental determination of the rate constants for the hydrogenation of acetone on nickel were not determined as a function of the reaction temperature by a series of constant temperature evaluations. The data obtained from single reaction, variable temperature determinations are more accurate in evaluating the temperature coefficient of the reaction.

b. Variable temperature measurements. Information from Figure 16 indicates that the metallic nickel produced from nickelocene was active in catalyzing the hydrogenation of acetone to isopropanol at temperatures above 130° and at hydrogen pressures above 100 psi. The rate constants for the hydrogenation reaction were determined over the temperature range 140-180° at five-degree intervals by means of the Variable Temperature Method in a modified form.⁴² The rate constants were calculated at each desired temperature within the 140-180° interval by the following equation:*

$$k = - \frac{1}{R w P_H} \left[\frac{v_g}{T_g} + \frac{v_b}{T_b} \right] \left[\left(\frac{dP}{dt} \right)_{\text{net}} - \left(\frac{dP}{dt} \right)_{\text{heating}} \right]$$

The previous method of calculating $(dP/dt)_{\text{heating}}$ at a given temperature, T_b , and bomb pressure, P, was (1) to evaluate $\left[\frac{1}{P} \frac{dP}{dt} \right]_{\text{blank}}$

*See the previous discussion of the Variable Temperature Method, pp. 53-55.

from time-temperature-pressure data obtained from a blank run in which no reaction occurred, and (2) to calculate $(dP/dt)_{\text{heating}}$ from the following equation:

$$\left(\frac{dP}{dt}\right)_{\text{heating}} = P_{\text{reaction}} \left[\frac{1}{P} \frac{dP}{dt} \right]_{\text{blank}}$$

The above equation is invalid when applied to the present system as a result of the relatively large change in the total pressure per unit time caused by the large increase in the acetone vapor pressure upon being heated from 140° to 180°. The acetone vapor pressure increases from 134 psi. at 140° to 288 psi. at 180° and, therefore, plays a dominant role in determining $(dP/dt)_{\text{heating}}$.⁴⁴

An attempt was made to derive an expression to correct $(dP/dt)_{\text{heating}}$ for the change in the vapor pressure of acetone with time and total pressure from a consideration of the Clausius-Clapeyron expression for the change in vapor pressure with temperature. An approximate equation was obtained, but little success was realized in applying the equation to the experimental data. Two factors which complicate such a calculation are the relatively large gas volume in the gage and the change in the solubility of hydrogen in acetone with temperature and pressure. The evaluation of $(dP/dt)_{\text{heating}}$ was ultimately made by empirical means. A series of four measurements of total pressure and temperature as a function of the time were made with the amount of hydrogen present being varied. The bomb charge was 10 ml. of acetone, and no catalytic materials were present. No liner was used. The pressure was measured by the 0-1000 psi. Laboratory Test Gauge, and

the bomb was heated on 60 v. input.

The slopes of the pressure versus time curves, which were $(dP/dt)_{\text{heating}}$, were measured at 140, 145, ..., 175° and 180° by means of a straightedge. The observation was made that $(dP/dt)_{\text{heating}}$ was essentially a constant at a given temperature and within a total pressure interval from 600-900 psi. Also, $(dP/dt)_{\text{heating}}$ appeared to be independent of small variations in the rate of heating, dT/dt , at a given temperature. The average value of dP/dt at each temperature was used as $(dP/dt)_{\text{heating}}$ in the calculation of the rate constants. A tabulation of these constants with the average for each temperature is given in Table XII.

Two determinations of the rate constants as functions of the reaction temperature were made with the average values of $(dP/dt)_{\text{heating}}$ from Table XII being used in the calculations. The reaction rate constants are recorded in Table XIII. Determination 2 is more accurate because the errors in the heating correction terms were minimized by a larger $(dP/dt)_{\text{net}}$.

Plots of the logarithms of the rate constants as functions of the reciprocal of the absolute temperature are given in Figure 18. Both curves were linear with the best straight line being obtained with the data of determination 2. The apparent activation energy, E_a , was calculated from the slope of each line by means of the differentiated Arrhenius equation:

$$E_a = - 2.303 R \frac{d \log k}{dT^{-1}}$$

TABLE XII

HEATING CORRECTION TERMS FOR THE VARIABLE TEMPERATURE DETERMINATION
OF THE RATE CONSTANTS FOR THE HYDROGENATION OF ACETONE IN THE
TEMPERATURE RANGE 140-180°

Bomb Temperature, Degrees Centigrade	$\left[\frac{dP}{dt}\right]_{\text{heating}}$, psi. min. ^{-1a}					av.	av. dev.
	Determination Number						
	1	2	3	4			
140	4.30	3.76	3.60	3.58	3.81	±0.24	
145	4.18	3.60	3.58	3.32	3.67	±0.25	
150	4.12	3.48	3.56	3.30	3.61	±0.25	
155	4.06	3.38	3.56	3.36	3.59	±0.23	
160	3.90	3.00	3.52	3.36	3.44	±0.26	
165	3.70	3.00	3.52	3.10	3.33	±0.28	
170	3.70	3.00	2.84	2.66	3.05	±0.46	
175	3.70	3.00	2.60	2.36	2.91	±0.43	
180	3.70	3.00	2.38	2.12	2.80	±0.55	

^aTen milliliters of acetone was added to the bomb without a liner. The total pressure, P, was measured with the 0-1000 psi. Laboratory Test Gauge. The heater voltage was 60 v. The total pressure range for which the calibration was made was 580-980 psi.

TABLE XIII

REACTION RATE CONSTANTS FOR THE HYDROGENATION OF ACETONE IN THE
TEMPERATURE RANGE 140-180° ON NICKEL FROM
BIS-(CYCLOPENTADIENYL)NICKEL(II)

Reaction Temperature, Degrees Centigrade	Reaction Rate Constant, $k \times 10^3$, ^a moles H ₂ /(min., psi. H ₂ , g. Ni)	
	Determination Number	
	1	2
140	1.84	1.19
145	2.18	1.42
150	2.42	1.78
155	2.81	2.11
160	3.52	2.48
165	3.92	3.01
170	4.18	3.48
175	4.44	4.22
180	5.08	5.18

^aThe nickel was added in the form of bis-(cyclopentadienyl)-nickel(II).

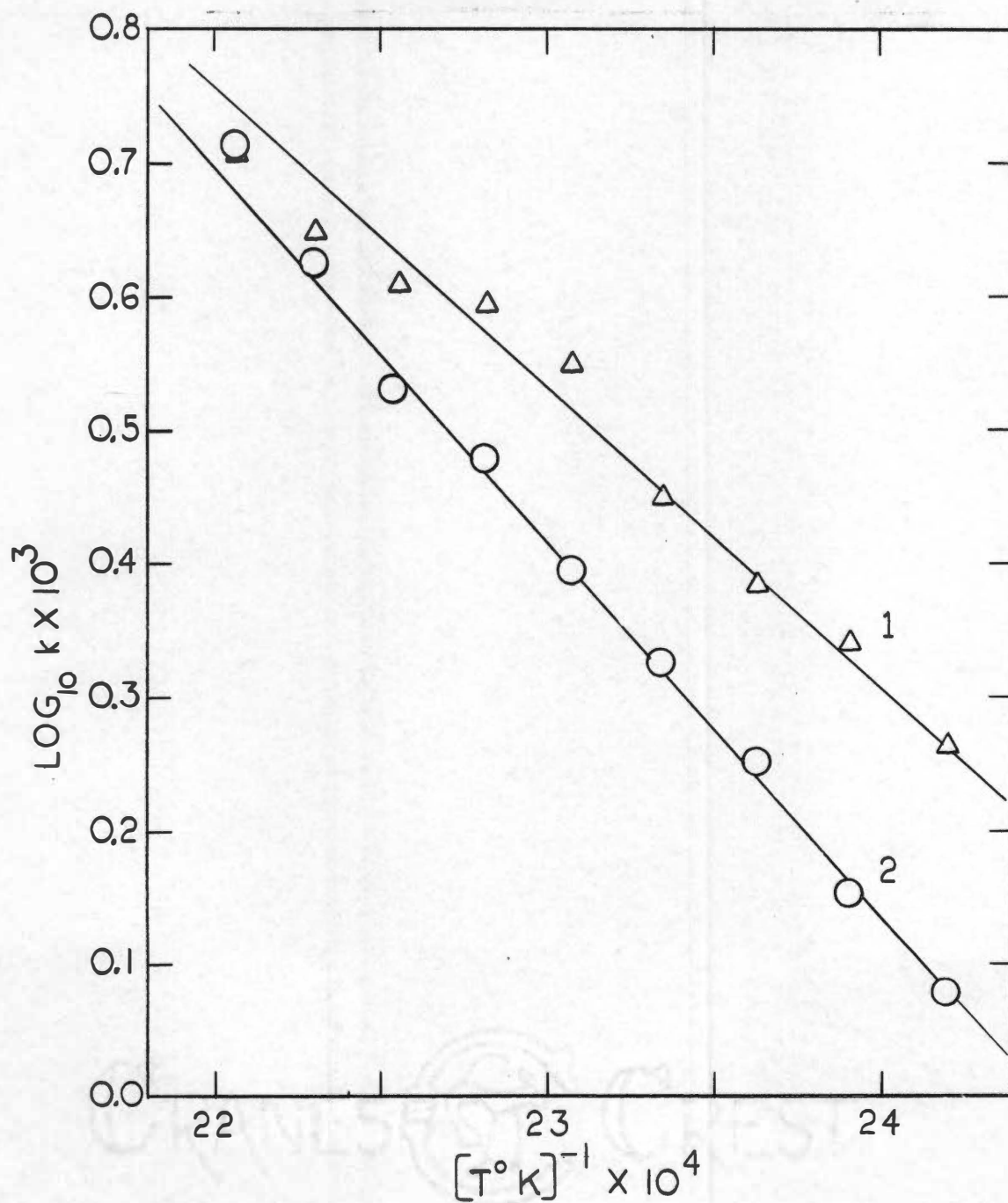


Figure 18. The logarithm of the reaction rate constant as a function of the reciprocal of the absolute temperature for the hydrogenation of acetone on nickel. Nickel added as nickelocene. The curve numbers correspond to the determination designation in Table XIV.

The values obtained for E_a are tabulated in Table XIV. Since more faith is placed in the rate constants in determination 2, the value of 12-13 kcal. mole⁻¹ is taken for the apparent activation energy for the hydrogenation of acetone to isopropanol on nickel from nickelocene in the temperature range 140-180°.

4. Hydrogenolysis of Ethyl Laurate

The behavior of nickelocene and ethyl laurate under hydrogen pressure was determined by means of temperature-pressure data (See Figure 19). The nickelocene was destructively hydrogenated at 95-105° under a hydrogen pressure of 1700-1750 psig. Metallic nickel was formed by the reaction in which approximately five moles of hydrogen was absorbed per mole of nickelocene present. Thus, the formation of two moles of cyclopentane was also indicated.

With the same charge in the bomb, the temperature was raised rapidly to 303-307°, and the pressure was recorded as a function of the shaking time (See Figure 20). The hydrogenolysis of ethyl laurate took place slowly on the surface of the deposited nickel. The reaction mixture was in two colorless layers when removed from the bomb. The heavy layer, which contained unreacted ethyl laurate, turned reddish-brown upon contact with air. The upper layer was immiscible with water and ethanol; a behavior characteristic of hydrocarbons and not alcohols which are the desired products in most hydrogenolysis reactions of esters.

A formal analysis of the products of the hydrogenolysis of ethyl laurate on the nickel catalyst was not made because of great difficulty in forming derivatives of the most possible products due to the presence

TABLE XIV

THE APPARENT ACTIVATION ENERGY FOR THE HYDROGENATION OF ACETONE
IN THE TEMPERATURE RANGE 140-180° ON NICKEL FROM
BIS-(CYCLOPENTADIENYL)NICKEL(II)

Determination Number ^a	Apparent Activation Energy, E_a , kcal. mole ⁻¹
1	9.99
2	12.95

^aThe determination designation corresponds with that in Table XIII and in Figure 17.

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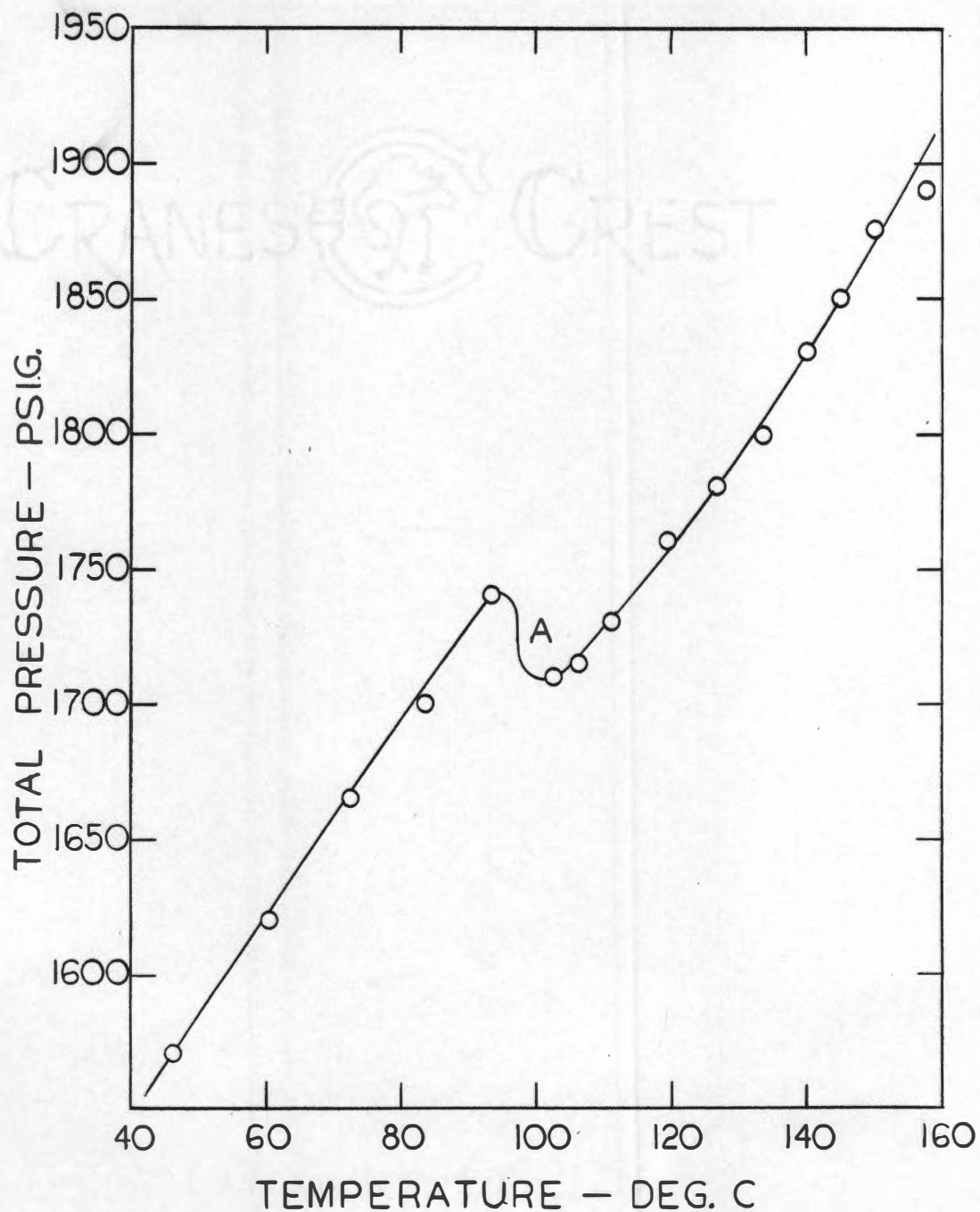


Figure 19. The total pressure as a function of the bomb temperature for a charge of hydrogen, ethyl laurate, and nickelocene. Heater voltage 70 v. Point A: reduction of nickelocene.

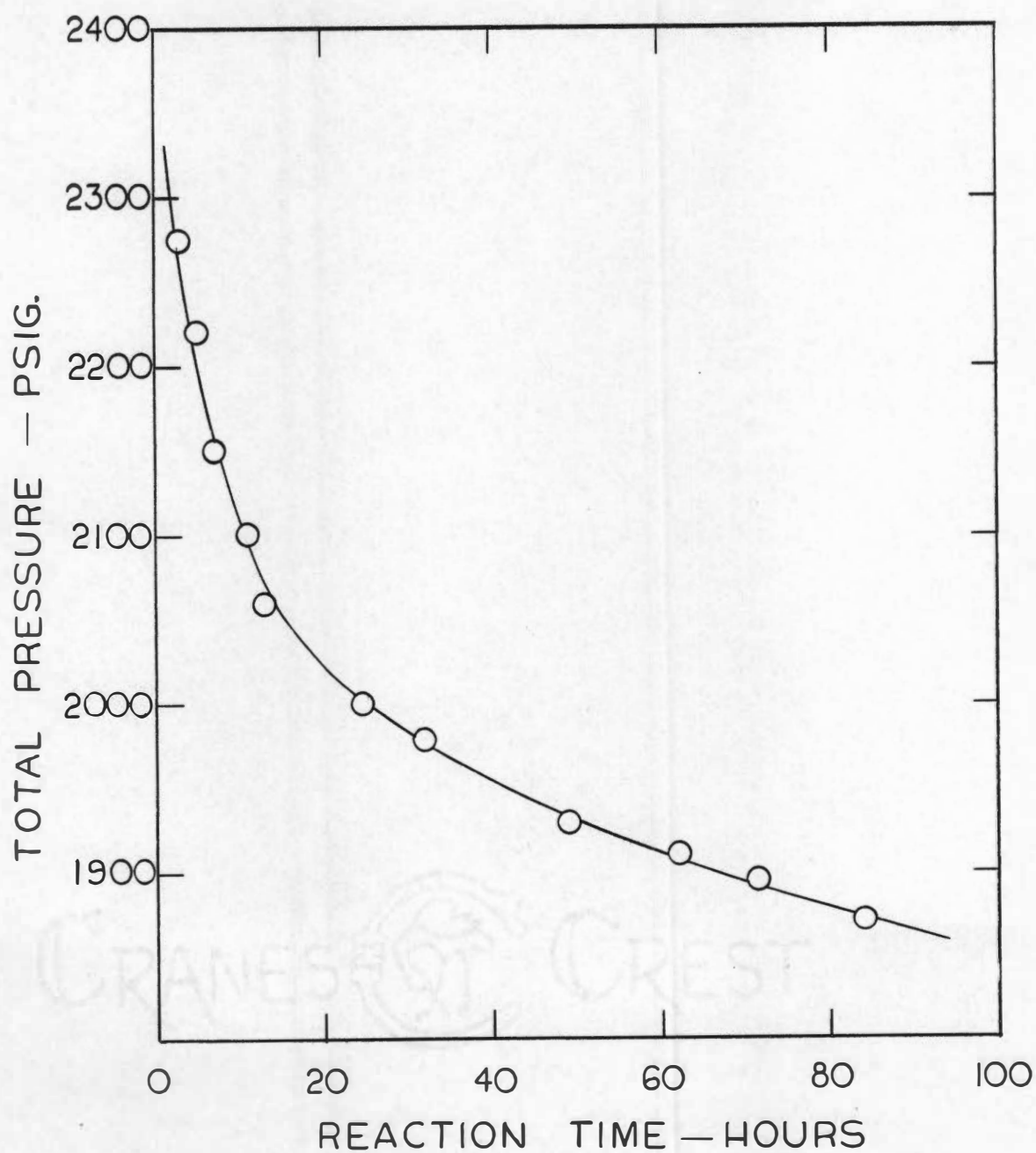


Figure 20. The total pressure as a function of the reaction time for the hydrogenolysis of ethyl laurate on nickel at 303-307°. Nickel added as nickelocene.

of interfering substances in the reaction products. Much decomposed material was present thus indicating complex products. The course followed by the nickel-catalyzed hydrogenolysis of esters usually leads to the formation of hydrocarbons rather than alcohols. The formation of a hydrocarbon in the reaction being considered in the present study is indicated by the product which was immiscible with ethyl laurate.

5. Hydrogenolysis of Dodecanol-1

A study was made to determine if dodecanol-1 is stable under the conditions which were required for the hydrogenolysis of ethyl laurate on nickel from nickelocene. This study was initiated in order to clarify the path of the ethyl laurate hydrogenolysis on nickel.

A charge of 0.153 g. of nickelocene dissolved in 10 ml. of dodecanol-1 was held at 310-315° under hydrogen pressure for twenty hours. The hydrogen pressure decreased from 2350 psig. to 2180 psig. corresponding to a 60 per cent reaction based on the formation of n-undecane as follows:



Approximately 8 ml. of colorless liquid and finely-divided nickel were obtained.

The reaction products were fractionally distilled through a 15-in. Vigreux column with 10 ml. of dodecanol-1 added as a high-boiling chaser. Five fractions having a total volume of 7.6 ml. were collected. The boiling points and refractive indices of the fractions were determined and are tabulated in Table XV. The constants for several possible

TABLE XV

THE BOILING POINTS AND REFRACTIVE INDICES OF CONSTANT BOILING FRACTIONS
FROM THE FRACTIONAL DISTILLATION OF THE REACTION PRODUCTS FROM THE
HYDROGENOLYSIS OF DODECANOL-1 ON NICKEL IN COMPARISON WITH THE
CONSTANTS FOR POSSIBLE REACTION PRODUCTS

Fraction Number or Compound	Volume Collected, ml.	Boiling Point, deg. C./mm. Hg	Refractive Index	
			n_D^{20}	n_D^{25}
1	1.4	192-193°/741	1.4171	1.4150
2	3.6	193-194°/741	1.4173	1.4151
3	1.9	194-195°/741	1.4173	1.4151
4	0.4	195-197°/741	1.4175	1.4153
5	0.3	197-205°/741	1.4181	1.4160
<u>n</u> -decane ⁴⁹		174°/760	1.4120	
<u>n</u> -undecane ⁴⁹		195.8°/760	1.4190	
<u>n</u> -dodecane ⁴⁹		216.3°/760	1.4217	
dodecanol-1 ⁴⁴		258.1°/740		1.4400

^aNo stem correction was applied to the boiling points obtained for the five constant boiling fractions.

products are also included in the table for the purpose of direct comparison.

The boiling points for fractions 1, 2, 3, and 4 agree quite well with the boiling point of n-undecane. Also, the refractive indices of the first four fractions agree fairly well with the refractive index of n-undecane. The data definitely rule out the lower and upper homologues, n-decane and n-dodecane, respectively, as possible products.

These experimental results show that n-undecane is formed in good yield by the hydrogenolysis of dodecanol-1 on nickel added in the form of nickelocene. Evidence is thus obtained that indicates that, should dodecanol-1 be produced in the hydrogenolysis of ethyl laurate on nickel, it would be unstable relative to n-undecane.

6. Hydrogenation of Nitrobenzene and Nitroethane

The hydrogenation of nitrobenzene and nitroethane on nickel added in the form of nickelocene was attempted at 130° using hydrogen pressures in the range 900-1000 psi. Tarry products and some ammonia were formed. Since the hydrogen uptake in the case of both nitro compounds corresponded to the hydrogenation of less than one-tenth of the available nitro groups, reactions other than the hydrogenation reaction must have been operative.

Nickelocene was found to be more stable in nitrobenzene and in nitroethane than in cyclohexane with regard to the destructive hydrogenation reaction. Nickelocene was found in both solvents after shaking for one hour at 130° under 1000 psi. hydrogen pressure. The presence of metallic nickel in the products was not definitely detected.

No hydrogen absorption was detected at temperatures below 100° , the region in which the nickelocene is relatively resistant to reduction by hydrogen. The hydrogenation of the nitro compounds must have taken place by a heterogeneous mechanism upon the surface of deposited nickel which was soon covered by tar-like products.

7. Reaction with Cyclohexene

Nickelocene and cyclohexene react at room temperature in cyclohexane to form a light green solid of unknown composition. The reaction is relatively fast and goes to completion if an excess of cyclohexene is present. The compound formation prevented the investigation of the behavior of nickelocene and cyclohexene under hydrogen pressure. The studies on the benzene-nickelocene system show that cyclohexene can be hydrogenated on nickel from nickelocene as cyclohexene is a short-lived intermediate in the process.

CHAPTER IV

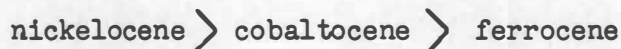
DISCUSSION OF RESULTS

A. Hydrogen Reduction of Bis-cyclopentadienyl

Metal Compounds

1. Comparison of Ferrocene, Cobaltocene, and Nickelocene

Under a hydrogen pressure of approximately 1000 psi., nickelocene undergoes hydrogen reduction to form metallic nickel and cyclopentane at temperatures as low as 56°. Under the same hydrogen pressure, cobaltocene reacts with hydrogen at temperatures above 160° to give metallic cobalt and cyclopentane as products. The reduction of ferrocene was not accomplished at 180° with a hydrogen pressure of 2000 psi. The reaction was attempted at 243° in the presence of platinum with no success. From these data the order of reactivity toward hydrogen is established as



Both nickelocene and cobaltocene gave finely-divided metals and also deposits of metallic mirrors when reduced by hydrogen in cyclohexane. Little reduction was achieved in the solid state although traces of mirror formation were observed. The reductions of nickelocene at 60° and of cobaltocene at 170° were characterized by induction periods before the start of hydrogen absorption. The induction periods were eliminated by carrying out the reductions at elevated temperatures (130° for nickelocene, 200° for cobaltocene).

2. Mechanism of Reduction Reaction

Nickelocene and cobaltocene are reduced by hydrogen in cyclohexane solution in the absence of a catalyst, but ferrocene resisted all attempts at hydrogen reduction on the most active hydrogenation catalysts (platinum and rhodium) for aromatic systems until just recently. The catalytic hydrogenation of ferrocene was accomplished at 265-345° over Raney nickel catalyst under a hydrogen pressure of 200-280 atm.⁵¹ The behavior by ferrocene implies that it possesses a higher degree of aromaticity than does benzene.

In comparing the conditions required for the hydrogenation of the neutral bis-cyclopentadienyl compounds of iron, cobalt, and nickel, the observation is made that the ease of hydrogen reduction is related inversely to the energy of the ring-to-metal bond. By means of molecular orbital theory, Dunitz and Orgel calculated the energy of the ring-metal-ring bond to be 286 kcal. mole⁻¹ in ferrocene and 194 kcal. mole⁻¹ in nickelocene.²⁵ The bond energy in cobaltocene was estimated to be intermediate between the energies in nickelocene and in ferrocene. The success of hydrogen reduction may depend largely upon these bond strengths. The failure of ferrocene to be reduced by hydrogen on platinum and on rhodium-on-alumina catalysts at temperatures below 200° indicates that this bond must be responsible for preventing the hydrogenation reaction.

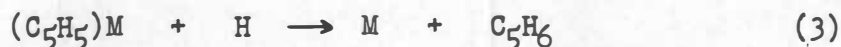
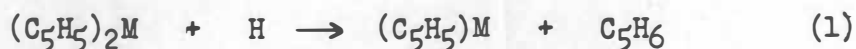
The hydrogen reduction of nickelocene and cobaltocene in the absence of catalytic materials has certain characteristics which may be considered in arriving at a mechanism for the reaction. First, the reaction goes through an induction period which can be shortened by

elevating the temperature. Hydrogen absorption either takes place very slowly or does not occur during this period.

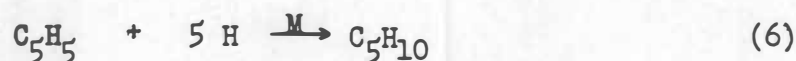
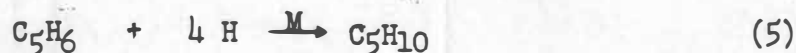
The second and final stage of the reaction features the rapidly-accelerating absorption of hydrogen to the extent of five moles per mole of bis-cyclopentadienyl compound. The metal is found deposited in two rather distinct forms: finely divided metal and metallic mirror. The ratio of fraction of metal in the mirror form to that in the finely divided particle form is diminished by carrying out the reduction at elevated temperatures.

The conclusion is reached that (1) during the induction stage, liberation of free metal occurs in micro amounts, perhaps with the formation of a mirror, and (2) during the second stage, an autocatalytic reduction of the bis-cyclopentadienyl compound takes place on the surface of the metal liberated prior to and during this second phase. The reactions given below are thought to take place.

induction stage (very slow):



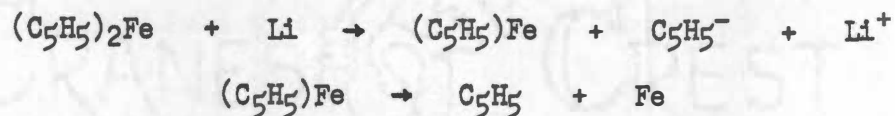
autocatalytic stage (accelerating fast reaction):



Observations during the present study indicate that hydrogen is required during the induction stage. For instance, nickelocene does not form a mirror at temperatures up to its melting point in the absence of hydrogen. It is also stable in the vapor phase at low pressures (less than one atmosphere) and up to 170° . Since the mirror is formed on the wall of the vessel at temperatures as low as 56° under hydrogen, obviously hydrogen must play a role in the mirror formation. Also, the wall of the glass liner may be involved in that the mirror deposition occurs on it.

The concentration of hydrogen atoms would be very small at the temperatures required to initiate the reduction of nickelocene and cobaltocene. For instance at 500° K, the fraction of hydrogen dissociated at 1000 psi. hydrogen pressure is 4.26×10^{-22} .⁵² Regardless, this induction stage is thought to be necessary for the formation of clusters of metal atoms which serve as catalyst sites for the autocatalytic reduction which follows.

Support is given the proposal of the induction period as outlined above in recent findings by Trifan and Nicholas who achieved the first reductive cleavage of ferrocene into free iron and cyclopentadiene with lithium in ethylamine solution at room temperature.⁵³ They concluded that the cleavage reaction proceeds by the attack of a lithium atom on carbon with the transfer of an electron to the ferrocene molecule. The π electrons in the cyclopentadienyl ring which is attacked are displaced directly to the resonance hybrid orbitals of the cyclopentadienide carbanion with the resulting detachment of that ion from the iron atom.



Mass spectrometer studies have shown that the $(\text{C}_5\text{H}_5)\text{Fe}$ fragment has appreciable stability.⁵⁴

In the system under consideration in the present study, the formation of cyclopentadiene is expected to occur in preference to the formation of the carbanion, C_5H_5^- , and hydrogen ion because the hydrocarbon would be only slightly ionized in the aprotic solvents used. Also, the $(\text{C}_5\text{H}_5)\text{M}$ fragments in the case of cobaltocene and nickelocene are expected to be very unstable relative to the $(\text{C}_5\text{H}_5)\text{Fe}$ radical so that reaction 2 should follow reaction 1 almost instantly. Reaction 3 should be relatively unimportant.

The autocatalytic stage is postulated to account for the sudden accelerated reduction of the bis-cyclopentadienyl compounds following the induction stage. This phase should commence as soon as the metal deposits have sufficient metal atoms present to function catalytically.

The autocatalytic reaction (reaction 4) can be justified in several ways. The metallic nickel and metallic cobalt produced in the reduction are active as hydrogenation catalysts for aromatic compounds such as benzene under the same conditions required for the reduction of the bis-cyclopentadienyl compounds of cobalt and nickel. In view of the reduction of ferrocene on Raney nickel under more severe conditions⁵¹ and of the greater instability of nickelocene and cobaltocene, the assumption that these compounds are reduced on their respective active free metal is reasonable.

Nickel and cobalt catalysts are known to activate molecular hydrogen to the atomic state on their surfaces. Thus, the reaction of these compounds with atomic hydrogen on the metal surfaces should proceed with the formation of two molecules of cyclopentadiene and one atom of metal. The metal atom adheres to the catalyst surface to continue building the particle of catalytically active metal. With the release of the molecules of cyclopentadiene in close proximity with the surface of the metal catalyst, the hydrocarbon should be quickly adsorbed and hydrogenated to cyclopentane. The migration of cyclopentadiene through the bulk of the solvent to the metal surface is, therefore, not a factor in the length of time required for its complete hydrogenation after liberation from the bis-cyclopentadienyl compound.

Being more stable than nickelocene, cobaltocene requires a higher temperature for its reduction. The cobaltocene is more resistant to attack by hydrogen atoms both in the homogeneous reaction of the induction period and in the heterogeneous reaction of the autocatalytic stage. Certainly, ferrocene has a high resistance toward heterogeneous catalytic reduction at temperatures below 280°.

B. Hydrogenation of Benzene

1. Comparison of Ferrocene, Cobaltocene, and Nickelocene

Benzene was hydrogenated to cyclohexane on nickel and cobalt produced by the hydrogen reduction of their respective bis-cyclopentadienyl compounds in the benzene prior to the hydrogenation reaction. Ferrocene was not reduced in benzene, and no observation was made of the

hydrogenation of benzene in which the dissolved bis-cyclopentadienyl compounds of iron, cobalt, or nickel functioned as homogeneous catalysts for the activation of molecular hydrogen. The nickel and cobalt catalysts slowly lost their activity upon being stored under methanol which did not have the dissolved oxygen removed.

The reaction on both nickel and cobalt was determined to be first order in hydrogen pressure and zero order in benzene concentration at temperatures between 120° and 170°. This same kinetic behavior has been observed in many previous investigations on the hydrogenation of benzene in the liquid phase, particularly on nickel and platinum.⁵⁵

The reaction rate constants were found to obey the Arrhenius equation at 130–170°, and the apparent activation energies are 8.78 kcal. mole⁻¹ for the reaction on nickel and 19.8 kcal. mole⁻¹ for cobalt. The same apparent activation energies were obtained irrespective of disagreement in the k values at a given temperature from one E_a determination to the next. This suggests that differences in the rate constants at a given temperature for either nickel or cobalt result from differences in the specific surface area which is controlled, in part, by the catalyst grain size. The formation of a metal catalyst with identical grain sizes in each reaction was impossible to achieve experimentally.

The following observations are made using the values of the rate constants and apparent activation energies: (1) The nickel is more active than cobalt at temperatures between 60° and 150°. (2) The two catalysts have approximately equal activity at 150–165°. (3) The cobalt catalyst should be more active above 170° provided the trend observed

up to 170° is not altered as the temperature is increased. (4) A more active catalyst results if the nickelocene or cobaltocene is reduced in solution with the compound to be hydrogenated rather than in a pre-reduction reaction in cyclohexane. External poisons and inhibitors from the atmosphere are eliminated by following the first procedure.

The catalytic activities of Raney nickel and Raney cobalt are compared with the catalytic activities found for nickel and cobalt in the present study. From data reported by Kirslis,⁴² the approximate rate constant for the hydrogenation of benzene on Raney nickel at 120° was estimated as 0.03 moles H_2 /(min., psi. H_2 , g. Ni), whereas the nickel produced in the present work had a rate constant of approximately 11×10^{-6} at 120° . Thus, the Raney nickel is estimated to be more active at this temperature by a factor of 3×10^4 . The apparent activation energy for the Raney nickel-catalyzed reaction was 15 kcal. mole⁻¹ at $50-80^{\circ}$ as compared with 8.8 kcal. mole⁻¹ at $130-165^{\circ}$ found for nickel from nickelocene.

Raney cobalt and cobalt from cobaltocene have approximately the same characteristics from the standpoint of the hydrogenation of benzene.⁵⁶ Both are catalytically active above 120° , and their apparent activation energies for this reaction are in the same range: 23 kcal. mole⁻¹ for Raney cobalt and 19.85 kcal. mole⁻¹ for cobalt from cobaltocene, both for the temperature range $150-170^{\circ}$. At 150° , Raney Cobalt is about three times more active than the cobalt prepared from cobaltocene.

2. Mechanism of Hydrogenation of Benzene

Two general mechanisms have been proposed to explain the observed kinetic laws in surface catalysis.⁵⁷ The Langmuir-Hinshelwood mechanism, which is also known as the "adjacent interaction" mechanism, has found the widest application. The second mechanism is the Rideal-Eley mechanism which is known as the "van der Waal's layer-chemisorbed layer interaction" mechanism. While the kinetic law observed in the hydrogenation of benzene on the nickel and cobalt catalysts can be accounted for on the basis of either mechanism, only the Langmuir-Hinshelwood mechanism will be discussed in detail because it seems to fit the present reaction under consideration much better.

The fundamental postulates are: (1) The reactants are involved in a dynamic adsorptive equilibrium with the surface of the catalyst, forming a monolayer on the surface. (2) Reaction takes place between molecules chemisorbed on adjacent sites with the rate of reaction being proportional to the concentrations of the reactants on the surface. (3) The products must desorb easily in order that the sites or active centers be vacated for the adsorption of more reactant molecules.

Applying these principles to the present system, benzene and hydrogen must both be chemisorbed on the surface of the nickel or cobalt, and reaction occurs between the chemisorbed species to form cyclohexane. The cyclohexane, which is less strongly chemisorbed than benzene, is rapidly displaced by benzene molecules. The displacement of cyclohexane must be faster than the hydrogenation reaction for the kinetic results to be meaningful.

According to the Langmuir-Hinshelwood mechanism, the rate of reaction, dn/dt , is given by the following equation:

$$-\frac{dn}{dt} = k' S \theta_H \theta_B \quad (1)$$

where k' is the reaction rate constant; S is the surface area of the catalyst; and θ_H and θ_B are the fractions of the surface covered by chemisorbed hydrogen and benzene, respectively. The values for θ must be obtained by the use of adsorption isotherms.

The Langmuir adsorption isotherms for two different types of surface systems are used in deriving the rate equation.

a. Case of the mutual displacement of hydrogen and benzene. If two gases, A and B, are adsorbed on the same surface at constant temperature, the fraction of the surface which is bare is $1 - \theta_A - \theta_B$. The rate of adsorption of A is given by

$$\text{rate adsorption} = M_A P_A (1 - \theta_A - \theta_B) \quad (2)$$

where M_A is a constant, and P_A is the partial pressure of A. The rate of desorption of A is given by

$$\text{rate desorption} = N_A \theta_A \quad (3)$$

where N_A is a constant.

At equilibrium, the rates of adsorption and desorption are equal.

Equations 2 and 3 are equated and solved for θ_A to give

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A} (1 - \theta_B) \quad (4)$$

where

$$K_A = M_A/N_A$$

In an identical manner, an expression for θ_B is obtained which is

$$\theta_B = \frac{K_B P_B}{1 + K_B P_B} (1 - \theta_A) \quad (5)$$

Equations 4 and 5 can be solved simultaneously for θ_A and θ_B to give

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B} \quad (6)$$

and

$$\theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B} \quad (7)$$

Returning to the problem of the liquid phase benzene-hydrogen system, with suitable modifications, the Langmuir-Hinshelwood mechanism can be applied to this system with only fair success. The Langmuir adsorption isotherm for two gases which are capable of mutual displacement should apply for the adsorption of hydrogen on the catalyst surface from the benzene solution because its concentration in the liquid phase is small thus simulating vapor phase behavior. With the pressure terms replaced by concentrations, equation 4 becomes the following equation for hydrogen adsorption:

$$\theta_H = \frac{K_H C_H}{1 + K_H C_H} (1 - \theta_B) \quad (8)$$

The use of the Langmuir isotherm (equation 7) for the determination of the fraction of the surface covered by benzene, θ_B , leads to an expression for the rate of hydrogenation which is not wholly compatible

with the experimental results. The possible failure of benzene to observe the adsorption isotherm is understandable in view of the high initial concentration of benzene in the liquid phase before reaction (approximately 10 molar). The surface of the catalyst is covered with a mechanical multilayer of benzene molecules which do not undergo the same type of energetic collision with the surface as would be found in adsorption phenomena in the vapor phase. Benzene is chemisorbed on the catalyst surface but not necessarily in a complete monolayer ($\theta_B = 1$).

Without a suitable adsorption isotherm for benzene in the liquid phase, the following rate equation is obtained by the substitution of the expression obtained in equation 8 for θ_H into equation 1:

$$-\frac{dn}{dt} = \frac{k' S K_H' C_H}{1 + K_H' C_H} (\theta_B - \theta_B^2) \quad (9)$$

Since the concentration of hydrogen in benzene is small and the chemisorption of benzene on the surface quite strong, the fraction of the surface covered by hydrogen, θ_H , should be small. The postulate is made that

$$\frac{K_H' C_H}{1 + K_H' C_H} \ll 1 \quad (10)$$

and

$$K_H' C_H \ll 1 \quad (11)$$

Equation 9 becomes

$$-\frac{dn}{dt} = k' S K_H' C_H (\theta_B - \theta_B^2) \quad (12)$$

The concentration of hydrogen in the liquid phase is directly proportional to the hydrogen pressure in the vapor phase over small pressure ranges (Henry's Law). The substitution

$$K'_H C_H = K_H P_H \quad (13)$$

is made in equation 12 to give

$$-\frac{dn}{dt} = k' S K_H P_H (\theta_B - \theta_B^2) \quad (14)$$

The assumption is made that, at a constant temperature, the value of θ_B is constant and independent of the concentration of benzene in the liquid phase with the mole fraction of benzene within the limits: $0.5 < N_B < 1.0$. This assumption is justified solely on the grounds that the observed rates of reaction were independent of the benzene concentration in this range of the benzene mole fraction. The independence of θ_B from the hydrogen pressure is also implied. The constant terms in equation 14 can be consolidated into a single constant, k :

$$-\frac{dn}{dt} = k S P_H \quad (15)$$

The surface area of a given weight of catalyst in a reaction is usually not known. If the catalyst is homogeneous with respect to the particle size, or with respect to being thoroughly mixed in the event particles of various sizes exist, then the surface area of a given sample will normally be a linear function of the catalyst weight, w . The surface area is therefore replaced in equation 15 by the catalyst weight.

$$-\frac{dn}{dt} = k w P_H \quad (16)$$

Equation 16 was found experimentally to be the kinetic law which governs the rates of hydrogenation of benzene on the nickel and cobalt catalysts.

b. Case of adsorption of reactants on different type sites. If two gases are adsorbed on a surface at constant temperature on different types of surface sites such that the adsorption of gas A does not interfere with gas B, then the problem of deriving the Langmuir adsorption isotherms for θ_A and θ_B reduces to that for the adsorption of a single gas on a surface. Let f_A and f_B be the fractions of the total surface on which only A molecules and only B molecules, respectively, can be chemisorbed. The fraction of the total surface which is available for the adsorption of A is $f_A - \theta_A$. The rate of adsorption of A is given by

$$\text{rate adsorption} = M_A P_A (f_A - \theta_A) \quad (17)$$

The rate of desorption is identical with the expression in equation 3, which is

$$\text{rate desorption} = N_A \theta_A \quad (18)$$

At equilibrium, the rates of adsorption and desorption are equal. Thus, equations 17 and 18 can be equated and solved for θ_A to give

$$\theta_A = \frac{f_A K_A P_A}{1 + K_A P_A} \quad (19)$$

A completely analogous expression can be obtained for θ_B which is

$$\theta_B = \frac{f_B K_B P_B}{1 + K_B P_B} \quad (20)$$

In applying these results to the hydrogenation of benzene, the assumption is made that benzene and hydrogen obey the Langmuir adsorption

isotherms (equations 19 and 20) in adsorbing from the liquid phase onto the nickel or cobalt catalysts. The values for θ_H and θ_B from equations 19 and 20 in terms of concentration of benzene and the hydrogen pressure (See equation 13) are substituted into equation 1 to give

$$-\frac{dn}{dt} = k' S \frac{f_H K_H P_H}{1 + K_H P_H} \frac{f_B K_B C_B}{1 + K_B C_B} \quad (21)$$

The assumption is made that hydrogen is weakly chemisorbed on the surface such that, under the experimental conditions of the present study, the following inequality holds:

$$K_H P_H \ll 1 \quad (22)$$

Also, the assumption is made that at the high benzene concentrations used, the following inequality holds:

$$K_B C_B \gg 1 \quad (23)$$

Using inequalities 22 and 23, equation 21 reduces to the following:

$$-\frac{dn}{dt} = k' S f_H K_H P_H f_B \quad (24)$$

Upon replacing the surface area term, S , with the catalyst weight, w , and consolidating all of the constants into one constant, k , equation 24 becomes:

$$-\frac{dn}{dt} = k w P_H \quad (16)$$

Equation 16 is the rate expression found experimentally.

c. Comparison of the two mechanisms. Insufficient information was obtained experimentally in the present study to distinguish between

the two modifications of the adjacent interaction mechanism as just presented. Certainly, the general rate equation obtained in the discussion of the second modification (equation 21) is more versatile than that obtained in the first discussion (equation 14) in that (1) a maximum in the reaction rate is predicted at high benzene concentrations and high hydrogen pressures; and (2) changes in the reaction order are predicted with large changes in concentrations and also in the temperature since the K 's are temperature dependent. The necessity of having to postulate that θ_B is independent of the benzene concentration and of the hydrogen pressure in describing a mechanism in which hydrogen and benzene are supposed to be mutually displaced from the catalyst surface would seem to invalidate the first mechanism.

The second mechanism in which benzene and hydrogen are postulated to be chemisorbed on different types of surface sites is believed to be operative. If benzene is chemisorbed on the surface in a flat position, then the idea that a different type of site is required for benzene adsorption than for hydrogen adsorption is not too remote. Hydrogen would be capable of adsorbing on sites that are inaccessible to the much larger benzene molecule.

C. Hydrogenation of Acetone

1. Comparison of Ferrocene, Cobaltocene, and Nickelocene

Nickelocene undergoes hydrogen reduction in acetone under identical conditions required for its reduction in cyclohexane. Acetone is hydrogenated to isopropanol at temperatures above 100° on the nickel

produced by the hydrogen reduction of nickelocene in the acetone solution. Acetone is hydrogenated on cobalt from cobaltocene at 170° and possibly at lower temperatures, but the process of forming active cobalt by hydrogen reduction of cobaltocene in acetone is complicated by an unexplained reaction between acetone and cobaltocene which results in the cobalt being tied up in a dark blue solid.

Acetone is not hydrogenated in the presence of dissolved ferrocene, and no hydrogen reduction of ferrocene occurs in the acetone solution below 180° and hydrogen pressures up to 1000 psi. The experimental evidence shows that the bis-cyclopentadienyl compounds of iron, cobalt, and nickel do not function as homogeneous catalysts for the activation of molecular hydrogen for the hydrogenation of acetone.

The nickel catalyst is not as active as the W-6 Raney nickel catalyst for the hydrogenation of acetone. Adkins and Billica report that acetone is hydrogenated to isopropanol on their W-6 Raney nickel catalyst at 25-30° under a hydrogen pressure of 15-45 psi.⁵⁸

2. Mechanism of Hydrogenation of Acetone

Acetone is hydrogenated on the nickel catalyst in a heterogeneous reaction that is first order in hydrogen pressure and zero order in acetone concentration. The Langmuir-Hinshelwood mechanism effectively accounts for the observed kinetics (See discussion of Langmuir-Hinshelwood mechanism, Chapter IV, Section B).

The Langmuir adsorption isotherm which was derived for the adsorption of two gases on different types of surface sites is most useful in deriving the rate expression for the hydrogenation of acetone. Using

the identical approach to the problem as made in the discussion on benzene (Chapter IV, Section B), the general rate equation for the hydrogenation of acetone is given by

$$-\frac{dn}{dt} = k' S \frac{f_H K_H P_H}{1 + K_H P_H} \frac{f_A K_A C_A}{1 + K_A C_A} \quad (1)$$

where the subscripts H and A refer to hydrogen and acetone, respectively. The f 's denote the fraction of the total surface capable of adsorbing only hydrogen or only acetone; the K 's are the equilibrium constants of adsorption; the P and C terms are pressure and concentration, respectively; and k' is the reaction rate constant in terms of the moles of hydrogen (n) reacting per unit time on the catalyst's surface which has a surface area, S .

The assumptions are made that (1) the hydrogen is weakly adsorbed on the catalyst such that $K_H P_H \ll 1$, and (2) acetone is strongly adsorbed on the catalyst at the high concentrations employed such that $K_A C_A \gg 1$. Equation 1 then reduces to

$$-\frac{dn}{dt} = k' S f_A f_H K_H P_H \quad (2)$$

which, upon consolidation of the constants, becomes

$$-\frac{dn}{dt} = k w P_H \quad (3)$$

Equation 3 was found experimentally for the hydrogenation of acetone on nickel.

No direct proof was obtained experimentally that hydrogen and acetone are not capable of displacing each other from the catalyst

surface. However, the use of the Langmuir adsorption isotherms for two gases capable of mutual displacement leads to difficulty in obtaining the experimentally determined rate equation.

Differentiation between the two modes of adsorption by experimental means is possible. If hydrogen and acetone are capable of mutual displacement, and if the Langmuir-Hinshelwood mechanism is operative, then a maximum rate of reaction should be achieved by increasing the hydrogen pressure and lowering the acetone concentration to the point where $\theta_H = \theta_A = 0.5$. Should hydrogen and acetone be adsorbed on different surface sites, a maximum in the reaction rate will be observed upon increasing the hydrogen pressure until $\theta_H/f_H = 1.0$ while maintaining the acetone concentration sufficiently high in order that $\theta_A/f_A = 1.0$. A plot of rate of reaction as a function of hydrogen pressure will give a curve which rises to a plateau if the molecules are adsorbed on different type sites, whereas a relatively sharp maximum should be obtained if mutual displacement takes place. Insufficient ranges in hydrogen pressure and in benzene concentration were covered in the present study to determine which adsorption mechanism is operative.

D. Hydrogenolysis of Ethyl Laurate

Nickelocene and cobaltocene are reduced with hydrogen to the free metal and cyclopentane in ethyl laurate solution under the same conditions of temperature and pressure as are required for the reductions in cyclohexane. Both the free nickel and free cobalt thus produced are active above 250° in catalyzing the hydrogenolysis of ethyl laurate at

hydrogen pressures above 2000 psi. A mixture of products is obtained, with dodecanol-1 and n-undecane being the principal products.

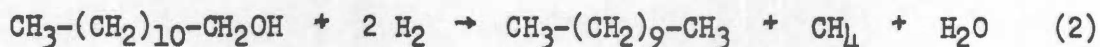
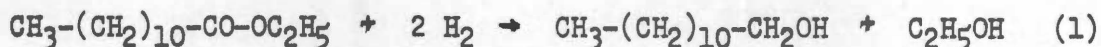
Ferrocene undergoes reaction in ethyl laurate at 300°, but catalytically active iron is not one of the products. Homogeneous catalysis was not observed with the three bis-cyclopentadienyl compounds.

The cobalt catalyst produced by hydrogen reduction of cobaltocene in ethyl laurate was more active than the nickel catalyst which was prepared from nickelocene. Conley found that cobalt(II) oxide was a suitable catalyst for the hydrogenolysis of ethyl laurate.³⁸ He did not obtain evidence that the cobalt oxide was reduced to metallic cobalt by hydrogen in the process.

Adkins points out that the products which are obtained in the hydrogenolysis of an ester are quite dependent upon such factors as the hydrogen pressure, temperature, ratio of catalyst to ester, and the reaction time.⁵⁹ In general, the yields of long-chain alcohols are improved by high hydrogen pressure, low temperature, and short reaction time. A high catalyst to ester ratio must often be used to achieve these conditions.

In the present study, the activities of the nickel and of the cobalt were quite low necessitating a higher reaction temperature than usually employed for the hydrogenolysis reaction. Undoubtedly, dodecanol-1 was produced in the initial reaction. However, at 280-320°, dodecanol-1 undergoes hydrogenolysis to n-undecane as was demonstrated in experiments with nickelocene and cobaltocene in dodecanol-1 with the hydrocarbon being formed on both the nickel and cobalt catalysts. The

following sequence of reactions best explains the formation of the observed products.



Palfray reported that the hydrogenolysis of ethyl laurate over a nickel catalyst gave as products dodecanol-1 (62 per cent), n-undecane, ethanol, and water.⁶⁰ The reaction was carried out at 240° under a hydrogen pressure of 150 kg. cm.⁻¹. Gault, Palfray, and Pao-Ting Hsu obtained almost theoretical yields of n-undecane from dodecanol-1 upon treatment with hydrogen at 100 kg. cm.⁻¹ over Raney nickel at 200°. ⁶¹ Wojcik and Adkins also obtained 100 per cent yields of n-undecane by the hydrogenolysis of dodecanol-1 over Raney nickel at 250° under a hydrogen pressure of 100-200 atm.⁶² These findings by other workers serve to substantiate the proposed reaction sequence.

Nickelocene and cobaltocene are concluded to be rather poor sources of nickel and cobalt for the hydrogenolysis of esters of long chain acids. The activity of the nickel and cobalt is low in comparison with that of copper chromite catalysts. Furthermore, the high reaction temperature which is required as a result of the low activity is conducive to the formation of hydrocarbons from the alcohols that are produced in the initial reaction. The reaction products are also contaminated with cyclopentane from the bis-cyclopentadienyl compound.

E. Discussion of Other Studies

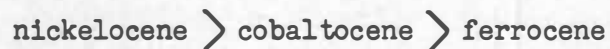
1. Nitroethane and Nitrobenzene

Nickelocene and cobaltocene are unsuitable compounds for adding nickel and cobalt to nitroethane and nitrobenzene solutions for the purpose of forming hydrogenation catalysts by reduction of the bis-cyclopentadienyl compounds with hydrogen. Interactions between the metal compound and the nitro compound prevent the complete hydrogen reduction of the nickelocene and cobaltocene. Some reduction of the nickel and cobalt compounds with liberation of the free metal did occur. The nitro compounds were hydrogenated on the liberated metals at a slow rate. The formation of much tarry material, particularly with nitrobenzene, made this approach to the hydrogenation of nitro compounds unsatisfactory.

Ferrocene was unattacked by hydrogen in solution with these nitro compounds and did not function as a homogeneous catalyst in activating molecular hydrogen for the reduction of the nitro compounds under the experimental conditions used.

2. Cyclohexene

Ferrocene, nickelocene and cobaltocene react with cyclohexene at room temperature to give compounds of unknown composition. The order of decreasing reactivity is



This order is identical with that decreasing ease of displacing the cyclopentadienyl rings. The reaction with ferrocene was very slow with

several weeks being required for the complete removal of 0.1 g. of ferrocene from 30 ml. of cyclohexene. Nickelocene and cobaltocene react within a few minutes.

One explanation for this phenomenon is that the bis-cyclopentadienyl compounds are capable of catalyzing the homogeneous polymerization of cyclohexene. This solution is suggested by the resinous products, particularly in the case of ferrocene. The metal compounds would be removed either physically or chemically from solution with the polymer. The observation was made that no interaction occurred when ferrocene and cyclohexene were heated under hydrogen pressure in the absence of oxygen which suggest that oxidation of cyclohexene might be occurring.

Ferrocene was found to be incapable of catalyzing the hydrogenation of cyclohexene to cyclohexane by homogeneous activation of hydrogen.

CHAPTER V

SUMMARY

The neutral bis-cyclopentadienyl metal compounds of iron, cobalt, and nickel were prepared and studied as possible sources of catalytically active iron, cobalt, and nickel. Nickelocene and cobaltocene are reduced to the free metal and cyclopentane in cyclohexane solution with hydrogen in the absence of a catalyst using hydrogen at 1000 psi. The reduction of nickelocene takes place at 60° , and the reduction of cobaltocene occurs at $160-170^{\circ}$. Induction periods were observed. The hydrogen reduction of ferrocene was not achieved. The hydrogenation reactions of benzene, cyclohexene, acetone, ethyl laurate, nitrobenzene, and nitroethane were studied with nickelocene and cobaltocene added as sources of nickel and cobalt, respectively.

The hydrogenation of benzene to cyclohexane occurs above 60° on the nickel from nickelocene and above 120° on the cobalt from cobaltocene at hydrogen pressures above 200-300 psi. The heterogeneous catalytic reactions were first order in hydrogen pressure and zero order in benzene concentration, and the reactions were explained on the basis of the Langmuir-Hinshelwood mechanism. The rate constants were determined by the Variable Temperature Method at $130-170^{\circ}$. The apparent activation energy is $8.78 \text{ kcal. mole}^{-1}$ for the reaction on nickel and $19.85 \text{ kcal. mole}^{-1}$ for the reaction on cobalt. The catalysts from the bis-cyclopentadienyl compounds are much less active than Raney nickel and have an activity comparable to Raney cobalt.

Acetone is hydrogenated to isopropanol on the nickel produced from nickelocene. The reaction proceeds above 100° at hydrogen pressures above 100 psi. The reaction is first order in hydrogen pressure and zero order in acetone concentration. The kinetics are explained on the basis of the Langmuir-Hinshelwood mechanism for the adsorption of hydrogen and acetone on different types of surface sites. The apparent activation energy is 12 kcal. mole⁻¹ at $140-180^{\circ}$. Very little active cobalt metal is produced by the hydrogen reduction of cobaltocene in acetone apparently because of compound formation involving acetone and cobaltocene. The free metal which was produced exhibited catalytic activity toward the hydrogenation of acetone.

Ethyl laurate undergoes hydrogenolysis on the nickel and cobalt catalysts above 250° at hydrogen pressures above 2000 psi. The principal products are dodecanol-1 and n-undecane with n-undecane being favored by long reaction times and high temperatures. The cobalt catalyst was more active than the nickel catalyst but less active than copper chromite.

The hydrogenation of nitrobenzene and nitroethane on the nickel and cobalt produced by the hydrogen reduction of nickelocene and cobaltocene in situ led to the formation of solid tar-like products. Considerable difficulty was experienced in reducing nickelocene and cobaltocene with hydrogen in the presence of nitrobenzene and nitroethane. Compound formation between cyclohexene and cobaltocene and nickelocene prevented a study of that system.

No instance of the homogeneous activation of molecular hydrogen by ferrocene, cobaltocene, and nickelocene was observed. Ferrocene acted as an inert substance in all of the hydrogenation reactions attempted in its presence with the exception of a possible reaction with ethyl laurate.

APPENDIXES

CRANES & CREST

APPENDIX I

COMMENTS ON THE VARIABLE TEMPERATURE METHOD

In his original derivation of the equations for the Variable Temperature Method of determining reaction rate constants, Kirsliis obtained the following equation:⁴²

$$\frac{dP}{dt} = \frac{P}{T} \frac{dT}{dt} \quad (1)$$

which relates the rate of change of the pressure, dP/dt , of n moles of an ideal gas at constant volume, v , to the temperature, T , the pressure, P , and the rate of heating or cooling, dT/dt . He shows that, at a given temperature and at a given rate of change of the temperature, the rate of change of the pressure is proportional to the pressure such that

$$\left[\frac{dP}{dt} \right]_2 = \frac{P_2}{P_1} \left[\frac{dP}{dt} \right]_1 \quad (2)$$

The subscripts 1 and 2 denote separate determinations of dP/dt in which the number of moles of gas present in the system are different in the two determinations.

Kirsliis uses equation 2 as a means of obtaining the rate of change of pressure due to heating, $(dP/dt)_{\text{heating}}$. Blank determinations of the quantity $\left[\frac{1}{P} \frac{dP}{dt} \right]$ are made under identical conditions as used in the constant volume hydrogenation reactions. Then, at a given temperature:

$$\left[\frac{dP}{dt} \right]_{\text{heating}} = P_{\text{reaction}} \left[\frac{1}{P} \frac{dP}{dt} \right]_{\text{blank}} \quad (3)$$

where P_{reaction} is the total pressure at the desired temperature during the hydrogenation reaction.

In obtaining equations 2 and 3, Kirslis does not consider the fact that the gas in the pressure gage is at a different temperature than the bomb temperature. While these equations (2 and 3) can be obtained through a derivation which takes into account this difference in bomb and gage temperatures, the derivation is non-trivial and, therefore, is given here.

If n moles of an ideal gas is enclosed in a hydrogenation apparatus, the application of the Ideal Gas Law to the system yields the following equations:

$$n = n_g + n_b \quad (4)$$

and

$$n = \frac{P}{R} \left[\frac{v_b}{T_b} + \frac{v_g}{T_g} \right] \quad (5)$$

where the subscripts b and g refer to the bomb and gage, respectively.

During a Variable Temperature Method determination, the gage temperature, T_g , remains constant at room temperature. The term v_g/T_g is constant and can be replaced by the constant, C . After solving for P , equation 5 becomes

$$P = \frac{n R T_b}{v_b + C T_b} \quad (6)$$

Equation 6 is differentiated with respect to the time, t , at constant n as follows:

$$\frac{dP}{dt} = \frac{n R}{(v_b + C T_b)^2} \left[(v_b + C T_b) \frac{dT_b}{dt} - C T_b \frac{dT_b}{dt} \right] \quad (7)$$

or

$$\frac{dP}{dt} = \frac{n R v_b}{(v_b + C T_b)^2} \frac{dT_b}{dt} \quad (8)$$

Equation 6 is solved for the moles of gas present, n , and the resulting expression is substituted for n in equation 8 to give

$$\frac{dP}{dt} = \frac{P v_b}{v_b T_b + C(T_b)^2} \frac{dT_b}{dt} \quad (9)$$

Equation 9 shows that dP/dt is directly proportional to the pressure at a given bomb temperature and given rate of heating. If the bomb is heated through a temperature interval in a manner such that a reproducible rate of heating is obtained at each temperature within the interval, then, for two measurements of dP/dt at the same temperature, the following equation holds:

$$\left[\frac{dP}{dt} \right]_2 / \left[\frac{dP}{dt} \right]_1 = \frac{P_2 v_b}{P_1 v_b} \cdot \frac{v_b T_b + C(T_b)^2}{v_b T_b + C(T_b)^2} \quad (10)$$

or

$$\left[\frac{dP}{dt} \right]_2 = \frac{P_2}{P_1} \left[\frac{dP}{dt} \right]_1 \quad (11)$$

Equation 11 is identical with equation 2. Equation 3 follows from equation 11 upon making the appropriate changes in the subscripts.

The use of equation 3 to correct the values of dP/dt obtained in the blank calibration runs for differences in the total pressure encountered in the blank runs and the hydrogenation runs is justified on the grounds that the rate constants obtained by the Variable Temperature Method agree favorably with those obtained by constant temperature

measurements. Usually, the difference between P_{reaction} and P_{blank} is less than 200 psi. with an average total pressure in the range 600-800 psi. Thus, the corrective factor seldom deviates from unity by more than ± 0.3 . The effect of the error incurred in $(dP/dt)_{\text{heating}}$ upon the reaction rate constant by the use of equation 3 is rather small because $(dP/dt)_{\text{net}}$ is quite often much larger than $(dP/dt)_{\text{heating}}$, especially as the upper limit of the reaction temperature range is approached.

The real system in the catalytic hydrogenation reactions which are conducted in the liquid phase is complicated by the non-ideal behavior of the gases in the vapor phase and by the presence of a liquid phase. Kirsliis made a thorough study of the variables which affect the accuracy of the calculation of $(dP/dt)_{\text{heating}}$ with equation 3.⁴² He concluded that the total error in the rate constants which were determined for the hydrogenation of benzene on Raney nickel by this method is less than 5 per cent. Information obtained in the present study indicates that $(dP/dt)_{\text{heating}}$ must be determined by other means if the liquid phase has a high vapor pressure which increases rapidly over the reaction temperature range (See Chapter III, Section C-3).

APPENDIX II

STUDIES ON THE INHIBITION OF THE HYDROGEN REDUCTION OF PLATINIC CHLORIDE BY NITROBENZENE

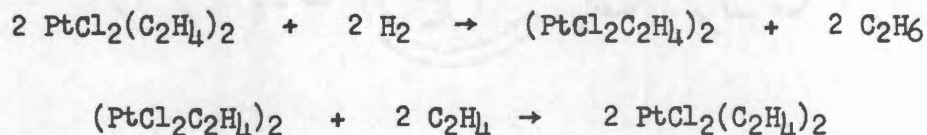
A. Introduction

Bedoit studied the action of platinum(IV) chloride as a promoter for Raney Nickel catalyst with respect to the hydrogenation of nitrobenzene in ethanol at 30° with hydrogen pressures up to 36 psi.⁶³ His experimental results indicate that platinum(IV) chloride acts as a promoter for Raney nickel in this reaction. He initiated an incomplete study of the hydrogenation of nitrobenzene in ethanol on platinum which was supplied by platinum(IV) chloride.

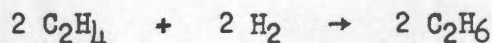
He found that platinum(IV) chloride is reduced by hydrogen to platinum which subsequently acts as a catalyst for the hydrogenation of nitrobenzene to aniline and cyclohexylamine. This study was performed also at 30° using hydrogen at pressures up to 40 psi. The results show that the catalytic activity of the platinum alone is equal to or greater than the activity of Raney nickel promoted by an equal amount of platinum.

During this study, the observation was made that hydrogen at 30-40 psi. fails to reduce the platinum chloride when the nitrobenzene concentration exceeds 1 ml. per 10 ml. of ethanol. Also, no hydrogenation of nitrobenzene occurs when the platinum remains in solution as the chloride. Cyclohexene acts as an inhibitor in a similar manner. Bedoit did not attempt an explanation of this phenomenon.

In order to obtain an explanation for the phenomenon of inhibition as observed by Bedoit, a study was made of the hydrogenation of nitrobenzene in ethanol with platinum(IV) chloride and chloroplatinic acid as sources of platinum. The present work was prompted also by the results of Flynn and Hulburt who studied the reduction of ethylene platinumous chloride by hydrogen in toluene and in acetone.⁶⁴ They found that ethylene platinumous chloride reacts with hydrogen at an appreciable rate in toluene at -40° with inhibition shown by olefins. The reaction was autocatalyzed by platinum. Evidence was found for the homogeneous hydrogenation of ethylene by hydrogen below -10° in acetone. A chain mechanism was proposed to explain the homogeneous activation of molecular hydrogen.



The net result of these reactions is



These findings are somewhat analogous to Bedoit's observations in that inhibition of the reduction of platinum by certain compounds is shown.

B. Experimental

The preparation and purification of many of the compounds used in this study have been described earlier in the text (See Chapter II, Sections B, C, and D).

1. Platinum(IV) Chloride

Anhydrous platinum(IV) chloride was prepared by thermally decomposing chloroplatinic acid hexahydrate at 275° in a stream of dry chlorine according to the method outlined by Keller.⁶⁵ The compound was stored in glass-stoppered bottles over Drierite. A stock solution of platinum(IV) chloride in ethanol was prepared by shaking 1.74 g. of PtCl_4 with 80 ml. of distilled absolute ethanol. The solution was filtered through a fine-pore fritted-glass funnel and diluted to 100 ml. with ethanol. The concentration of platinum was determined by evaporating aliquot portions in porcelain crucibles and igniting over a Fisher burner to convert the chloride to the free metal for weighing. The concentration was 0.045 molar in platinum(IV) chloride corresponding to a platinum content of 8.8 mg. per milliliter.

2. Chloroplatinic Acid

Baker and Company chloroplatinic acid hexahydrate was used without further purification. A stock solution was prepared by dissolving 2.8 g. of the compound in 80 ml. of distilled absolute ethanol. The solution was filtered through a fine-pore fritted-glass filter and diluted to 100 ml. with ethanol. The concentration was determined by evaporating aliquot portions in a porcelain crucible and igniting over a Fisher burner to convert the chloroplatinic acid to the free platinum metal. The solution was 0.0488 molar in chloroplatinic acid hexahydrate corresponding to a platinum content of 9.5 mg. per milliliter.

3. Ethanol

One gallon of absolute ethanol was shaken with 0.8 lb. of Drierite and added to the pot of a 13-ft. glass helix-packed column. One-fourth pound of Drierite was added to the pot of the still, and the ethanol was fractionally distilled at a 10:1 reflux ratio, b.p. 77.7-77.8°/736-740 mm., n_D^{20} 1.3617. The solvent was stored in a brown screw-cap bottle.

4. Hydrogenation Studies

a. Apparatus. The hydrogenation reactions were conducted at constant pressure in a variable volume system in which the pressure was maintained at that of the atmosphere with a mercury leveling bulb arrangement. The reaction flasks were constructed from 41-mm. Pyrex tubing and had a volume of 100 ml. The necks of the flasks were 6 in. long and were constructed from 12-mm. tubing. The reaction flasks were secured in a water jacket which was mounted on a variable speed shaker. The shaker violently agitated the solutions in the reaction flasks at constant rates within the range of 240-350 cycles per minute.

The reaction flasks were maintained at constant temperature by means of water which was circulated through the water jacket from a constant temperature bath. Temperatures between room temperature and 70° were obtained and maintained constant to within $\pm 0.2^\circ$.

The reaction flasks were attached by means of heavy rubber vacuum tubing to a Pyrex glass manifold which had outlets to a hydrogen tank, to an evacuation system, and to a 100-ml. Pyrex gas buret. The gas buret was mounted adjacent to a second Pyrex tube of equal size which

was open to the atmosphere at the top. The two tubes were attached through a common base tube to a mercury leveling bulb. The use of the adjacent tube in leveling the mercury columns greatly increased the accuracy of the volume readings over that realized in using only a mercury leveling bulb to maintain atmospheric pressure in the system. The volume of hydrogen in the gas buret was quite sensitive to small pressure changes resulting from unbalanced mercury columns.

b. Procedure. A reaction mixture with a volume of approximately 25 ml. was added to a reaction flask which was then attached to the gas buret system and placed in the water jacket. The entire system was filled with hydrogen by alternately evacuating for twenty seconds with a water aspirator and filling to atmospheric pressure with hydrogen. This cycle was repeated six times. After the mercury levels had been adjusted to the 100-ml. mark, the system was closed with the hydrogen pressure equal to the atmospheric pressure (735-745 mm.).

After the reaction flask attained temperature equilibration with the water from the constant temperature bath, the shaker was started, and the absorption of hydrogen was measured as a function of the time by observing the volume of hydrogen in the gas buret at atmospheric pressure and room temperature. The gas buret system was useful in measuring the rate of hydrogen absorption up to a maximum of 10 ml. per minute. Difficulty was experienced in keeping the mercury columns leveled when the rate of absorption was faster.

c. Calculations. The moles of hydrogen absorbed were calculated from the volume of hydrogen absorbed at atmospheric pressure and room

temperature using the Ideal Gas Law:

$$\Delta n = \frac{P}{R T} \Delta v \quad (1)$$

where Δv is the volume of hydrogen absorbed which corresponds to the reaction of Δn moles of hydrogen. This method of calculating the rate of hydrogen absorption is valid even when the volume of gas in the reaction flask is at a different temperature than room temperature because of the rapid temperature equilibration of hydrogen entering the reaction flask.

Although the rate of the reaction can be determined without correcting for the vapor pressure of the liquid phase, the partial pressure of hydrogen in the flask must be used in rate expressions which are pressure-dependent.

5. Spectral Measurements

The Beckman DU Quartz Spectrophotometer was used in all of the spectral studies. A pair of matched quartz cells with a light path of 10.00 mm. in length were used in conjunction with the spectrophotometer.

C. Results and Discussion

1. Hydrogen Reduction of Platinic Chloride*

Both platinum(IV) chloride and chloroplatinic acid are rapidly reduced to platinum in ethanol solution by hydrogen at atmospheric

*The term "platinic chloride" will be used to denote both platinum(IV) chloride and chloroplatinic acid unless differentiation between the two compounds is required.

pressure and temperature. The reaction takes place immediately upon contact of the solution of the chloride with hydrogen. The reduced platinum first appears as a suspension and then collects into larger aggregates. The reduction reaction is thought to be initiated by a homogeneous reaction involving dissolved hydrogen and the dissolved platinic chloride.

2. Hydrogenation of Nitrobenzene

Nitrobenzene is hydrogenated to cyclohexylamine on the platinum formed in the hydrogen reduction of platinic chloride (See Figure 21). Bedoit and Smith showed that the kinetics of the hydrogenation of nitrobenzene are first order in hydrogen pressure and zero order in nitrobenzene concentration for the reduction of both the nitro group and the benzene ring.⁶⁶ They used Adams platinum catalyst and acetic acid solvent in their studies.

The same kinetics were observed in the present study with ethanol as the solvent. The rate of absorption of hydrogen is constant with constant hydrogen pressure for the reduction of both the nitro group and the benzene ring. A reaction was carried out at constant volume in the hydrogenation equipment described in Chapter II, Section G. The rate of reaction was observed to be first order in hydrogen pressure for the nitro group. The reaction was not carried on through hydrogenation of the benzene ring.

3. Effect of Nitrobenzene on Reduction of Platinic Chloride

Platinic chloride is reduced by hydrogen in ethanol solution in the presence of nitrobenzene providing the concentration of nitrobenzene

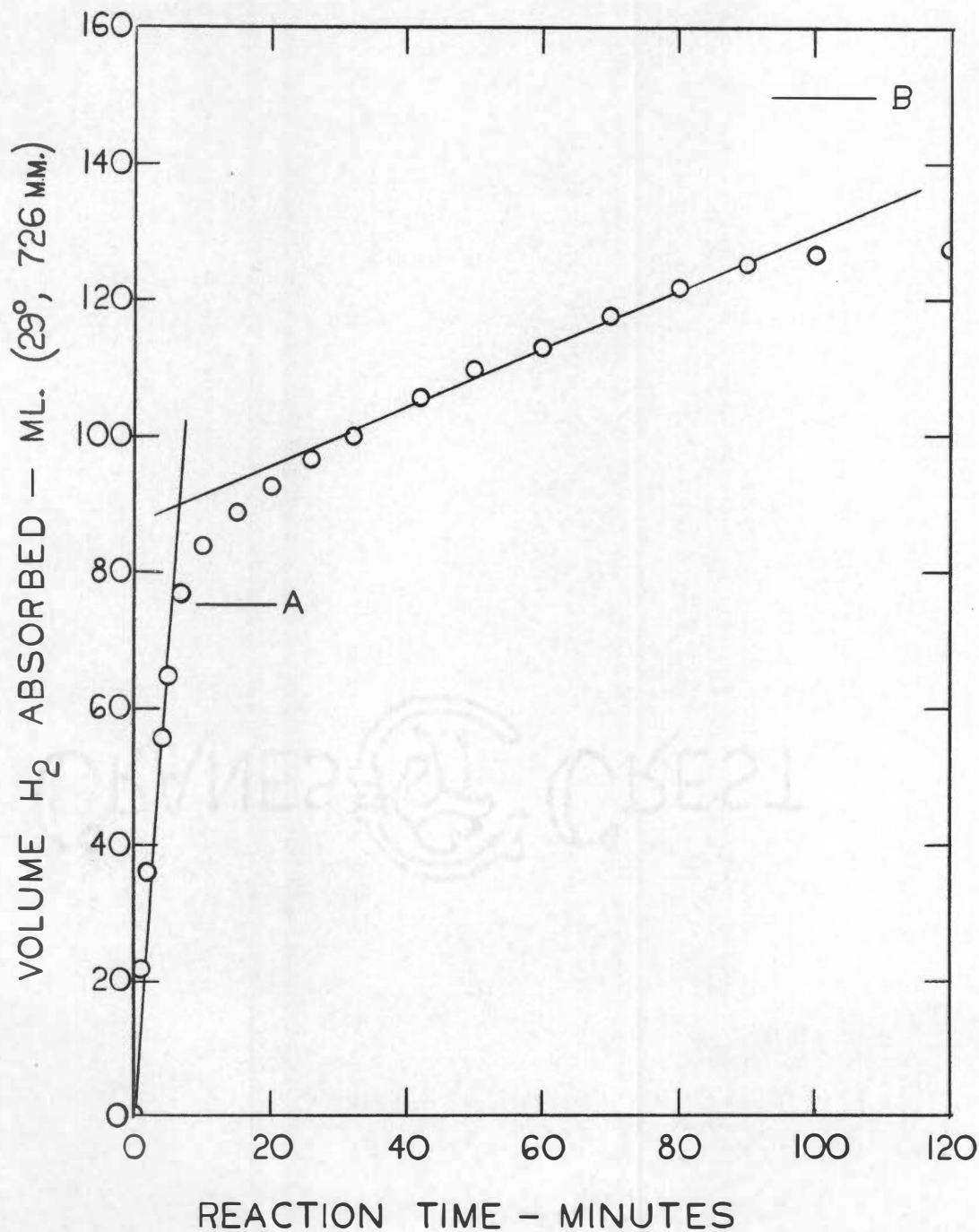


Figure 21. The volume of hydrogen absorbed as a function of the reaction time for the hydrogenation of nitrobenzene at 30° on platinum from chloroplatinic acid. Wt. platinum: 9.5 mg. Solvent: ethanol. Hydrogen pressure: 726 mm. Point A: complete hydrogenation of nitro group. Point B: complete hydrogenation of benzene ring.

is not too high. A study was made to determine the maximum concentration of nitrobenzene which would inhibit the reduction of platinic chloride at 30°. Hydrogen at atmospheric pressure was used. While an accurate evaluation of the upper concentration limit was not obtained, a ratio of 20 ml. of nitrobenzene to 5 ml. of ethanol was found, without exception, to be sufficiently large to inhibit the reduction of the platinum salts. Inhibition was observed at nitrobenzene-ethanol ratios as low as 10:15 in some cases. The concentration of platinic chloride was held constant at approximately 0.002 M. Platinum(IV) chloride and chloroplatinic acid gave similar results.

Trace amounts of platinum(IV) oxide fail to initiate the reduction reaction. The reduction of the platinum salts takes place very slowly at 60° in the presence of nitrobenzene in high concentration. Also, hydrogen at 100 psi. is capable of reducing the platinum, regardless of the nitrobenzene concentration.

An apparent anomaly to the above results was found during studies with a solution of platinum(IV) chloride in pure nitrobenzene. The salt is readily reduced to metallic platinum in this solution by hydrogen at 30° and atmospheric pressure. In this instance, the platinum is deposited on the walls of the reaction vessel as a mirror rather than as a highly divided solid. An additional exception to the inhibiting action was found in experiments in which ethanol was added to the solution of platinum(IV) chloride in nitrobenzene. The addition of ethanol in sufficient quantity to form a solution with a concentration of nitrobenzene and ethanol comparable to those found to inhibit the reduction of platinum(IV) chloride

failed to produce the same inhibiting effect. An irreversible process must be operative with an important factor being which solvent, nitrobenzene or ethanol, is used to dissolve the platinum(IV) chloride initially.

4. Effect of Water

Water was present in most of the hydrogen reduction experiments. In particular, the ethanol solution of chloroplatinic acid hexahydrate which was used in preparing reaction solutions contained 0.005 ml. of water per milliliter of solution. Also, the ethanol solution of platinum(IV) chloride undoubtedly contained trace amounts of water as the salt is very hygroscopic. The effect of water upon the reduction of platinum(IV) chloride by hydrogen was studied at 30° and at a hydrogen pressure equal to atmospheric pressure.

Water does not inhibit the hydrogen reduction of platinum(IV) chloride in pure nitrobenzene, but, on the contrary, it acts to accelerate the reduction.

Platinum(IV) chloride was shown to be completely resistant to hydrogen reduction at 30° and at hydrogen pressures up to 929 mm. when in a solution which contained 10 ml. of nitrobenzene, 15 ml. of ethanol, and 8.8 mg. of platinum as platinum(IV) chloride. The platinum(IV) chloride was rendered susceptible to reduction upon the addition of 1 ml. of water. As the nitrobenzene concentration was increased, the effect of water became less.

This series of experiments shows that the molecular system which is responsible for preventing the reduction of platinum chloride is disrupted

more easily by water than by ethanol. Should a molecular complex between platinum(IV) chloride and nitrobenzene be responsible for the inhibiting action, then water might be capable of breaking up the complex due to its strong affinity for platinum(IV) chloride.

5. Platinum(IV) Chloride-Nitrobenzene Complex

Flynn and Hulburt found that the hydrogen reduction of ethylene platinous chloride is completely inhibited by ethylene in sufficiently high concentration.⁶⁴ Ethylene would tend to stabilize the ethylene platinous chloride by reversing the dissociation reaction of the compound. Other effects may also be operative. In like manner, if a platonic chloride-nitrobenzene complex is responsible for the inhibition of the hydrogen reduction of the chloride, then an increase in the nitrobenzene concentration would be expected to tie up the platonic chloride and thus prevent its reduction by hydrogen. No stable compound between nitrobenzene and either platinum(IV) chloride or platinum(II) chloride has been reported.

a. Attempted isolation of a complex. Several of the reaction solutions in which the reduction of platonic chloride was inhibited were kept at 0° for several months in an attempt to effect the crystallization of any complex that might have formed in the solutions. No crystals were obtained. Attempts to induce crystallization by supercooling the solutions in a Dry Ice bath were fruitless.

Kharasch and Ashford outlined a fairly general procedure for preparing the olefin platinous chloride complexes which are stable at room conditions.⁶⁷ In order to test the procedure, cyclohexene platinous

chloride, $\text{C}_6\text{H}_{10}\text{PtCl}_2$, was prepared in good yield by treating 1 g. of platinum(IV) chloride with 1.3 ml. of dry cyclohexene in 15 ml. of glacial acetic acid. The desired compound precipitates out as it is formed. No reaction took place when nitrobenzene was substituted for cyclohexene.

b. Spectral studies. The absorption spectra of nitrobenzene, platinum(IV) chloride, and mixtures of these compounds were determined over the wavelength range 220-800 m μ . using ethanol as a solvent in an attempt to show the existence of a compound between platinum(IV) chloride and nitrobenzene. This approach to the problem proved to be of limited value because of the necessity of working with solutions in which the concentration of nitrobenzene was much lower than that required to inhibit the reduction of platinum(IV) chloride.

Platinum(IV) chloride absorbs strongly at wavelengths below 500 m μ . with no sharp maxima being observed. The intensity of the absorption increases as the wavelength decreases with a molar extinction coefficient of 4600 being attained at 220 m μ . Nitrobenzene absorbs strongly below 440 m μ . A maximum is exhibited at 259 m μ . with a molar extinction coefficient of 8200. No separated absorption maxima which would permit the study of one species without interference from the second species were found.

The only evidence for interaction between platinum(IV) chloride and nitrobenzene was obtained in absorption studies with a series of solutions which had the same platinum(IV) chloride concentration (0.009 M.) and varied nitrobenzene concentrations. The following ratios of volume of nitrobenzene to volume of ethanol were used in both the platinum solutions

and the standards: 0:25, 1:24, 5:20, and 10:15. Increased absorption was observed in the region 520-620 m μ . as the concentration of nitrobenzene increased. While the increase in absorption was rather small, the presence of a third species is indicated.

6. Inhibition by Other Compounds

Benzene, cyclohexene, and nitroethane also inhibit the reduction of platinum(IV) chloride when present in high concentration.

7. Conclusions

The inhibition of the hydrogen reduction of platinic chloride by nitrobenzene is due to a weak association between the two compounds rather than to the formation of a stable complex. The inhibition effect is weakened upon increasing the temperature and upon increasing the hydrogen pressure with the latter being completely effective. The reduction of platinum(IV) chloride in pure nitrobenzene is not explained by the data obtained. When diluted with ethanol, the solution of platinum(IV) chloride in pure nitrobenzene yielded solutions with a darker yellow color than that of similar solutions prepared by diluting ethanol solutions of platinum(IV) chloride with nitrobenzene. This fact indicates that colloidal platinum(IV) chloride or even free platinum may be present.

The hydrogenation of nitrobenzene takes place only by a heterogeneous mechanism on the surface of the reduced platinum. The hydrogenation reaction did not occur in the absence of the platinum under the conditions used in this study. The homogeneous activation of molecular hydrogen in the platinic chloride-nitrobenzene system does not appear

feasible because of the apparent absence of a compound between these molecules which is capable of activating a hydrogen molecule.

D. Summary

The hydrogen reduction of platinum(IV) chloride and chloroplatinic acid to platinum in ethanol was investigated in ethanol solution. The free platinum metal was shown to be catalytically active in the hydrogenation of nitrobenzene at 30° with hydrogen at atmospheric pressure. The reduction of the platinum compounds was shown to be inhibited by high concentrations of nitrobenzene, nitroethane, benzene, and cyclohexene.

No evidence was found to confirm definitely the existence of a platinum chloride-nitrobenzene compound in ethanol solution. The homogeneous activation of molecular hydrogen by platonic chloride for the reduction of nitrobenzene was not observed.

APPENDIX III

STUDIES WITH RANEY COBALT CATALYST⁵⁶

A. Introduction

Smith, Chadwell, and Kirsliis measured the surface area and catalytic activity of Raney nickel as functions of the amount of dissolved hydrogen in the catalyst.⁶⁸ They found that Raney nickel contained from 92 to 157 standard milliliters of hydrogen per gram of catalyst and that the catalytic activity of the catalyst toward the hydrogenation of benzene at 80° decreased linearly with the removal of the hydrogen upon evacuation of the catalyst. They also found that the surface area of the catalyst, as measured by the chemisorption of palmitic acid from benzene solution, decreased slowly as hydrogen was removed from the catalyst.

In the present work, Raney cobalt was studied from the standpoint of its hydrogen content, its surface area, and its catalytic activity.

B. Experimental

1. Preparation of Raney Cobalt

Raney cobalt alloy was supplied in a powder form by the Raney Catalyst Company, Chattanooga, Tennessee. Fifty grams of the alloy, which contained 40 per cent cobalt and 60 per cent aluminum, was leached with a solution of 200 g. of reagent sodium hydroxide in

1 l. of distilled water. The reaction mixture was digested for one hour at 50° with constant stirring. The catalyst was transferred to a washing tube. The washing operation was performed by passing 8 l. of distilled water through the apparatus while the catalyst was being stirred. The wash water was saturated with hydrogen for fifteen minutes prior to its use.

The catalyst was removed from the washer and washed five times with absolute ethanol by centrifugation and decantation. The ethanol washings were cloudy. The catalyst was stored under ethanol at 0°.

Raney cobalt is easier to wash free of alkali than is Raney nickel. The wash solution was neutral to phenolphthalein after 1 l. of water had passed through the washer. Often 10-12 l. was required to remove the alkali from Raney nickel.

2. Palmitic Acid

Eastman white label palmitic acid was used in the adsorption studies.

3. Behenic Acid

Behenic acid was prepared from erucic acid by catalytic hydrogenation. The crude product was purified by recrystallization.

4. Benzene

LaPine thiophene-free benzene was purified according to the procedure given in Chapter II, Section B.

5. Determination of Dissolved Hydrogen

A description of the apparatus and the technique employed is given in the author's M.S. thesis⁶⁹ and in the paper by Smith, Chadwell, and Kirsliis.⁶⁸

6. Adsorption of Fatty Acids

The adsorption of palmitic acid and behenic acid on Raney cobalt was measured at 25° according to the method outlined by Smith and Fuzek.⁴³

7. Hydrogenation of Benzene

The apparatus and technique employed in carrying out the hydrogenation of benzene on Raney nickel were used in the study of Raney cobalt.^{68,69}

C. Experimental Results and Discussion

1. Hydrogen Content

Raney cobalt has less dissolved hydrogen than does Raney nickel. The volume of dissolved hydrogen in Raney cobalt ranged from 40 to 70 standard milliliters of hydrogen per gram of cobalt. Also, the hydrogen in Raney cobalt is held more strongly as is evidenced by the fact that evacuations of the catalyst for thirty minutes at room temperature will remove only 6 per cent of the total dissolved hydrogen. The remaining hydrogen is removed by heating the catalyst in the evacuated tube with a Bunsen flame. The residual hydrogen after this treatment was determined by weighing the water formed in the oxidation of the decomposed catalyst with pure oxygen. The results showed that 99 per cent

of the original dissolved hydrogen is removed.

Raney cobalt does not "explode" when heated rapidly to 100° in vacuo as does Raney nickel. A slow liberation of hydrogen from Raney cobalt occurs under these conditions.

2. Catalytic Activity

Benzene is hydrogenated to cyclohexane on Raney cobalt with hydrogen at pressures above 500 psi. The reaction is slow at 120° and becomes rapid at 150°. The rate of the reaction is proportional to the hydrogen pressure and independent of the benzene concentration when a freshly-prepared sample of Raney cobalt is used. As the catalyst ages, the kinetic behavior becomes more complex with deviation from the strictly first-order kinetics.

The first order reaction rate constant, k , is defined by the following equation:

$$-\frac{dn}{dt} = k w P_H$$

where dn/dt is the rate of change of the number of moles of hydrogen; w is the weight of Raney cobalt added; and P_H is the hydrogen pressure. The constant, k , has a value of approximately 6×10^{-5} moles of hydrogen/(min., psi. H_2 , g. catalyst) at 150°.

The apparent activation energy of the reaction was determined by the Variable Temperature Method as outlined by Kirsliis.⁴² A value of 23 kcal. mole⁻¹ was obtained over the temperature range 155-180°.

Conley found that a catalyst composed of 90 per cent cobalt oxide and 10 per cent copper oxide was active in catalyzing the hydrogenation of long chain fatty acids to alcohols.³⁸ An attempt was made during the present study to hydrogenate five grams of lauric acid to dodecanol-1 on 0.3 g. of Raney cobalt. The reaction mixture was held at 300° under a hydrogen pressure of 2300 psig. for four hours without a detectable decrease in the hydrogen pressure. Dark, resinous products were obtained. Raney cobalt appears to be ineffective as a catalyst for the hydrogenation of acids to alcohols. A study should be made to determine its usefulness in the hydrogenolysis of the methyl or ethyl esters of fatty acids.

3. Adsorption of Fatty Acids

A study was made of the adsorption of palmitic acid from benzene solution on Raney cobalt at 25°. Accurate data were not obtained because of the contamination of the benzene solution by a cobalt compound which is formed during the adsorption process. The compound is probably a cobalt soap, *i. e.*, cobalt palmitate. The blue compound was present in the benzene solution in the largest amounts when the concentration of palmitic acid was high.

Behenic acid, $\text{CH}_3-(\text{CH}_2)_{20}-\text{COOH}$, was substituted for the palmitic acid, $\text{CH}_3-(\text{CH}_2)_{14}-\text{COOH}$, in an attempt to reduce the solubility of the cobalt soap. Behenic acid is less soluble in benzene than palmitic acid. Also, oxygen was removed from the adsorption tubes with argon prior to shaking the Raney cobalt with the benzene solution of behenic acid.

Little contamination of the benzene solution with the cobalt soap of behenic acid took place. A relatively smooth adsorption isotherm was obtained (See Figure 22). The plateau obtained with equilibrium acid concentrations above 0.0044 M. is good evidence that behenic acid is adsorbed on the Raney cobalt in a unimolecular layer.

The surface area of the Raney cobalt was calculated with the assumptions (1) that only the carboxyl group is attached to the surface with the alkyl radical extending out perpendicularly to the surface, and (2) that the carboxyl groups completely cover the surface. Using a value of 20.5 square angstrom units for the cross section area of fatty acid molecules,⁷⁰ a value of 15.6 square meters per gram was calculated for the surface area. A surface area of 18-22 square meters per gram is normally obtained by the adsorption of palmitic acid on Raney nickel.

4. Aluminum Content of Raney Cobalt Catalyst

The total aluminum content of Raney cobalt catalyst was determined by the method of Willard and Tang.⁷¹ A value of 3.31 ± 0.04 per cent aluminum was obtained for the catalyst prepared by leaching the alloy in a single alkali solution for thirty minutes. The amount of aluminum in the catalyst is reduced to 2.76 ± 0.11 per cent by treating the alloy with several batches of fresh alkali solution for ten-minute periods. The aluminum content of Raney nickel is 10-12 per cent.⁶⁸

D. Summary

The hydrogen content of Raney cobalt catalyst was determined by measuring the volume of hydrogen liberated upon heating the catalyst

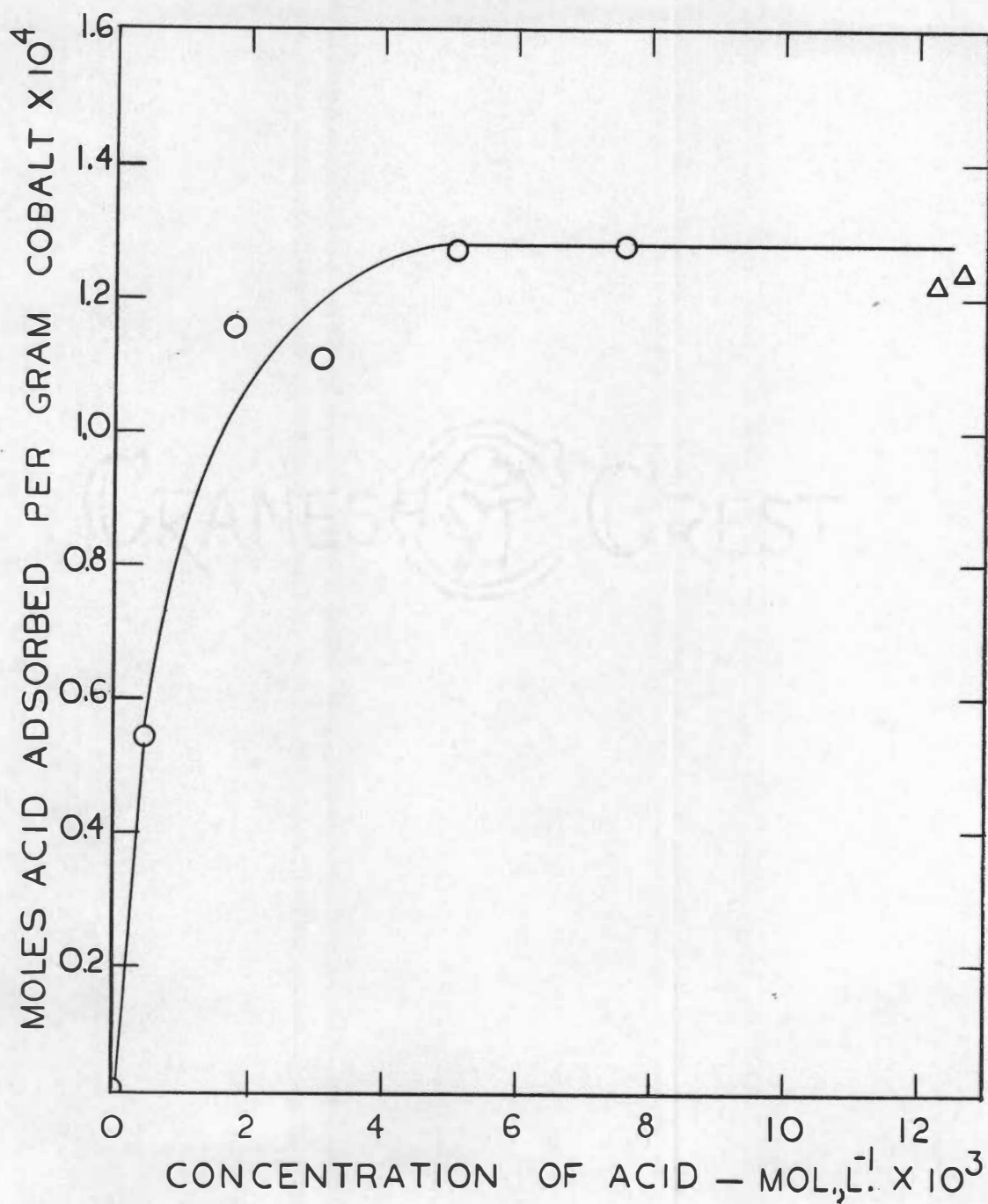


Figure 22. The moles of acid adsorbed per gram of Raney cobalt as a function of the equilibrium concentration of acid for the adsorption of behenic acid and palmitic acid on Raney cobalt from benzene solution at 25°. Behenic acid: ○. Palmitic acid: Δ.

in vacuo. The volume of dissolved hydrogen is 40-70 standard milliliters per gram of catalyst. Raney cobalt is active in catalyzing the hydrogenation of benzene above 120°. Its activity in this reaction is much less than that of Raney nickel catalyst. Raney cobalt is unsatisfactory as a catalyst for the hydrogenation of lauric acid to dodecanol-1.

The surface area of Raney cobalt is 15.6 square meters per gram as determined by the adsorption of behenic acid from benzene solution. Palmitic acid is unsuitable for determining the surface area of Raney cobalt because the formation of a benzene-soluble cobalt soap interferes with the analytical method.

GRANES & CREST

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He entered the University of Tennessee in September 1949 and was graduated with the degree of Bachelor of Science in Chemistry in August 1953. As an undergraduate he was elected to membership in Phi Kappa Phi and the Society of the Sigma Xi. He was recipient of the Armed Forces Chemical Association Award, the Student Medal of the American Institute of Chemists, and the Outstanding Chemistry Senior Award from the East Tennessee Section of the American Chemical Society. He was employed on a part-time basis from April 1950 to August 1953 by the Rhenium Research Laboratory where, under the direction of Dr. A. D. Melaven, he engaged in the production and study of the element rhenium and some of its compounds.

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