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A Study of the Catalytic Hydrogenation of Methoxybenzenes Over Platinum and Rhodium Catalysts

Robert Gene Thompson
University of Tennessee, Knoxville

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To the Graduate Council:

I am submitting herewith a dissertation written by Robert Gene Thompson entitled "A Study of the Catalytic Hydrogenation of Methoxybenzenes Over Platinum and Rhodium Catalysts." 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.

Hilton A. Smith, Major Professor

We have read this dissertation and recommend its acceptance:

Ron Boarts, M. J. Jovicich, H. Johnson

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

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

August, 1956

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R M Boarts
M J Joncich
H Johnson
C A Buehler

Accepted for the Council:

Dean of the Graduate School

A STUDY OF THE CATALYTIC HYDROGENATION OF METHOXYBENZENES OVER PLATINUM AND RHODIUM CATALYSTS

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

Robert Gene Thompson

August, 1956

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CHAPTER I

INTRODUCTION: HISTORICAL AND THEORETICAL

A. Aromatic Ether Hydrogenations and Cleavages

1. Chemical Cleavage

It has been recognized for many years that the carbon-oxygen bond in ether linkages may undergo fission under a number of conditions. Perhaps the best-known cleavage reaction is the chemical cleavage induced by acidic reagents. Since the oxygen atom of an ether can serve as a base, it is expected that acidic reagents would induce cleavage *via* the oxonium intermediate. Aliphatic and aromatic ethers have been observed to undergo this bond rupture in strong mineral acid media, the most common reagents being concentrated hydriodic acid or constant boiling hydrobromic acid. For example, guaiacol is converted to catechol in 87 per cent yield by constant boiling hydrobromic acid.[1]

Certain aromatic ethers may also undergo chemical cleavage under the influence of strong *alkali*. This reaction occurs only when the aromatic ring of the ether contains strong electron-attracting groups *ortho* or *para* to the ether group, i. e., ethers of strongly acidic phenols. Anisole reacts very sluggishly with alkalies even at 180-200°, whereas 2,4-dinitroanisole is converted to 2,4-dinitrophenol by alcoholic potassium hydroxide.[2] It should be noted that this cleavage, as well as those in acidic media, does not involve the carbon-oxygen bond adjacent to the aromatic ring.

Schwenk[3] has shown that methoxyl groups can be cleaved from certain aromatic rings by boiling the ether with nickel-aluminum alloy in the presence of 10 per cent sodium hydroxide. As in the cleavage by alkali alone, this reaction takes place only with methyl ethers derived from strongly acidic phenols. For example, neither anisole, the methylanisoles, nor m-methoxybenzoic acid undergo cleavage; o- and p-methoxybenzoic acid give benzoic acid.[3]

2. Catalytic Hydrogenolysis

The ether cleavage with which this work is chiefly concerned involves the process of catalytic hydrogenolysis. In molecules in which a carbon-oxygen ether bond is β with respect to a carbon-carbon double bond, cleavage is quite easy. Such a linkage is shown below:

$$-\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}\cdots\cdots O-$$

The double bond may be a part of an aromatic ring as in benzyl alkyl ethers. That such an ether bond is labile is in agreement with the well-known fact that a double bond in the $\beta-\gamma$ position weakens carbon-oxygen, carbon-nitrogen, carbon-halogen, and other bonds throughout a wide series of compounds. For aromatic ethers, such a bond may be catalytically cleaved under conditions too mild for ring hydrogenation. For example, alkyl ethers of benzyl alcohol may be cleaved quantitatively to toluene and alkyl alcohol by use of palladium in alcohol solution.[4] Also, palladium will catalyze the reduction of α,α-dimethoxydiphenylmethane to diphenylmethane plus methanol.[5] This reaction is not observed for aliphatic acetals, illustrating the labilizing of the ether linkage by the β-double bond of the aromatic compound.

It is of interest to note that hydrogenolysis of a p-methoxybenzyl ether, using palladium in alcohol solution, gives only p-methoxytoluene and alkyl alcohol.[6] The methoxyl group on the aromatic ring is not cleaved under these conditions--conditions which are also too mild for ring hydrogenation.

The catalytic hydrogenolysis which has received less attention is that involving cleavage of methoxyl (and alkoxyl, in general) groups from aromatic nuclei during the hydrogenation or ring saturation of these compounds. Under the conditions necessary for catalytic hydrogenation, cleavage of the ether linkage is quite common. Despite this, little work has been done on the problem of methoxyl cleavage as such. Most of the literature articles simply relate that an ether group (or sometimes hydroxyl) of a certain compound was cleaved during hydrogenation.

The splitting of a methoxyl group may or may not be complete depending upon the catalyst, compound, and reaction conditions. Also, the cleavage of an aromatic methoxy compound may occur either on the carbon-oxygen bond adjacent to the ring or the corresponding bond involving the methyl group. Probably both cleavages occur in most cases, but the cleavage of the carbon-oxygen bond adjacent to the ring predominates. In fact, the latter cleavage is the only one reported for most hydrogenations of aromatic ethers. Cleavages involving the carbon-oxygen bond of the methyl group have usually been observed for high-temperature (200-250°) catalytic reactions. At these temperatures cleavage by mechanisms other than those found at lower temperatures are undoubtedly becoming important.

Ipatiev and Lugovoy[7] reported that hydrogenation of anisole in the presence of nickel (oxide) at 240° and 50 atmospheres gave 50 per cent hexahydroanisole plus some cyclohexane and cyclohexanol. Cleavage of the diethyl ether of catechol and the dimethyl ethers of resorcinol and hydroquinone was also found to accompany hydrogenation of these molecules. Ipatiev and Filipov[8], using the same conditions as above, found that diphenyl ether gave cyclohexane and cyclohexanol in addition to the expected dicyclohexyl ether. Skita and Brunner[9] reported that quinine, <u>dihydroquinine</u>, and quinidine lost methoxyl groups when hydrogenated at 40-45° using platinum. Skita and Rolfes[10] reported that ethoxyl groups are also split under similar conditions, ethoxyacetanilide giving hexahydroacetanilide.

Grave[11] found that 2-methoxypyridine absorbed 4 moles of hydrogen to give piperidine when the former compound was hydrogenated using platinum catalyst. The platinum black-catalyzed hydrogenation of <u>p</u>-methoxyphenylethylamine gave 81 per cent hexahydrophenylethylamine.[12]

Marty[13] has found that the hydrogenation of phenetole at 180° over nickel gave only cyclohexane and ethanol as cleavage products. The same reaction carried out at 250° gave some cyclohexanol also. Thus at higher temperatures one observes cleavage of both carbon-oxygen bonds in the phenyl alkyl ether.

Waser[14] found that splitting occurred for several phenyl alkyl ethers when hydrogenations were carried out at room temperature with platinum black as the catalyst. For anisole these workers reported about 50 per cent of the normal product, 30 per cent cyclohexane, and 10 per cent cyclohexanol. Ruggli[15] attempted to prepare 4-methoxycyclohexaneacetic acid by hydrogenation of p-methoxyphenylacetic acid over platinum, but he obtained principally cyclohexaneacetic acid. He also found that p-hydroxyanisole gave about 25 per cent cyclohexanol in addition to the expected product when nickel (oxide) was employed; platinum resulted in a greater amount of cleavage for the same hydrogenation.

Amatasu[16] has hydrogenated aromatic compounds containing hydroxyl, methoxyl, and the $-CCH_2O-$ linkage (as in safrole) using nickel at pressures of 50-60 atmospheres and temperatures of 140-200°. He concluded that the ease of cleavage of the carbon-oxygen bond is:

$$-OCH_2O- \rangle -OCH_3 \rangle -OH \cdot$$

Duzee and Adkins[17] have also studied the relative stabilities of various ether linkages with respect to hydrogenolysis over Raney nickel. These workers reported that the order of increasing stability of ether linkages is:

$$\text{Benzyl} \rangle \text{aryl-alkyl} \rangle \text{diaryl} \rangle \text{dialkyl.}$$

This order of stability was determined by observation of the temperature necessary for hydrogenolysis. As previously observed, these workers found that the benzyl ethers underwent cleavage at conditions too mild for catalytic hydrogenation. From the products isolated from the hydrogenation-hydrogenolysis of various phenyl alkyl ethers, it appears that the only cleavage involved the carbon-oxygen bond adjacent to the ring. However, a small amount of cleavage leading to cyclohexanols may have occurred without detection.

Levin and Pendergrass[18] have studied the effect of acidic and basic media on the cleavage of hydroxyl and methoxyl groups. For p-hydroxy- and p-methoxybenzoic acid in alcohol solution, at room temperature and using platinum catalyst, they observed 38 and 74 per cent cleavage, respectively, during hydrogenation. In weakly acidic ethanol the hydroxy compound exhibited 47 per cent cleavage, while only 22 per cent occurred in alkaline ethanol. The cleavage was also found to be greater in acetic acid than in ethanol. The cleavage product was cyclohexanecarboxylic acid in each case.

There are a few isolated examples of hydrogenations in which little or no cleavage of alkoxyl groups occurred. Skita and Rolfes[10] reported that hydrogenation of anisole and phenetole with colliodal platinum gave quantitative yields of the simple hydrogenated products. Also, Ruggli[15] found that Raney nickel at 100-120° and 160-180 atmospheres gave about 90 per cent of the simple hydrogenated product of p-hydroxyanisole. Nickel and platinum (oxides) catalysis resulted in extensive cleavage in this case.

B. Supported Catalysts

Since this research represents the first study of supported catalysts in this laboratory, it is of value to discuss briefly the functions of a catalyst support or carrier. For a detailed review, the reader may refer to Volume I of "Catalysis."[19] A catalyst support is defined by Innes as "a major catalyst constituent that serves as a base, support, carrier, or binder for the active constituent but which by itself has little, if any, catalytic activity." Some of the functions of a support are given below. 1. It serves as a framework for the catalytic component. The support may reduce shrinkage, lend physical strength, etc. in this capacity. 2. It may prevent sintering of the catalyst surface during a reaction by dissipating the heat of reaction over a much larger area than that of the active metal itself. 3. It may prevent catalyst poisoning during a reaction by selective adsorption of species which would cover the active metal. 4. It may increase the activity per unit weight of catalytic metal. This increase may be due to an increase in the number of available active sites or to a change in the electronic or crystal structure of the active constituent.

The nature of the support itself may vary widely depending upon the particular property desired in the final catalyst. Examples of widely used supports are alumina, silica, carbon, pumice, diatomaceous earths, and bauxite.

Little work has been done on the relative merits of supported and unsupported catalysts for ether hydrogenations. Duzee and Adkins[17] have reported that nickel supported on kieselguhr is superior to Raney nickel for hydrogenation of aromatic ethers with minimum cleavage. Nickel on kieselguhr gave a 42 per cent yield of dicyclohexyl ether from diphenyl ether[20] as compared with a negligible yield with Raney nickel. Zartman[21] has reported that 1,4-dimethoxybenzene gave 70 per cent 1,4-dimethoxycyclohexane when the hydrogenation was carried out with nickel on kieselguhr; almost none of this product was obtained by a Raney nickel hydrogenation.

Based on the work above, Duzee and Adkins state that supported catalysts are much better than the corresponding unsupported ones for catalytic hydrogenation without hydrogenolysis. This is not necessarily true, but depends on the nature of the support and other reaction conditions. For example, acidic supports such as silica promote dehydration or cleavage during high-temperature hydrogenations. Taylor, Rose and Alderson[22] have reported that acidic supports lead to hydrogenolysis during the dehydrogenation of cyclohexanol to phenol.

C. Rhodium Catalysis

It is beyond the scope of this work to include a review of the great amount of research done on the catalytic hydrogenation of aromatic compounds using platinum catalysts. However, the use of rhodium for reduction of aromatic rings is relatively new.

Zelinski[23] has reported that not only platinum, but also rhodium (also ruthenium and iridium) is excellently adapted to hydrogenation of the benzene ring. The catalysts used in this work were supported on asbestos. The activity of the rhodium appeared to be about the same as that of platinum. For the catalysts studied, it was found that rhodium and platinum were superior with respect to resistance to sintering at high reaction temperatures. Of the series platinum, rhodium, iridium, ruthenium, and palladium, only platinum and rhodium continued to catalyze the hydrogenation of benzene at 300-310°.

Zenghelis and Stathis[24] have reported that colloidal rhodium is superior to colloidal platinum for the reduction of many unsaturated molecules. They further stated that the rhodium-catalyzed reduction did not require an acidic medium, while for some of the platinum hydrogenations such a medium was necessary. Minacher[25] has found that 1 per cent rhodium on alumina and on carbon have about the same activity with respect to hydrogenation of benzene as do the corresponding platinum catalysts. Recently, workers at Baker and Company[26] (supplier of commercial catalysts) have shown that 5 per cent rhodium on alumina is effective for the reduction of many substituted aromatic and heterocyclic compounds. This catalyst was shown to be somewhat more active than 5 per cent platinum on alumina.

Hernandez and Nord, who worked with colloidal rhodium and rhodium on carbon, have some evidence that the mechanism for rhodium reductions may be different from that in platinum and palladium reductions. With rhodium supported on colloidal polyvinyl alcohol[27], they found that the rate of reduction of nitro groups attached to aromatic nuclei was dependent upon the electronic nature of other substituents on the aromatic ring. Also, the rate of hydrogenation of nitrobenzene over the colloidal rhodium was sensitive to pH; the reaction was not sensitive to pH when carried out over colloidal palladium.[28] The rate of dehydrogenation of isopropyl alcohol to acetone increased with addition of elemental sulfur. Catalytic hydrogenations and dehydrogenations are usually poisoned by sulfur.

D. Purpose of Present Research

1. Methoxyl Cleavage

As previously mentioned, most of the work that has been published on the cleavage of aromatic ethers does not deal with the ultimate nature of the phenomenon and the factors influencing it. There are sufficient data available for one to realize that the problem is complex and that both the existence and extent of cleavage are influenced by many factors. It was the purpose of this research to investigate as many of these factors as possible. It appeared that the nature of the catalyst, its physical structure as well as its chemical constitution, would be of prime importance. Also to be considered were the effects of temperature, solvent, and the structure of the compound being hydrogenated. An investigation of these factors would aid not only in the prediction of the course of a hydrogenation reaction, but also in control of the reaction for a desired product. It was hoped that some insight into the mechanism of cleavage might be obtained, as well as a further understanding of the difficult problem of heterogeneous catalysis.

2. Effect of Substitution on Reaction Rates

For many years this laboratory has been active in the study of the effect of substituents and substitution on the platinum-catalyzed hydrogenation of the benzene nucleus. It was desired to extend these data to include various methoxyl substituted benzenes and other catalysts. To compare the rates of hydrogenation of methoxybenzenes with the corresponding methylbenzenes was of particular interest.

CHAPTER II

EXPERIMENTAL

A. Materials

1. Adams Platinum Catalyst

This catalyst was prepared by essentially the same procedure as that given in "Organic Syntheses."[29] Two modifications of the procedure described by Adams were employed. After fusion of the platinum nitrate to platinum oxide, the mass was allowed to cool only until solidification occurred before addition of distilled water. Also, during filtration of the platinum oxide, the solid was washed with distilled water until the oxide tended to become colloidal. American Platinum Works platinum chloride and Merck Reagent Grade sodium nitrate were employed. Several batches of catalyst prepared in this manner were ground in an agate mortar and put through a 100-mesh sieve.

2. Rhodium oxide, 5 Per Cent Rhodium on Alumina, Rhodium Black, and 5 Per Cent Platinum on Alumina

These catalysts were used as obtained from Baker and Company, Inc., Newark, New Jersey. All catalysts were stored in glass bottles which were kept in a desiccator.

3. Acetic Acid

Glacial acetic acid, the solvent for most of the hydrogenations, was obtained by fractionation of du Pont C. P. glacial acetic acid through either a 5-ft. helix-packed column or an 8-ft. Vigreux column.

4. Benzoic Acid

Eastman white label (sublimed) benzoic acid was used without further purification.

5. Hydrogen

Commercial hydrogen obtained from the National Cylinder Gas Company was used without further purification. This hydrogen has been previously shown to be satisfactory for use in catalytic hydrogenations.

6. Anisole

Eastman white label material was fractionated through an 8-ft. Vigreux column and the fraction boiling at 152.4°/743 mm. was collected, n_D^{20} 1.5165.

7. 1,4-Dimethoxybenzene

Eastman white label material was purified by recrystallization from absolute ethanol. The melting point was 54.9-55.0°.*

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*All melting points were taken on an aluminum melting point block using Anscheutz thermometers.

8. 1,3-Dimethoxybenzene

Eastman white label material was fractionated in vacuo through an 8-ft. Vigreux column and the fraction boiling at 71.5°/15 mm. was collected, n_D^{25}1.3216.

9. 1,2-Dimethoxybenzene

Eastman white label material was fractionated in vacuo through an 8-ft. Vigreux column and the fraction boiling at 112.4-112.6°/28 mm. was collected, n_D^{25}1.5295.

10. 1,2,3-Trimethoxybenzene

This compound was prepared by the addition, with stirring, of a mixture of 1.0 mole of 2,6-dimethoxyphenol and 1.2 mole of methyl iodide to a solution of potassium hydroxide in methyl alcohol. After a reaction time of one hour, the methyl alcohol was removed from the reaction mixture by distillation. Aqueous sodium hydroxide was then added so that the trimethoxy compound could be steam distilled while any unreacted phenolic compound remained in solution. The steam distillation yielded a colorless oil that readily solidified upon stirring. The solid was again steam distilled from an aqueous sodium hydroxide solution after which it was further purified by recrystallization from dilute ethanol. The compound melted at 42.0-42.5°. A melting point of 47° has been reported.[30]

Anal.* Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.30; H, 7.37.

11. Cyolohexane

Mathieson (Coleman and Bell Division) cyclohexane was fractionated through an 8-ft. Vigreux column and the fraction boiling at 80.0° was collected, n_D^{20} 1.4262.

12. Phenol

Mallinckrodt U. S. P. phenol was fractionated *in vacuo* through an 4-ft. Vigreux column and the fraction boiling at 104.5°/48 mm. was collected. The colorless product was stored in a brown bottle in the dark.

13. Methoxytoluenes

Eastman white label *ortho-*, *meta-*, and *para*-methoxytoluenes were fractionated *in vacuo* through a 4-ft. Vigreux column. The fractions collected boiled at 85.6°/40 mm. (n_D^{15} 1.5197), 88.9°/40 mm. (n_D^{20} 1.5131), and 89.9-91°/43 mm. ($n_D^{19.3}$ 1.5120), respectively.

14. Methoxybenzoic Acids

Ortho-, *meta-*, and *para*-methoxybenzoic acids were purified by recrystallization from absolute ethanol. The *ortho* and *meta* isomers were Eastman white label materials; the *para* isomer was Fisher Scientific Co. C. P. material. The melting points for *ortho*, *meta*, and *para* isomers were 101.4-102.4°, 106.1-106.3°, and 184.8-186°, respectively.

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*All analyses were done by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

15. Cyclohexene

A sample of cyclohexene that had been previously purified by Louis H. Cross[31] was again fractionated through a 4-ft. Vigreux column and the fraction boiling at 81.0°/740 mm. was collected, n_D^{20} 1.4455.

16. Benzene

The benzene used was purified by A. Jack Chadwell, Jr. by fractionation of LaPine C. P. material through a 5-ft. helix-packed column. The fraction boiling at 79.5° was collected, n_D^{20} 1.5010.

B. Low-Pressure Hydrogenations

1. Apparatus and Procedure

A low-pressure Parr apparatus containing certain modifications which allowed more accuracy in the determination of reaction rates was used. The hydrogen pressure gauge employed was calibrated to the nearest quarter of a pound in order that pressures could be estimated to the nearest tenth of a pound. The standard hydrogen tanks provided were replaced with smaller tanks so that small samples could be hydrogenated with a relatively large drop in pressure. The volumes, including reaction bottles and connections, of the two systems used in this work were 1.24 and 1.97 liters.[32] The general procedure for carrying out a hydrogenation was the same as that previously described.[33]

The initial hydrogen pressures for each hydrogenation were 40-60 p.s.i.g. The changes in pressure during the course of the reactions were of the order of 5-15 p.s.i.

The reaction bottle of the apparatus was enclosed in a metal jacket through which water from a constant-temperature bath was circulated. This bath was maintained within 0.05° of the desired reaction temperature for most of the runs; the temperature never varied more than 0.1°. The constant-temperature bath did not contain a refrigeration unit. Thus for the runs at 20° the temperature was maintained by a combination of heating and circulation of the water from the main bath through a copper coil contained in an ice-water bath. In the summer this procedure was also necessary to maintain the bath at 30°. The rate of the water circulation was large enough that the temperature drop of the water returning to the bath was negligible. For the runs at 20°, 40°, and 50°, the solvent and reaction bottle were brought to the approximate temperature of that run before the bottle was placed in the apparatus. Then an additional time of five to ten minutes was allowed for temperature equilibrium while the bottle was being evacuated and filled with hydrogen. In almost every case shaking of the heterogeneous reaction mixture and timing began immediately after the vessel was filled with hydrogen. However, no pressure drop was noted when the apparatus was allowed to stand ten to twenty minutes before shaking.

Unless otherwise specified, 25 ml. of glacial acetic acid was used as the solvent in all runs. The weights of catalyst and acceptor were of the order of 0.05-0.30 g. and 0.9-2.0 g., respectively.

2. Calibration

In order that the amount of hydrogen absorbed in each hydrogenation might be determined, it was necessary to calibrate each hydrogenation apparatus. This was done by hydrogenating several weighed samples of benzoic acid which is known to absorb three moles of hydrogen for every mole of benzoic acid. The pressure drops for the absorptions of one mole of hydrogen, as calculated from the benzoic acid hydrogenation, were 197.5 and 324 pounds when the large and small tanks, respectively, were employed. Thus the ΔP for any hydrogenation could be related to the number of moles of hydrogen required to complete the reaction. Simple hydrogenation of any benzene nucleus would require 3.0 moles of hydrogen per mole of aromatic compound, while complete cleavage of the methoxyl group at the carbon-oxygen bond adjacent to the ring in addition to ring saturation, would require 4.0, 5.0, and 6.0 moles for mono-, di-, and trimethoxybenzenes, respectively. For a given hydrogenation run on a methoxybenzene, ring saturation is always complete; cleavage of the methoxyl group is not usually complete. Thus a value of 3.40 for anisole indicated complete ring hydrogenation accompanied by cleavage of 40 per cent of the methoxyl groups.

In order to allow for variation in catalyst activity for various batches of Adams platinum catalyst prepared, each batch was standardized with benzoic acid and referred to a common basis. Smith, Alderman, and Nadig[34] prepared several batches of Adams catalyst and measured the rate of hydrogenation of benzoic acid for each batch. The average value for the rate constant was 0.1120 l. min^{-1} which was taken as the standard. For the other catalysts, a single batch was used for the entire work.

In the determination of rate constants in heterogeneous catalysis it is important to remember that for a given shaking rate the amount of catalyst can only be varied over a limited range for which equilibrium exists. Otherwise, the rate of reaction is no longer proportional to the catalyst weight. The same is true, of course, for the choice of shaking rates with a given quantity of catalyst. In this work the rate of hydrogenation for each compound was found to be proportional to the catalyst weights used (approximately 0.05-0.1 g. for platinum; 0.05-0.3 g. for rhodium) at a shaking speed of about 250 cycles per minute. Also $k_{1.0}$ (the specific rate constant referred to one gram of catalyst) was found to be constant when the shaking rate was changed from 200 to 280 cycles per minute, the only two shaking rates used.

C. High-Pressure Hydrogenations

The Parr high-pressure bomb and shaker used have been described in detail by J. F. Fuzek[35] and S. S. Kirslis.[36] The bomb was a standard steel high-pressure bomb with an inside volume of 52.9 ml. The attached valve-block and 2000 p.s.i. Bourdon gauge had a volume of 11.8 ml. The gauge had been calibrated with a dead-weight tester by Kirslis. During shaking, the bomb had an oscillation of 46 cycles per minute through an angle of about ninety degrees. There was an electric heating coil in the shaker jacket by which the bomb could be either heated at a constant rate or maintained at some desired temperature. The bomb was fitted with a 3-inch deep thermocouple well. A calibrated iron-contantan thermocouple attached to a Leeds and Northrup portable potentiometer was used to measure the temperature of the bomb. The temperature could be measured to ±0.2.

After addition of the catalyst and acceptor to the bomb, it was sealed and the pressure gauge with valve attached. The bomb was then connected to a hydrogen tank and flushed twice with hydrogen from a pressure of about 1200 p.s.i. The bomb was then filled to about 1200-1400 p.s.i. and the valve closed. After testing the bomb for leaks by immersion in water, it was secured in the heater jacket. The thermocouple was inserted into the well and initial pressure and temperature readings recorded. For constant temperature hydrogenations, the bomb was heated to the desired temperature and shaking was begun. Pressure was recorded as a function of time during the hydrogenation. The bomb was maintained at the desired temperature by adjusting the heater voltage to a previously determined equilibrium voltage corresponding to that temperature.

For variable temperature runs, the bomb heater was maintained at a constant voltage which was above the equilibrium voltage for the highest temperature desired. The shaker was started when the temperature was a few degrees below the beginning of the desired range. Readings were then recorded of temperature, pressure, and time as the bomb was heated through about a forty degree temperature range with the hydrogenation taking place.

After completion of a run, the bomb was cooled to room temperature by immersion in water. The bomb was opened and the catalyst removed from the organic product by filtration.

It was found that catalyst decay or poisoning during a run could be considerably decreased by use of a glass liner. This glass liner was constructed of 15 mm. Pyrex tubing to which a ground-glass joint with plug was attached. A pinhole in the side of the liner permitted hydrogen to enter and maintain the same pressure inside the liner as that measured by the gauge.

D. Calculations

1. Constant Temperature Runs

As shown previously for the hydrogenation of benzene and various substituted benzenes, the kinetics for the methoxybenzenes were found to be first order with respect to hydrogen pressure, zero order with respect to concentration of hydrogen acceptor, and directly proportional to catalyst weight. These kinetics were obeyed for both the platinum and rhodium catalysts. For a heterogeneous reaction obeying these kinetics, the rate is given by:

$$-\frac{dn}{dt} = k'P \qquad (1)$$

where n is moles of acceptor, t is time, P is pressure, and k' is a constant.

For the ideal gas law:

$$P = \frac{nRT}{V} \qquad (2)$$

where R, T, and V are the gas constant, the absolute temperature, and volume, respectively.

For constant temperature and volume,

$$\frac{dP}{dt} = \frac{dn}{dt}\frac{RT}{V} \qquad (3)$$

Substituting the value of $\frac{dn}{dt}$ from equation (3) into equation (1) and rearranging:

$$-\frac{dP}{dt} = \frac{k''RT}{V}P \qquad (4)$$

where k'' is now the specific rate constant in moles atm^{-1} time^{-1}.

In order to compare the rate constants obtained with those previously calculated for various hydrogenations, specific rate constants were calculated from the expression given by Fuzek and Smith[32] in which RT is absorbed in the constant.

$$-\frac{dP}{dt} = \frac{k}{V}P \qquad (5)$$

where k is now given in liters time^{-1}.

This expression is correct when one is working at a constant and specified temperature, but is in slight error when used for comparison of rate constants at different temperatures and for calculation of activation energies. The error in an activation energy calculated from k is well within experimental error when one is dealing with short temperature ranges and when most of the hydrogen remains at room temperature even though the temperature of the reaction flask is changed.

Integration of (5) above gives:

$$\log P = \frac{-kt}{2.303V} + \log P_o \qquad (6)$$

To obtain values of k, the slope of the straight line obtained by plotting log P versus t was multiplied by -2.303 V. All rate constants were referred to 1.0 gram of catalyst ($k_{1.0}$) by dividing k by the catalyst weight.

Figure 1 shows a typical hydrogenation plot. In most cases a drift from linearity was observed after about 60-80 per cent reaction. This was due to catalyst poisoning which reduced the number of active spots. That this is due to poisoning and not to a deviation from zero order kinetics for acceptor was shown by two observations. First, the rate constants as determined from the linear portion of the plots were identical over a large range of initial acceptor concentration. For some of the preparatory hydrogenations requiring long periods of time, the reaction rate fell almost to zero long before absorption of the theoretical amount of hydrogen. A new addition of catalyst to the reaction mixture caused hydrogenation.

The amount of catalyst decay during a hydrogenation appeared to be less for the 5 per cent rhodium on alumina than for Adams platinum catalyst.

The Arrhenius equation, relating the change in rate constant with temperature is:

$$k = Ae^{-\Delta Ha/RT} \qquad (7)$$

Integrating,

$$\log k = \frac{-\Delta Ha}{2.303RT} + \log A \qquad (8)$$

where ΔH_a is activation energy, A is a constant, and the other symbols are as previously defined. Activation energies were determined from the slopes of the lines obtained by plotting log k versus $^1/T$. The reaction rates for these plots were determined at temperatures of 20°, 30°, 40°, and 50°. For a heterogeneous reaction true activation energies are obtained only for a zero order reaction. Since the reactions studied here are dependent upon hydrogen pressure, only apparent activation energies (and, indeed, rate constants) can be calculated. However, the deviation in true and apparent activation energies here involves only the heat of adsorption of hydrogen which should be approximately the same for a given catalyst regardless of the compound studied. Thus the relative activation energies for a series of compounds on a given catalyst should be the same as for a zero order reaction.

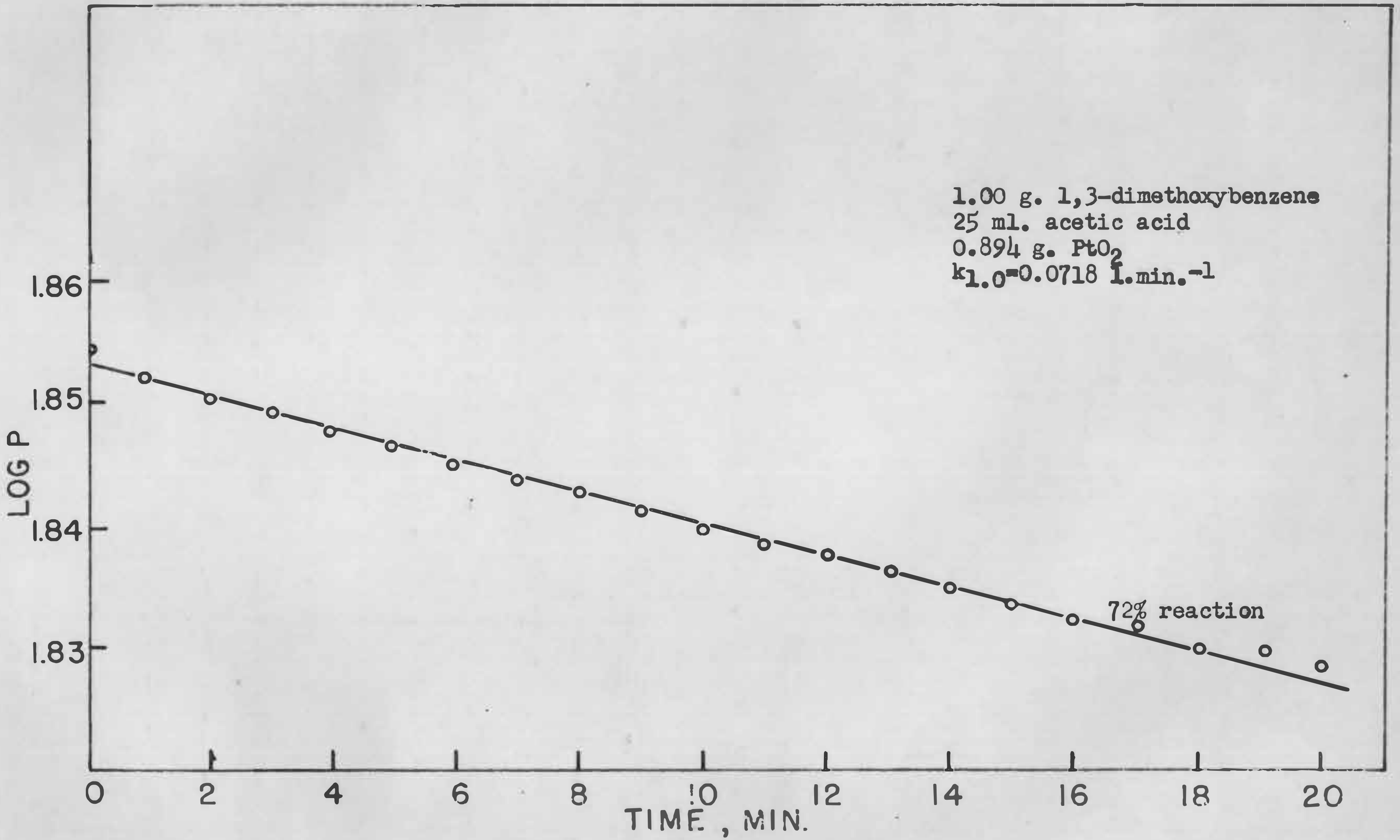

Figure 1.- Typical Low-Pressure Hydrogenation Plot.

2. Variable Temperature Activation Energy

Kirslis and Smith[36] have worked out a rapid method for determination of the activation energy for a reaction which is first order in hydrogen pressure and zero order in acceptor. The general method would be applicable for any reaction order with appropriate changes in the calculations. In this method reaction rates are measured at several temperatures while making only a single hydrogenation. Pressure, time, and temperature are recorded during a hydrogenation run in which the bomb is being heated at a constant and measured rate. The heater voltage during such a run is such that approximately one third of the original pressure remains by the time the temperature reaches the upper limit of the range of interest. A pressure *versus* time curve such as that shown in Figure 2 is obtained. Also shown in this figure is a plot of temperature *versus* time. From the latter plot one can find the temperature at any given time and corresponding pressure. Then by graphically determining the slope of the pressure-time curve at this temperature, one gets dP'/dt directly.

From equation (5):

$$k''' = -\frac{1}{P}\frac{dP}{dt}$$

where k''' is k/V.

The dP'/dt measured above must be corrected for the gas law increase in pressure with increasing temperature before the rate constant

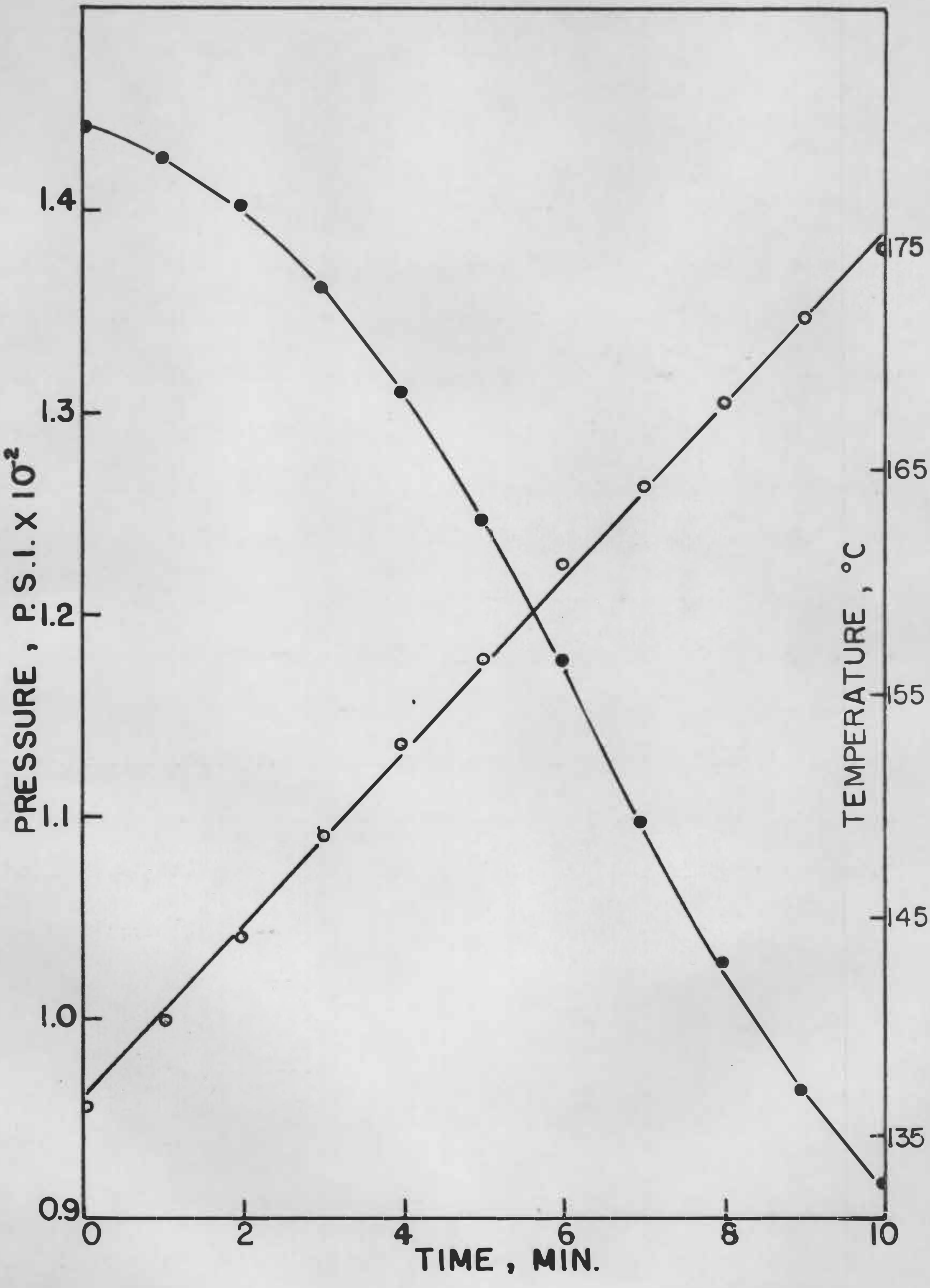

Figure 2.- Variable-Temperature Hydrogenation of 1,4-Dimethoxybenzene: ●, Pressure *vs.* Time; ○, Temperature *vs.* Time.

can be calculated. The correction term, $\frac{dP''}{dt}$, was determined from a blank run of acceptor and hydrogen with no catalyst present.

The final expression for the rate constant at a given temperature, k''', is:

$$k''' = -\frac{1}{P'}\frac{dP'}{dt} + \frac{1}{P''}\frac{dP''}{dt}$$

The units of k''' are min^{-1}.

Kirslis and Smith have shown that this method, while being much faster, is just as accurate as making several constant temperature runs. These workers have made a detailed study of other corrections that might be made to this method such as solubility of hydrogen in acceptor and deviation of hydrogen from ideal gas law. These corrections were found to be within experimental error.

For both the high-pressure and low-pressure runs, rate constants were usually reproducible within 5 per cent.

CHAPTER III

RESULTS AND DISCUSSION

A. Cleavages of Methoxybenzenes

1. Effect of Catalyst

As previously found by many investigators, the methoxyl group may be split from an aromatic nucleus during catalytic hydrogenation. The extent of cleavage was quite large when Adams platinum catalyst was employed. At 30°, anisole absorbed 3.40 moles of hydrogen per mole which corresponded to 40 per cent cleavage of the methoxyl group to give, finally, methanol and cyclohexane. Since most of the earlier work had shown that platinum promoted cleavage more than other catalysts such as Raney nickel, it was of interest to try new catalysts in the hope that they would catalyze the hydrogenation of the benzene ring with little cleavage of methoxyl groups. It was desired, at the same time, to obtain a catalyst sufficiently active to catalyze the hydrogenation at room temperature and atmospheric pressure.

Five per cent rhodium on alumina was found to catalyze readily the hydrogenation of the benzene nucleus at room temperature and ordinary pressures. With this catalyst anisole absorbed 3.06 moles of hydrogen per mole, corresponding to only 6 per cent cleavage. Thus the nature of the catalyst is very important in determining the amount of cleavage.

The hydrogenation of 1,4-dimethoxybenzene was carried out using platinum oxide, 5 per cent platinum on alumina, rhodium black, and 5 per cent rhodium on alumina. The rates of hydrogenation, as well as the amounts of cleavage, were measured. These data are presented in Tables I and II. These hydrogenations were made in order to compare: (1) the influence of the metal and/or support on the extent of cleavage, (2) the catalytic activity of platinum and rhodium, and (3) the catalytic activity of supported and unsupported catalysts.

From Table I it is seen that about 50 per cent of the methoxyl groups were cleaved during hydrogenation with the platinum catalysts, while only about 12 per cent underwent cleavage when rhodium was employed. Under the conditions here, it appears to be an intrinsic metal property that governs the amount of cleavage rather than a difference in surface properties of the catalyst. Supported and unsupported catalysts for each metal led to about the same amount of cleavage. Actually, it is possible for these particular catalysts that the alumina surfaces are covered with active metal so that each active surface is essentially the same for the supported and unsupported catalysts.

On a total weight basis, the pure metal catalysts are more active in each case. Adams platinum is almost six times as active as platinum on alumina; rhodium black is over twice as active as rhodium on alumina. The higher ratio for platinum is probably due to the fact that this catalyst is stored as the stable oxide before use, and the active metal

TABLE I

CLEAVAGE AND RATES OF HYDROGENATION FOR 1,4-DIMETHOXYBENZENE OVER PLATINUM AND RHODIUM CATALYSTS

Catalyst	$k^{a}_{1.0}(30^{o})$	Moles H_2/Mole Cpd.	$k_{sup.}/k_{unsup.}$
Adams Platinum	0.1604	4.05	0.17
5 Per Cent Platinum on Alumina	0.0280	3.92	
Rhodium Black	0.0764	3.05	0.47
5 Per Cent Rhodium on Alumina	0.0362	3.19	

[a] The $k_{1.0}$ is given per unit weight of total catalyst.

TABLE II

COMPARISON OF SUPPORTED AND UNSUPPORTED PLATINUM AND RHODIUM CATALYSTS

Catalyst	$k^{a}_{1.0}(30^{\circ})$	$k_{sup.}/k_{unsup.}$
Adams Platinum	0.1378	4.1
5 Per Cent Platinum on Alumina	0.5600	
Rhodium Black	0.0764	9.5
5 Per Cent Rhodium on Alumina	0.7240	

[a] The $k_{1.0}$ is given per unit weight of active metal.

is present only after reduction by hydrogen at the beginning of a hydrogenation.

When one compares the rates of hydrogenation on the basis of weight of catalytic metal, it is seen from Table II that the supported catalysts are much superior.

2. Point of Cleavage of Anisole

The cleavage of anisole at room temperature was shown to involve the carbon-oxygen bond adjacent to the aromatic ring; thus within experimental error all the cleavage led to methanol and cyclohexane. This is in agreement with earlier work on the cleavage of methoxybenzenes catalyzed by a number of catalysts.

A 0.252 mole sample of anisole plus 2 ml. of glacial acetic acid was hydrogenated at 25° and 3-4 atmospheres pressure using Adams catalyst. The mixture absorbed 3.16 moles of hydrogen per mole of anisole. This corresponds to 16 per cent total cleavage if all the cleavage involves the carbon-oxygen bond adjacent to the benzene ring. Any cleavage of the other ether linkage leading to methane and cyclohexanol would not be accurately detected by the pressure drop. One mole of hydrogen used for this cleavage would lead to 1 mole of methane.

After removal of the catalyst from the reaction mixture, the mixture was fractionated through a 2-ft. Vigreux column. The first fraction collected was an immiscible liquid pair boiling at 53.3°. Methanol and cyclohexane form an azeotrope boiling at 54.2°; this azeotrope contains 37.2 per cent methanol and 62.8 per cent cyclohexane by weight. After the first fraction, a mixture of cyclohexane and acetic acid was collected. The remainder of the distillation gave only methoxycyclohexane. There was no cyclohexanol (b.p. 161°) detected, the entire mixture being distilled except about 0.5-1.0 ml. hold-up in the column. The n_D^{20} was 1.4365 for this residue indicating a very slight amount of cyclohexanol may have been present; n_D^{20} is 1.4344 for methoxycyclohexane.[14]

The contents of the immiscible liquid pair were shown to be methanol and cyclohexane in the following manner. The mixture was extracted with two 10-ml. portions of cold water and the water solution fractionated. The first fraction boiled at 64.5°; n_D^{20} was 1.3290. For the organic layer, n_D^{20} was 1.4257 after drying over sodium hydroxide. The refractive indices are in agreement with accepted values for methanol and cyclohexane.

From the weights of cyclohexane and methanol obtained from the distillation, 21 per cent cleavage of anisole had occurred during the hydrogenation. This is in fair agreement with the value calculated directly from the drop in hydrogen pressure.

Waser[14] has reported the detection of 0.38 per cent methane in the gaseous mixture resulting from the hydrogenation of anisole at room temperature using platinum black. Some cleavage to methane and cyclohexanol was also shown by separation of reaction products. However, his catalyst was platinum black and caused 66 per cent cleavage of anisole compared to 40 per cent for Adams platinum in this work.

3. Effect of Temperature

The amount of cleavage of anisole and the dimethoxybenzenes was determined as a function of temperature over the range 20°-50°. These data are shown in Tables III and IV for platinum and rhodium, respectively. It is of interest to note that the amount of cleavage for the dimethoxybenzenes is a linear function of temperature over the range studied, increasing as the temperature increases. For both catalysts, the change in cleavage of anisole with temperature is negligible. The data for trimethoxybenzene seem to indicate that the amount of cleavage for this compound increases with temperature. Because of the scattering of the experimental points, however, one cannot conclude whether or not the cleavage is linear with temperature as observed for the dimethoxybenzenes. For the purpose of calculating the temperature coefficient, linearity was assumed. The "least-squares" slopes were used for this calculation. The scattering of the experimental points probably resulted from the fact that the rate of hydrogenation of this compound was extremely slow, and considerable catalyst poisoning occurred toward the end of the reactions. Poisoning was so pronounced in some runs that fresh catalyst had to be added to cause complete hydrogenation.

Plots of cleavage as a function of temperature are shown as Figures 3 and 4.

TABLE III

CLEAVAGE OF METHOXYL GROUPS OVER ADAMS PLATINUM AS A FUNCTION OF TEMPERATURE

Compound	Temperature				T coeff.[a]
	20°	30°	40°	50°	
Anisole	3.38[b]	3.40	3.36	3.40	0
1,2-Dimethoxybenzene	3.92	3.96	4.07	4.15	0.24
1,3-Dimethoxybenzene	3.95	4.01	4.11	4.18	0.23
1,4-Dimethoxybenzene	3.93	4.05	4.17	4.30	0.37
1,2,3-Trimethoxybenzene	3.95	4.31	4.20	4.27	0.26

[a] Change in moles of hydrogen absorbed per mole of acceptor for temperature change from 20° to 50° as determined from plots (Figure 3).

[b] Values are given in moles of hydrogen absorbed per mole of acceptor.

TABLE IV

CLEAVAGE OF METHOXYL GROUPS OVER 5 PER CENT RHODIUM ON ALUMINA AS A FUNCTION OF TEMPERATURE

Compound	Temperature				T coeff.[a]
	20°	30°	40°	50°	
Anisole	3.07[b]	3.06	3.04	3.02	0
1,2-Dimethoxybenzene	3.09	3.17	3.21	3.23	0.15
1,3-Dimethoxybenzene	3.25	3.35	3.51	3.59	0.39
1,4-Dimethoxybenzene	3.07	3.19	3.35	3.50	0.43
1,2,3-Trimethoxybenzene	3.32	3.34	3.49	3.47	0.18

[a] Change in moles of hydrogen absorbed per mole of acceptor for temperature change from 20° to 50° as determined from plots (Figure 4).

[b] Values are given in moles of hydrogen absorbed per mole of acceptor.

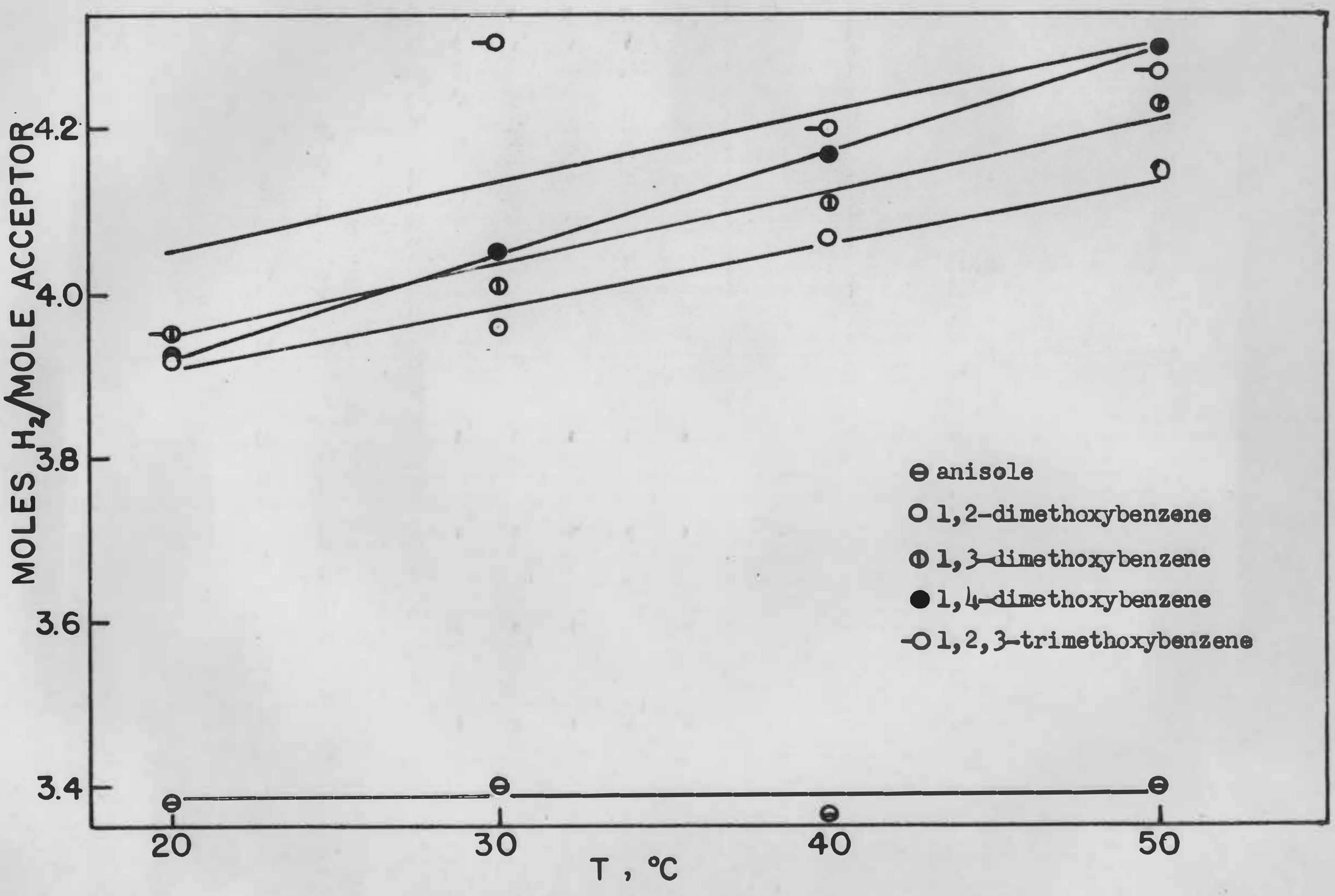

Figure 3.- Cleavage of Methoxybenzenes as a Function of Temperature for Hydrogenations over Adams Platinum.

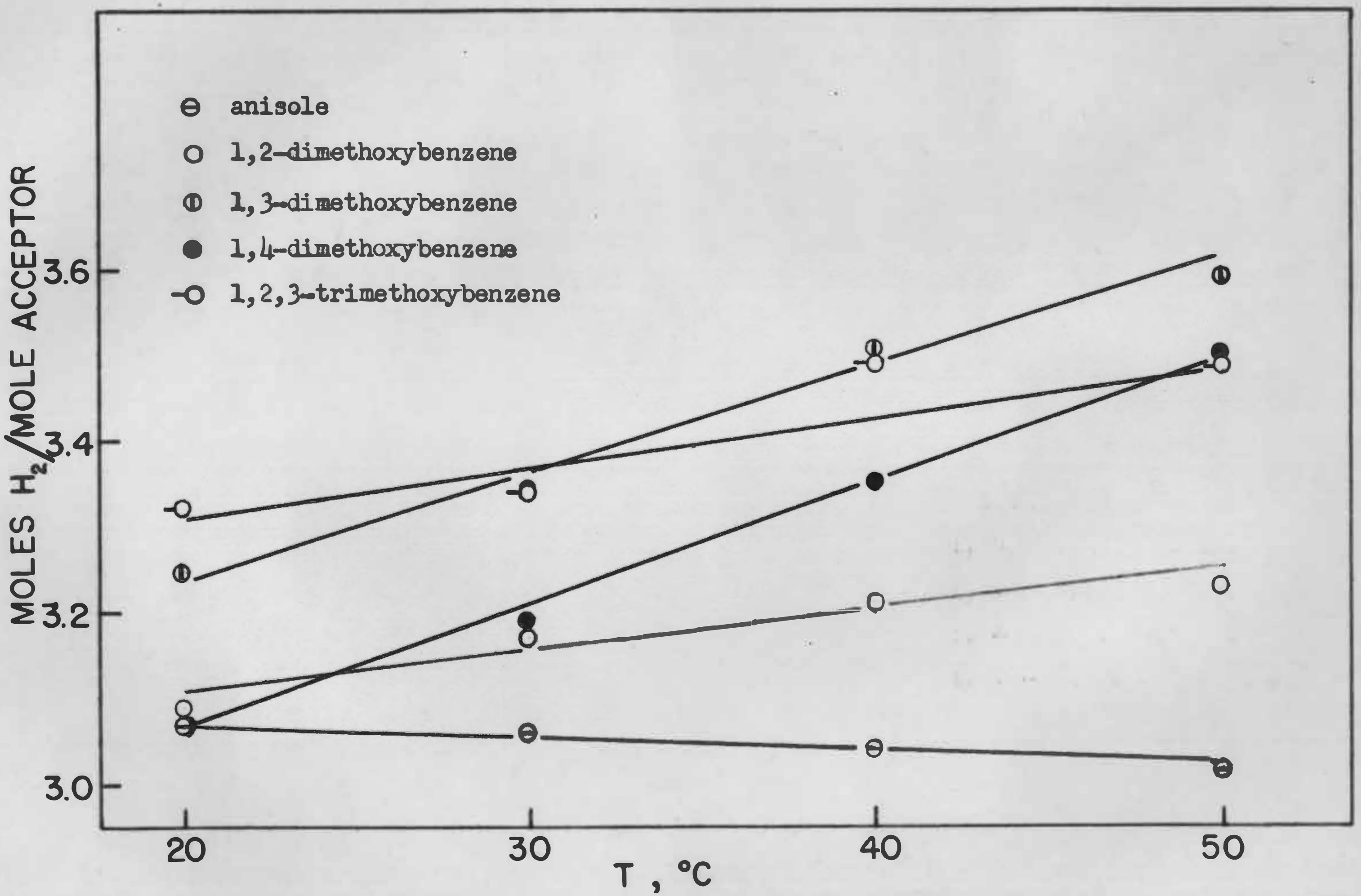

Figure 4.- Cleavage of Methoxybenzenes as a Function of Temperature for Hydrogenations over Rhodium on Alumina.

4. Effect of Acetic Acid

The cleavage of anisole appears to be dependent not only upon the catalyst and temperature, but also upon the amount of acetic acid used. This was shown by hydrogenations of anisole involving different acid concentrations. The hydrogenations were at 25° and 3-4 atmospheres. Rate constants and percentages of cleavage are shown in Table V.

This behavior is logical since acidic media are known to promote ether cleavages. Levin and Pendergrass[18] have observed that in the hydrogenation of p-hydroxybenzoic acid with Adams platinum a mixture of cyclohexanecarboxylic acid and 4-hydroxycyclohexanecarboxylic acid was obtained. They observed that acidic reagents increased the amount of cyclohexanecarboxylic acid while basic reagents reduced it.

It is also seen in Table V that the rates of hydrogenation vary slightly with the amount of acetic acid, the fastest reaction occurring for the greatest acetic acid concentration. The same reaction orders appear to be followed, however, for each acetic acid concentration. It has been shown by Keenan, Giesemann and Smith[37] that Adams platinum catalyst contains basic sodium salts or oxides. The platinum will not catalyze the hydrogenation of the aromatic ring unless the reaction is either carried out in an acid medium or the platinum oxide is washed free of base before use. The decrease in reaction rate observed here may result from a decreased catalytic activity due to incomplete removal of the basic constituents at lower acid concentrations.

TABLE V

EFFECT OF ACETIC ACID ON CLEAVAGE AND RATE OF HYDROGENATION OF 1,4-DIMETHOXYBENZENE OVER ADAMS PLATINUM

% Acetic Acid[a]	% Cleavage	$k_{1.0}$
7	16	0.0886
17		0.0926
67	21	
93	38	0.1280

[a] By weight.

5. Possibility of Ketone as Intermediate

It has been shown conclusively that the hydrogenation of phenol goes through the cyclohexanone intermediate. See CHAPTER III, Part E. Therefore, it was of interest to determine whether any ketone is present as an intermediate during the hydrogenation of anisole.

a. Room temperature hydrogenation of anisole using Adams catalyst. A mixture of 10.4 g. of anisole and 2 ml. of acetic acid was hydrogenated to 26.5 per cent completion. The reaction was then stopped and the partially hydrogenated mixture shaken with an excess of a saturated sodium bisulfite solution. No precipitation of ketone-addition product occurred after one hour of shaking. The mixture was allowed to stand for two days during which a small amount of solid separated. Qualitative tests showed this material to be only sodium bisulfite.

For the hydrogenation of phenol, the ketone addition product separated within five minutes of shaking with aqueous sodium bisulfite. It appears that no ketone is present as an intermediate during the hydrogenation of anisole under these conditions. This result is logical on the basis of the following considerations. First, if the reaction were to proceed through a ketone intermediate this would be expected to lead to complicated kinetics as is observed for phenol. Second, anisole and the dimethoxybenzenes hydrogenated at about the same rate as the corresponding methylbenzenes. Finally, the only cleavage products detected were methanol and cyclohexane. If before the hydrogenation there were appreciable hydrogenolysis to phenol and methane, one would then expect this phenol to undergo hydrogenation to cyclohexanol via cyclohexanone as found in the hydrogenation of pure phenol.

Waser[14] has hydrogenated anisole with platinum black as the catalyst and in the presence of semicarbazide hydrochloride. He reported that some semicarbazone of cyclohexanone was isolated; no values were given for the amount of semicarbazone, however. This reaction was repeated using Adams platinum catalyst. The reaction mixture absorbed 3.32 moles of hydrogen per mole of anisole compared to 3.40 moles for the hydrogenation with no semicarbazide present. The reaction carried out by Waser consumed 3.7 moles of hydrogen compared to 3.66 when anisole alone was hydrogenated. In this work the reaction rate was found to be the same for the two reactions: $k_{1.0}$ was 0.157 and 0.159 liters min.$^{-1}$ for reactions with and without semicarbazide, respectively.

From the above data it seems obvious that only a very small amount of semicarbazone of cyclohexanone could have been obtained by Waser. For each mole of cyclohexanone reacting with semicarbazide only 2 moles of hydrogen would be required. The small amount of ketone present undoubtedly resulted from some cleavage to phenol and methane under the conditions used by Waser.

b. High-temperature hydrogenation of anisole using rhodium (oxide) catalyst. Most high-temperature hydrogenations of aromatic ethers give a small amount of cleavage of the carbon-oxygen bond involving the alkyl group in addition to the usual cleavage adjacent to the aromatic ring. Thus one might expect some ketone intermediate via phenol if this cleavage precedes hydrogenation.

Using rhodium oxide and no solvent anisole was hydrogenated to 27.6 per cent completion at 144° and about 1300 p.s.i. initial pressure. The n_D^{20} for the partially hydrogenated mixture was 1.4928. A synthetic mixture of 27.6 mole per cent methoxycyclohexane (n_D^{20} 1.4340) and 72.4 mole per cent anisole (n_D^{20} 1.5165) gave an n_D^{20} of 1.4906. Thus it is seen that the reaction mixture probably contained almost entirely unreacted anisole and hydrogenated anisole.

The reaction mixture was then treated with an excess of saturated sodium bisulfite solution. After about five minutes of shaking a precipitate separated, indicating presence of some ketone in the reaction mixture. After the mixture had been allowed to stand for several hours for complete precipitation, the product was isolated as described for partially hydrogenated phenol (See part E). The addition product corresponded to 2 mole per cent cyclohexanone present in the reaction mixture. The product was shown to be the sodium bisulfite addition product of cyclohexanone by dissolving the solid in water and adding sodium carbonate. An oil separated and the mixture possessed the characteristic odor of cyclohexanone. The 2,4-dinitrophenylhydrazone melted at 157°-159° without recrystallization; the dinitrophenylhydrazone of cyclohexanone melts at 162°.[38]

The small amount of ketone observed in comparison with that in the phenol hydrogenation and the various factors discussed above rule out the possibility of a reaction proceeding principally through the ketone. It is assumed that under the reaction conditions used here a small amount of cleavage of anisole to phenol occurs. This phenol then undergoes hydrogenation to cyclohexanol via the ketone. The assumption that cleavage at these conditions for anisole results in some cyclohexanol is supported by the values for the refractive indices of completely hydrogenated anisole. These values were usually slightly higher than for pure methoxycyclohexane. For methoxycyclohexane n_D^{20} is 1.4344;[14] for cyclohexanol, n_D^{20} is 1.4667.[39]

It should be noted that this cleavage of the carbon-oxygen bond involving the methyl group apparently occurs before hydrogenation of the aromatic ring. Hydrogenation first to methoxycyclohexane followed by cleavage to cyclohexanol would not be expected to involve a ketone intermediate.

6. Effect of Structure

Tables VI and VII show the amount of cleavage of methoxyl groups for catalytic hydrogenation of methoxybenzenes, methoxybenzoic acids, and methoxytoluenes. It is apparent from these data that the catalyst is far more important in determining the extent of cleavage than the structure of the molecule hydrogenated. For each compound, the cleavage reaction was of considerable importance when the hydrogenation-hydrogenolysis was catalyzed by platinum; the cleavage reaction was of minor importance in the case of rhodium on alumina.

It appears that there is little or no electrical influence of substituents on cleavage. From a comparison of the platinum-catalyzed

TABLE VI

CLEAVAGE OF METHOXYL GROUPS AT 30° FOR LOW-PRESSURE HYDROGENATIONS OVER ADAMS PLATINUM

Compound	$\frac{\text{Moles } H_2}{\text{Mole Cpd. } (30^\circ)}$	$\frac{\text{Moles } H_2}{\text{Mole Methoxyl Group}}$
Anisole	3.40	0.40
o-Dimethoxybenzene	3.96	0.48
m-Dimethoxybenzene	4.01	0.50
p-Dimethoxybenzene	4.05	0.52
1,2,3-Trimethoxybenzene	4.31	0.44
o-Methoxybenzoic acid	3.43	0.43
m-Methoxybenzoic acid	3.39	0.39
p-Methoxybenzoic acid	3.64	0.64
o-Methoxytoluene	3.20	0.20
m-Methoxytoluene	3.35	0.35
p-Methoxytoluene	3.35	0.35

TABLE VII

CLEAVAGE OF METHOXYL GROUPS AT 30° FOR LOW-PRESSURE HYDROGENATIONS OVER 5 PER CENT RHODIUM ON ALUMINA

Compound	$\frac{\text{Moles } H_2}{\text{Mole Cpd.}}$ (30°)	$\frac{\text{Moles } H_2}{\text{Mole Methoxyl Groups}}$
Anisole	3.06	0.06
o-Dimethoxybenzene	3.17	0.08
m-Dimethoxybenzene	3.35	0.18
p-Dimethoxybenzene	3.19	0.10
1,2,3-Trimethoxybenzene	3.34	0.11
o-Methoxybenzoic acid	3.17	0.17
m-Methoxybenzoic acid	3.07	0.07
p-Methoxybenzoic acid	3.08	0.08
o-Methoxytoluene	3.00	0.10
m-Methoxytoluene	3.04	0.04
p-Methoxytoluene	3.00	0.00

hydrogenation of methoxybenzoic acids and methoxytoluenes in Table VI, it is seen that the carboxyl group does cause more cleavage than the methyl group. However, it is not apparent whether this is an electrical effect or one involving perhaps the relative sizes of the groups. Since the methoxyl group itself, while opposite in electrical influence on the aromatic ring, causes more cleavage than the methyl also, the effect is probably due to relative sizes of substituents. Also, it can be seen in Table VI that the *ortho* isomer usually undergoes less cleavage than the *meta* or *para*. This may be due to a slight steric inhibition of cleavage for the *ortho* isomer.

B. Saturated Methoxyl Compounds

In connection with the mechanism of methoxyl cleavage, it was of interest to determine whether the cleavage that accompanies hydrogenation of methoxybenzenes at room temperature would occur when the saturated methoxyl compounds were subjected to hydrogenation conditions.

Table VIII summarizes the runs made on saturated ethers. All the runs were made at room temperature, 3-4 atmospheres, and using Adams platinum. The platinum catalyst was chosen since this catalyst led to the most cleavage during hydrogenation of the aromatic ethers.

It is apparent from these data that the extensive cleavage (about 40 per cent for anisole and 50 per cent for the dimethoxybenzenes)

TABLE VIII

STABILITY OF SATURATED METHOXYL COMPOUNDS TOWARD HYDROGENOLYSIS

Compound	Solvent	Moles H_2/Mole Cpd.
1,4-Dimethoxycyclohexane	Acetic Acid	0.02
1,4-Dimethoxycyclohexane	Acetic Acid	0.07
1,4-Dimethoxycylohexane	Acetic Acid[a]	0.00
1,4-Dimethoxycylohexane	Cyclohexane	0.01
Methoxycyclohexane	Acetic Acid	0.02
Methoxycyclohexane	Cyclohexane	0.01

[a] No catalyst used.

which takes place during hydrogenation does not occur as a secondary reaction after ring saturation is complete. Although the data in Table VIII indicate that some cleavage of the saturated compounds occurred, this could be within experimental error. The pressure drops involved were quite small and the correction for the consumption of hydrogen for the reduction of platinum oxide represented a considerable percentage of the pressure drop. There is other evidence that the saturated ethers are stable toward hydrogen. For each hydrogenation the cleavage was never complete even though the reaction was continued until no further pressure drop occurred.

Adkins and Duzee[17] have shown that dihexyl ether, ethoxycyclohexane, methoxycyclohexane, 1,3- and 1,4-dimethoxycyclohexane, and various other cyclic ethers are stable toward hydrogen over Raney nickel at 200°. This temperature is sufficient to promote hydrogenation of the corresponding aromatic ethers with accompanying cleavage. For example, phenetole at 200° over Raney nickel gave 85 per cent ethoxycyclohexane, 15 per cent ethanol, and 5 per cent cyclohexane. Levin and Pendergrass[18] reported that 3-hydroxcyclohexanecarboxylic acid was recovered unchanged after shaking with hydrogen over Adams platinum for eight hours. Treatment of m-hydroxybenzoic acid under the same conditions gave cyclohexanecarboxylic acid in addition to the expected hydroxycyclohexanecarboxylic acid.

Evidence will be presented later to show that hydrogenolysis also does not precede the hydrogenation, or specifically, does not precede the rate-determining step of the hydrogenation.

C. Effect of Substitution on Reaction Rates

1. Polymethylbenzenes

For the platinum-catalyzed hydrogenation of methylbenzenes by Smith and Pennekamp,[40] it has been shown that as the number of adjacent substituents increase, the rate constants decrease, *e.g.*,

Acceptor	$k_{1.0}$ at 30°
benzene	0.288
toluene	0.180
o-xylene	0.093
hemimellitene	0.042
prehnitene	0.028
pentamethylbenzene	0.010
hexamethylbenzene	0.002

Also, for those compounds which have the same number of substituents, the one in which the arrangement is symmetrical has the highest rate, the vicinal isomer has the lowest rate, and the unsymmetrical isomer has an intermediate rate, *e.g.*,

Acceptor	$k_{1.0}$ at 30°
o-xylene	0.093
m-xylene	0.143
p-xylene	0.185
hemimellitene	0.042
pseudocumene	0.085
mesitylene	0.168

There exists an overlapping of these phenomena such that a symmetrical compound with a certain number of substituents has a higher rate than a vicinal compound with one less substituent, *e.g.*,

Acceptor	$k_{1.0}$ at 30°
toluene	0.180
p-xylene	0.188
o-xylene	0.093
mesitylene	0.168
hemimellitene	0.042
durene	0.053

It has been shown that symmetrical substitution rather than molecular symmetry is actually the important factor in influencing the rate.

2. Methoxybenzenes

a. Comparison of rates of hydrogenation of methoxybenzenes with those of methylbenzenes. There exists a striking similarity between the rates of hydrogenation of the methylbenzenes and the corresponding methoxybenzenes. It may be seen in Table IX that the rate constants of the methoxybenzenes reveal the same effect of symmetry, number of groups, etc. as for the methylbenzenes. The relative rates are not only in the same order, but fair quantitative agreement also exists. The somewhat slower rates for the methoxybenzenes are probably attributable to the difference in size of the methoxyl and methyl group.

It must be remembered that for the methylbenzenes only aromatic hydrogenation occurred with the absorption of 3 moles of hydrogen in

TABLE IX

COMPARISON OF RATE CONSTANTS AT 30° FOR HYDROGENATION OF METHYLBENZENES AND METHOXYBENZENES OVER PLATINUM

Compound	$k_{1.0}$	Compound	$k_{1.0}$	$\frac{k_{methyl}}{k_{methoxyl}}$
Anisole	0.1588	Toluene	0.1800	1.13
o-Dimethoxybenzene	0.0843	o-xylene	0.0932	1.11
m-Dimethoxybenzene	0.1013	m-xylene	0.1434	1.41
p-Dimethoxybenzene	0.1604	p-xylene	0.1882	1.20
1,2,3-Trimethoxybenzene	0.045	Hemimellitene	0.042	0.94

each case. However, for the methoxybenzenes, the absorption of hydrogen indicated about 50 per cent of the methoxyl groups had been cleaved from the ring. It appears that for either series the symmetry and number of groups govern the rate of formation of activated complexes of catalyst, acceptor, and hydrogen. In the case of the methoxybenzenes cleavage must then occur after the rate-determining step. The cleavage cannot take place to an appreciable extent before hydrogenation or a parallel between the behavior of methoxy- and methylbenzenes would not exist. If cleavage preceded the hydrogenation of anisole, for example, the products would be benzene and methanol. The rate of hydrogenation observed would then be that characteristic of benzene. Instead, anisole undergoes hydrogenation about one-half as rapidly as benzene which is approximately the same ratio observed for the hydrogenations of toluene and benzene. For both anisole and toluene, the aromatic substituent influences the rate of reaction markedly. Also, the clear-cut kinetics of zero order with respect to acceptor and first order with respect to hydrogen pressure seem to indicate that independent simultaneous hydrogenation and hydrogenolysis reactions do not exist.

There are some literature data which support the conclusion that hydrogenolysis does not precede the hydrogenation reaction, but occurs only during the hydrogenation of a particular aromatic ring. Stark[41] has studied the hydrogenation of β-methoxynaphthalene at 85° using Raney nickel. By adjusting the pH of the reaction mixture either aromatic ring of the substituted naphthalene could be hydrogenated selectively. In acid solution Stark obtained reduction of the unsubstituted ring to give 6-methoxytetralin without cleavage of the methoxyl group. When the reaction was carried out in basic solution, the substituted ring hydrogenated. The latter hydrogenation was accompanied by methoxyl cleavage to give tetralin as the final product. Thus methoxyl cleavage occurred only as a part of the hydrogenation reaction.

The rates of hydrogenation at 30° for the methoxybenzenes using 5 per cent rhodium on alumina show the same general effect of symmetry as observed for the corresponding compounds with platinum. However, the differences in rates for ortho-, meta, and para-dimethoxybenzenes are not nearly as pronounced as for platinum. Workers at Baker and Company[26] have reported that the three compounds hydrogenate at about the same rate over 5 per cent rhodium on alumina.

b. Activation energies. Tables X and XI show the hydrogenation rates as a function of temperature for methoxybenzenes. The activation energies were calculated from the "least-squares" slopes of activation energy plots. The activation energy plots are shown as Figures 5 and 6. For each compound the activation energy was greater for hydrogenation with the supported rhodium catalyst than for Adams platinum.

3. Methoxytoluenes and Methoxybenzoic Acids

The comparison of rates of hydrogenation of methoxy compounds with the corresponding methyl compounds was extended to include the three isomeric methoxytoluenes and methoxybenzoic acids.

TABLE X

REACTION RATES AND ACTIVATION ENERGIES OF METHOXYBENZENES FOR HYDROGENATIONS OVER ADAMS PLATINUM

Compound	T°C	$k_{1.0}$(l. min.$^{-1}$g.$^{-1}$)	H_a(Kcal. mole^{-1})
Anisole	20	0.1240	
	30	0.1588	
	40	0.1997	
	50	0.2481	4.36
1,2-Dimethoxybenzene	20	0.0579	
	30	0.0843	
	40	0.1125	
	50	0.1576	6.20
1,3-Dimethoxybenzene	20	0.0818	
	30	0.1013	
	40	0.1273	
	50	0.1736	4.58
1,4-Dimethoxybenzene	20	0.1193	
	30	0.1604	
	40	0.2277	
	50	0.3276	6.35
1,2,3-Trimethoxybenzene	20	0.023	
	30	0.045	
	40	0.074	
	50	0.117	9.44

TABLE XI

REACTION RATES AND ACTIVATION ENERGIES OF METHOXYBENZENES FOR HYDROGENATIONS OVER 5 PER CENT RHODIUM ON ALUMINA

Compound	T°C	$k_{1.0}$(l. min.$^{-1}$g.$^{-1}$)	H_a(Kcal. mole^{-1})
Anisole	20	0.0687	
	30	0.0876	
	40	0.1177	
	50	0.1537	5.10
1,2-Dimethoxybenzene	20	0.0210	
	30	0.0315	
	40	0.0456	
	50	0.0633	6.87
1,3-Dimethoxybenzene	20	0.0227	
	30	0.0360	
	40	0.0611	
	50	0.0896	8.73
1,4-Dimethoxybenzene	20	0.0226	
	30	0.0362	
	40	0.0559	
	50	0.0850	7.93

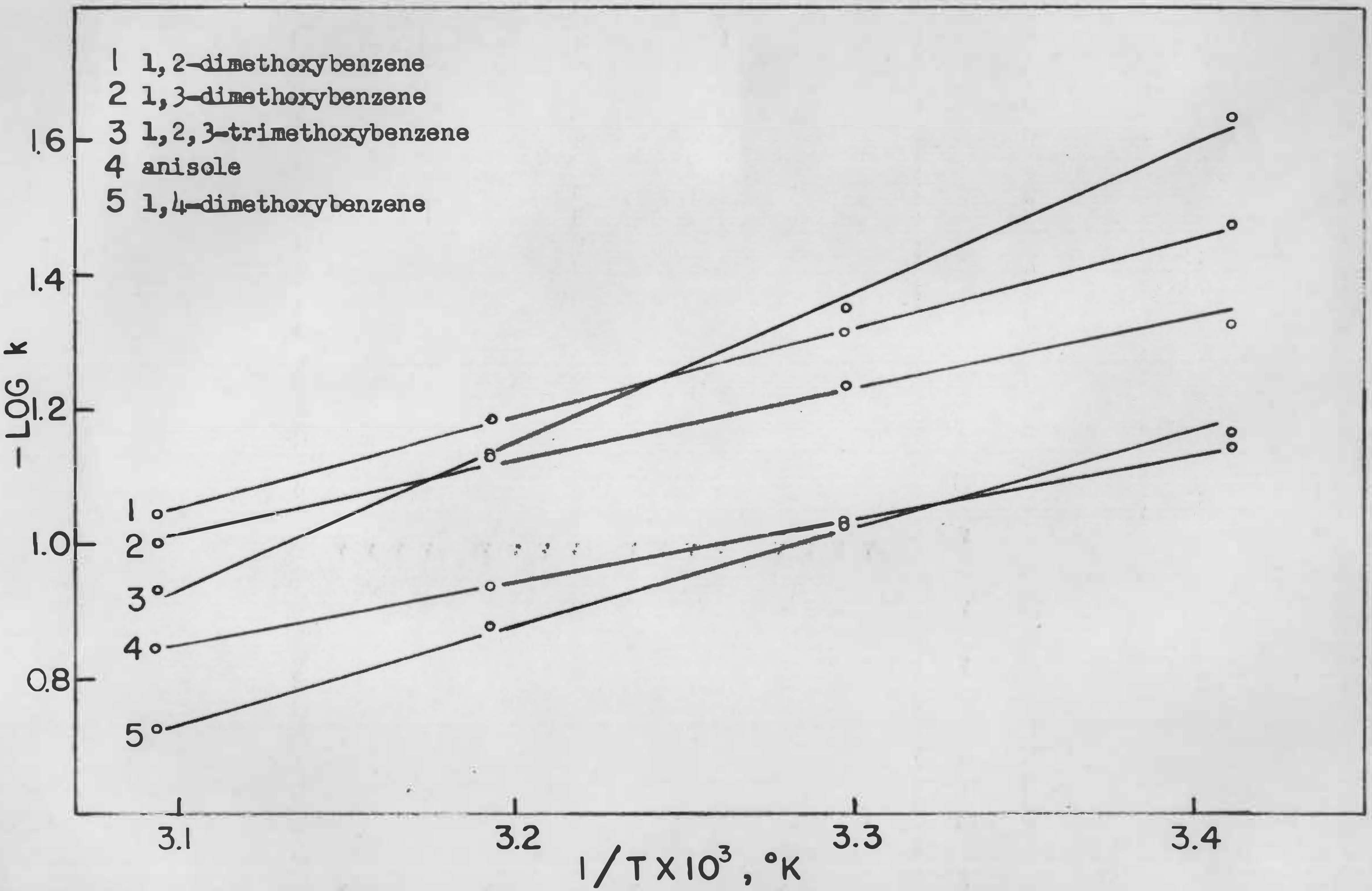

Figure 5.- Activation Energy Plots for Hydrogenations of Methoxybenzenes over Adams Platinum.

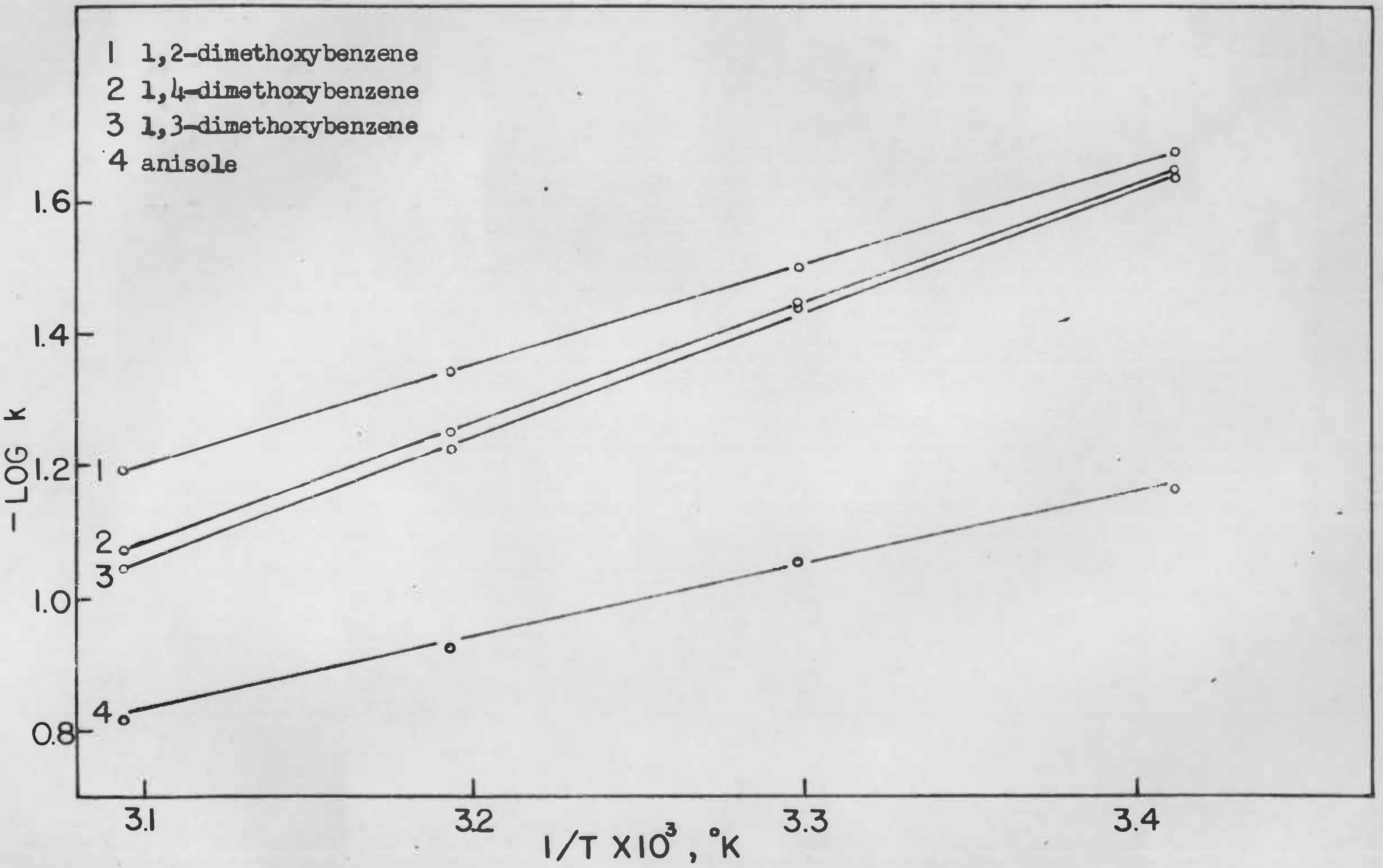

Figure 6.- Activation Energy Plots for Hydrogenations of Methoxybenzenes over Rhodium on Alumina.

a. Adams platinum catalyst. Table XII shows a comparison of the rates of hydrogenation of the methylbenzoic acids with the corresponding methylbenzenes. This work was done by Smith and Stanfield.[42] It is seen that replacement of a methyl group with a carboxyl group lowers the rate by approximately one half. This change in rates has been attributed to the larger size of the carboxyl group. The fact that benzoic acid, phenylacetic acid,[34] and even ethylbenzene all hydrogenate at about the same rate indicates that the effect is not electrical.

Table XIII shows the rates of hydrogenation of methoxytoluenes and methoxybenzoic acids and comparisons with the rates for methylbenzenes. It is seen that for the methoxyl compounds the same effects of symmetry and number of groups exist as for methylbenzenes and methylbenzoic acids. The ratios $k_{methyl}/k_{carboxyl}$ are essentially the same for the methoxyl compounds as for the methyl compounds shown in Table XII. Also, the ratios $k_{methoxyl}/k_{methyl}$ are essentially the same as those determined in this work for the comparison of methoxybenzenes and methylbenzenes (See Table IX). These data for the methoxybenzoic acids and methoxytoluenes furnish further confirmation that symmetrical substitution rather than molecular symmetry is the important factor in influencing rates.

It is of interest to note that the relative rates for the hydrogenations of methylbenzenes, methoxybenzenes and methyl- or methoxybenzoic acids are:

TABLE XII

COMPARISON OF RATE CONSTANTS AT 30° FOR HYDROGENATION OF METHYLBENZENES AND BENZOIC ACIDS OVER PLATINUM

Compound	$k_{1.0}$	Compound	$k_{1.0}$	$\frac{k_{methyl}}{k_{carboxyl}}$
Benzoic Acid	0.1120	Toluene	0.1800	1.6
o-Methylbenzoic Acid	0.0312	*o*-Xylene	0.0932	3.0
m-Methylbenzoic Acid	0.0813	*m*-Xylene	0.1434	1.8
p-Methylbenzoic Acid	0.0942	*p*-Xylene	0.1882	2.0

TABLE XIII

COMPARISONS OF RATE CONSTANTS AT 30° FOR HYDROGENATION OF METHYLBENZENES, METHOXYBENZOIC ACIDS, AND METHOXYTOLUENES OVER PLATINUM

Compound	$k_{1.0}$	Compound	$k_{1.0}$	$\frac{k_{methyl}}{k_{carboxyl}}$
Benzoic Acid	0.1120	Toluene	0.1800	1.6
o-Methoxybenzoic Acid	0.0591	o-Xylene	0.0932	1.7
m-Methoxybenzoic Acid	0.0903	m-Xylene	0.1434	1.6
p-Methoxybenxoic Acid	0.0945	p-Xylene	0.1882	2.0
				$\frac{k_{methyl}}{k_{methoxyl}}$
Anisole	0.1588	Toluene	0.1800	1.13
o-Methoxytoluene	0.0747	o-Xylene	0.0932	1.25
m-Methoxytoluene	0.1336	m-Xylene	0.1434	1.08
p-Methoxytoluene	0.1410	p-Xylene	0.1882	1.33

methylbenzenes $\rangle$ methoxybenzenes $\rangle$ methyl- or methoxybenzoic acids. The decrease in rates here parallels the increase in the size of the substituents.

b. Five per cent rhodium on alumina. Table XIV shows the rates of hydrogenation of the methoxytoluenes and methoxybenzoic acids for the rhodium catalyst. The effect of symmetry on the rate is the same (qualitatively) for this catalyst as for Adams platinum, *i.e.*, the rates are *para* $\rangle$ *meta* $\rangle$ *ortho*. Replacing the carboxyl group with a methyl group increases the rate approximately 2-2.5 times.

D. Rhodium Oxide as a Catalyst

1. Preliminary Work

Rhodium oxide, as commercially obtained, did not catalyze the hydrogenation of benzoic acid in glacial acetic acid at room temperature. The oxide as obtained was somewhat granular. However, grinding the material to a fine powder in an agate mortar did not change its behavior. Since no pressure drop was observed even at the beginning of the attempted hydrogenation, it appeared that the oxide was not reduced to catalytically active metal under the mild conditions used.

The oxide was heated in a steel bomb to 300° at about 1200 p.s.i. pressure of hydrogen. The rhodium thus obtained did catalyze the hydrogenation of benzoic acid at room temperature. Apparently reduction of the oxide to metallic rhodium had occurred at the elevated temperature. Even though this rhodium did catalyze the benzoic acid hydrogenation,

TABLE XIV

RATES OF HYDROGENATION OF METHOXYBENZOIC ACIDS AND METHOXYTOLUENES OVER 5 PER CENT RHODIUM ON ALUMINA

Compound	$k_{1.0}$	Compound	$k_{1.0}$	$\frac{k_{toluenes}}{k_{acids}}$
o-Methoxybenzoic	0.0096	o-Methoxytoluene	0.0230	2.40
m-Methoxybenzoic	0.0118	m-Methoxytoluene	0.0302	2.56
p-Methoxybenzoic	0.0227	p-Methoxytoluene	0.0432	1.90

the reaction was quite slow ($k_{1.0}$ (25°) 0.0003 l. min.$^{-1}$. Other reductions of the oxide at 240° and 200° gave values of $k_{1.0}$ of approximately 0.002. These hydrogenation rates are seen to be about sevenfold faster, illustrating the effect of high temperatures on catalytic activity. The reduction at 300° undoubtedly produced considerable sintering of the catalyst surface. In order to find the minimum temperature for reduction to catalytically active rhodium, a sample of oxide was heated slowly in the bomb while temperature and pressure were observed. A plot of pressure *versus* temperature showed a break at about 125° indicating that reduction occurred at this temperature.

The activity of prereduced rhodium was much lower than for the other catalysts studied, *e.g.*,

Catalyst	$k_{1.0}$(25-30°)
Adams platinum	0.1120
5 per cent rhodium on alumina	0.0285
rhodium (from oxide)	0.002

where the values of $k_{1.0}$ are given per gram of total catalyst weight. Since the catalyst gave such slow rates at room temperature and low pressure, further hydrogenations were carried out in the high-pressure bomb at temperatures of 125-150° and pressures of 1200-1600 p.s.i. For these reactions, there was an added advantage of not having to transfer the active catalyst from one system to another after preparation.

Before measuring reaction rates for rhodium (oxide) hydrogenations in the high-pressure bomb, it was necessary to determine the catalyst weight range for which the reaction rates were proportional to catalyst weight. For the hydrogenation of anisole, the most rapidly reacting compound studied, the rate was found to be proportional to catalyst weight for weights below about 40 milligrams.

2. Ether Hydrogenations

It was found that anisole and 1,4-dimethoxybenzene undergo hydrogenation readily in the bomb at temperatures of 125-150°. The rhodium (from oxide) was effective even in the absence of a solvent. This behavior is in contrast to Adams platinum catalyst which requires an acidic medium or special treatment of the catalyst before use to remove basic salts. The advantages of hydrogenations in absence of a solvent are obvious. If no side reactions occur the final product is obtained directly and in excellent purity. For hydrogenations of aromatic ethers such as anisole or 1,4-dimethoxybenzene, the absence of an acid medium should reduce methoxyl cleavage greatly.

The kinetics for the hydrogenations at high temperatures and pressures were the same as those observed for the low pressure and temperature work; namely, first order in hydrogen pressure and zero order in acceptor concentration. The kinetic behavior was the same for reactions run in solvents and in the absence of solvents. It was noted, however, that catalyst decay during a run was more pronounced for hydrogenations at high temperature and pressure than for those carried out under the milder conditions.

The activation energy for rhodium (oxide) catalyst was determined using the variable temperature method developed by Smith and Kirslis.[36] The acceptor was 1,4-dimethoxybenzene; no solvent was used. The slope of the activation energy plot (shown as Figure 7) gave a value of 22.8 Kcal. mole^{-1}. The activation energies for platinum (oxide) and rhodium on alumina at 20-50° were of the order of 4-8 Kcal. mole^{-1}. From a comparison of the rates of hydrogenation for rhodium (oxide) and these two catalysts at room temperature, it is obvious that rhodium (oxide) is not nearly as active. However, its activity increases much more rapidly with temperature by virtue of its higher activation energy.

Table XV lists other hydrogenations carried out with rhodium (oxide) in the bomb. From the refractive indices of the products, it appears that very little cleavage occurred for these hydrogenations in absence of acetic acid. For the hydrogenations of anisole, the refractive indices of the products were usually higher than the literature value for pure methoxycyclohexane. This probably indicates that slight cleavage to cyclohexanol (n_D^{20}1.4667) occurred. Cleavage leading to appreciable methanol and cyclohexane would have given a refractive index lower than that for methoxycyclohexane (n_D^{20}methanol is 1.3288; n_D^{20} cyclohexane is 1.4262). The cleavage to cyclohexanol <u>via</u> phenol was also indicated by the isolation of cyclohexanone from partially hydrogenated anisole. The average values for moles of hydrogen absorbed per mole of acceptor were 3.18 and 3.16 for anisole and 1,4-dimethoxybenzene, respectively. These values were calculated using the ideal gas equation and are not corrected for such things as the consumption of hydrogen

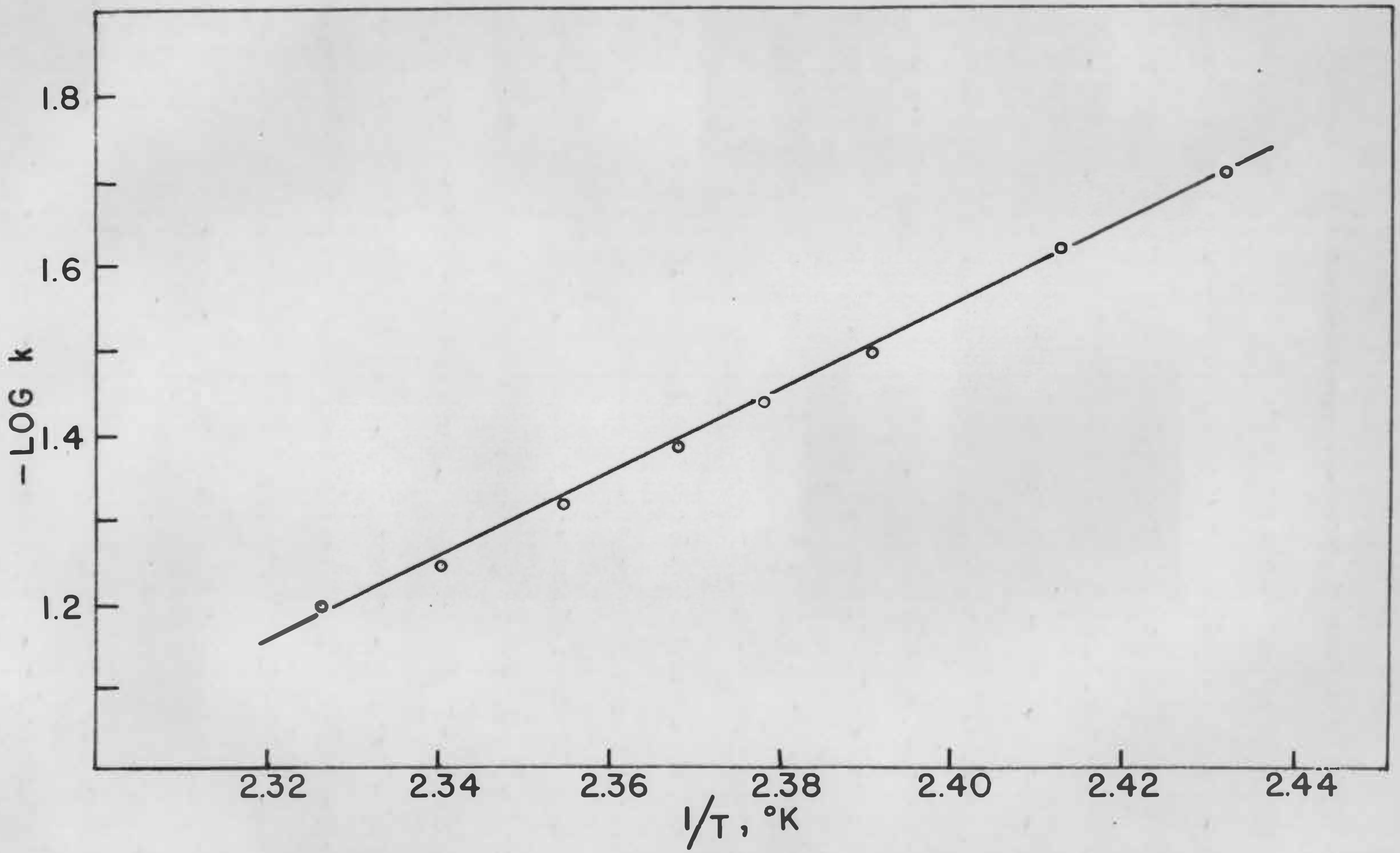

Figure 7.- Activation Energy for Variable-Temperature Hydrogenation of 1,4-Dimethoxybenzene over Rhodium (Oxide).

TABLE XV

HYDROGENATIONS OVER RHODIUM (OXIDE) IN HIGH-PRESSURE BOMB

Compound	T°C	$k_{1.0}$	Solvent	$\frac{\text{Moles } H_2}{\text{Mole Cpd.}}$	n_D^{20}(Prod.)
Anisole	133	0.3066	None	3.15	1.4340[a]
Anisole	125		None	3.21	1.4350
Anisole	170		None		1.4356
Anisole	130		None		1.4352
p-Dimethoxybenzene	144	0.0691	None	3.02	1.4468[b]
p-Dimethoxybenzene	145	0.0678[c]	None	3.32	1.4430
p-Dimethoxybenzene	140		None	3.23	
p-Dimethoxybenzene	143	0.0806	Cyclohexane		
p-Dimethoxybenzene	143	0.0766	Acetic Acid		
m-Methoxybenzoic Acid	133	0.0158	None		

[a] Literature n_D^{20} methoxycyclohexane is 1.4344.[44]

[b] Literature $n_D^{18.5}$ cis-1,4-dimethoxycyclohexane is 1.4440; $n_D^{18.5}$ trans-1,4-dimethoxycyclohexane is 1.4430.[43]

[c] By the variable temperature method.

for reduction of rhodium oxide and solubility of hydrogen in the organic phase.

The conclusion reached above that little methoxyl cleavage occurred for rhodium (oxide) hydrogenations in absence of acetic acid was checked by fractionation of the hydrogenation product of anisole. The product with n_D^{20} of 1.4352 (See Table XV) was fractionated through a 2-ft. Vigreux column. The initial equilibrium temperature of the distillate indicated that it was methoxycyclohexane. However, the first few drops of distillate that collected in the head were cloudy and had a n_D^{20} of 1.4336. This first fraction probably contained a small amount of methanol and cyclohexane which accounted for the cloudy appearance and the low refractive index. The trace of water (n_D^{20} 1.3330) resulting from the rhodium oxide reduction may also have contributed to this cloudy appearance and low refractive index. The distillation was then continued until the pot was dry, 88 per cent of the original mixture being collected. After the column cooled, the refractive index of the material held up in the column was measured. The n_D^{20} was 1.4482 indicating that a small amount of cyclohexanol was probably present. One can safely conclude from these data that less than 3-5 per cent cleavage of methoxyl groups occurred during the hydrogenation.

No attempt was made to determine whether the hydrogenation of 1,4-dimethoxybenzene gave the _cis_ or _trans_ isomer or a mixture. The _cis_ isomer is usually formed in catalytic hydrogenations, but subsequent isomerization may occur. For either case, however, the refractive indices are so close that it is apparent that very little cleavage occurred.

From the rate constants for anisole, 1,4-dimethoxybenzene, and m-methoxybenzoic acid, it is seen that the same order of reactivity exists as for 5 per cent rhodium on alumina at room temperature.

A comparison of the rates of hydrogenation of 1,4-dimethoxybenzene in absence of solvent with the corresponding rates in cyclohexane and acetic acid shows that the reaction is faster in the presence of a solvent. It is possible for the reaction carried out in absence of solvent that the large concentration of reactant molecules on or near the catalyst surface interfered with the approach of hydrogen, and thereby lowered the rate. This phenomenon is known as reactant poisoning. For the rhodium (oxide) catalyst, an acidic medium does not increase the reaction rate. In fact, the reaction is somewhat faster in inert cyclohexane than in acetic acid.

With the rhodium (oxide) catalyst and elevated temperatures, it is possible to hydrogenate compounds that are solids at room temperature without having to use a solvent. For example, m-methoxybenzoic acid melts at 106° and hydrogenates readily at 133°. This is not possible, of course, if the material is not stable above its melting point under the conditions used. An example of this is 2,2′-dimethoxybenzilic acid which decarboxylated at about 135°.

It was found that rhodium (oxide) would not catalyze the hydrogenation of 1,4-dimethoxybenzene in absolute methanol at temperatures up to 180°.

Rhodium black and 5 per cent rhodium on alumina did not catalyze the hydrogenation of 1,4-dimethoxybenzene in the absence of solvent at temperatures up to about 160°. Apparently these catalysts require an acidic medium as in the case of Adams platinum.

E. Hydrogenation of Phenol

It has been shown by Coussemant and Jungers[39] that the Raney nickel-catalyzed hydrogenation of phenol to cyclohexanol goes through the cyclohexanone intermediate. These workers found that no simple kinetic picture could be formulated due to the intervention of the ketone intermediate. The reaction was found to approach first order in phenol at low temperatures and zero order at higher temperatures.

The hydrogenation of phenol was carried out in this work using rhodium (oxide) catalyst. The reaction temperature was 146° and the initial pressure was 1500 p.s.i. Neither first nor zero order kinetics with respect to phenol were followed accurately. A plot of log P *versus* t (for zero order in phenol and first order in hydrogen pressure) was fairly linear up to approximately 50 per cent reaction. See Figure 8 for zero and first order plots.* The rate calculated from the linear

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*The kinetic expression for a reaction which is first order in acceptor concentration and zero order in hydrogen pressure has been derived in detail by H. A. Smith and W. C. Bedoit, Jr. See *J. Phys. & Colloid Chem.*, *55*, 1090(1951).

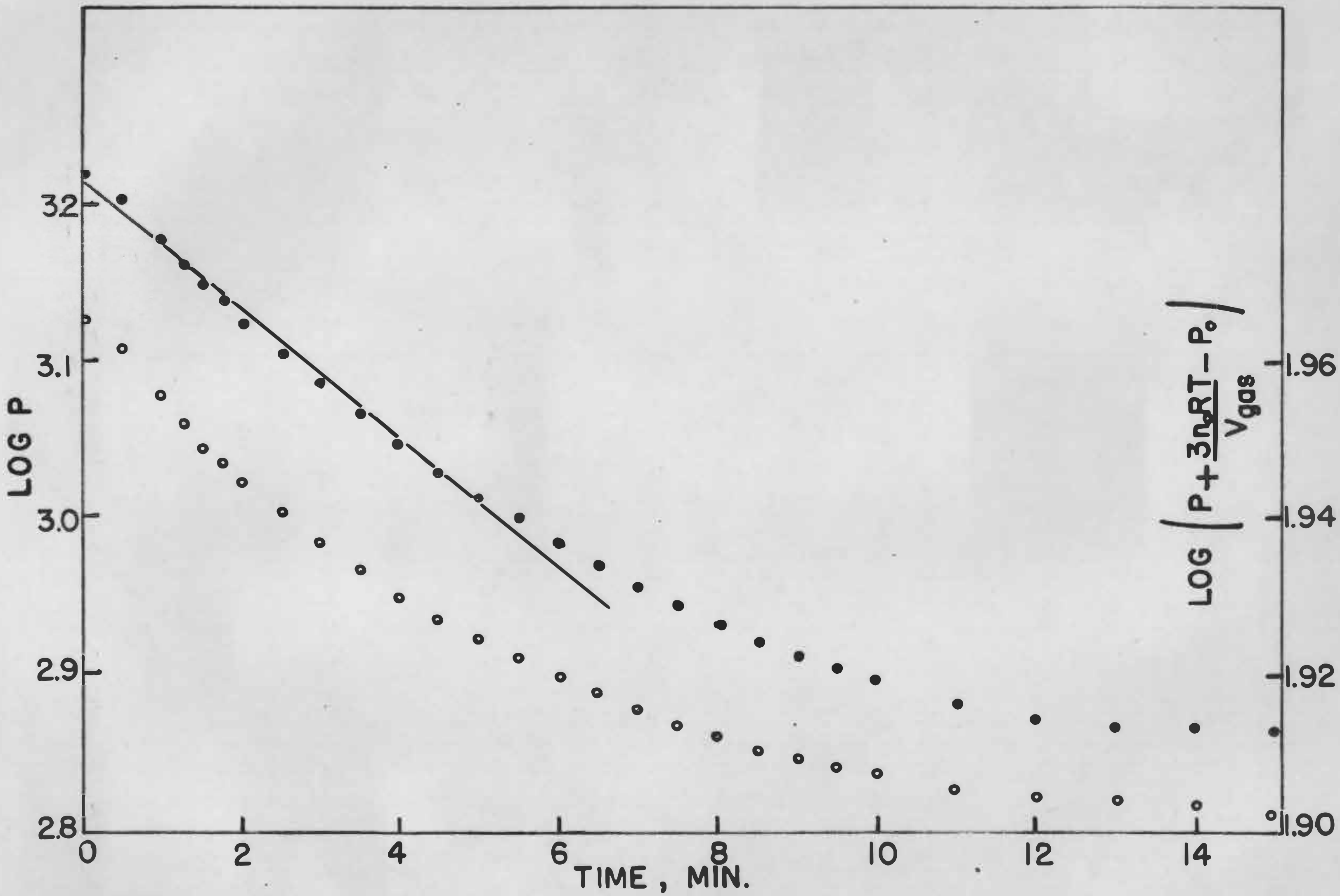


Figure 8.- Zero and First Order Plots for Hydrogenation of Phenol: ●, Zero Order in Phenol (left axis); ○, First Order in Phenol (right axis).

portion of this plot was 0.214 l. min.$^{-1}$ This value was also found from the same type plot for the hydrogenation of phenol to 26 per cent completion. Since the partially hydrogenated reaction mixture was found to consist largely of cyclohexanone, it is likely that the value for $k_{1.0}$ above is approximately that for the hydrogenation of phenol to cyclohexanone. A maximum was found to exist in a plot of d(H)/dt *versus* per cent hydrogenation. Such a maximum was also observed by Coussemant and Jungers.

From the moles of hydrogen absorbed per mole of phenol (3.09) and the refractive index of the product, it appears that some cleavage to cyclohexane and water occurred. For the product, n_D^{20} was 1.4624; n_D^{20} of cyclohexanol is 1.4667. The refractive indices of both water and cyclohexane are lower than that of cyclohexanol. Coussemant and Jungers indicated that with Raney nickel a slight deviation of the refractive index was observed toward the end of the reaction, and they attributed this to "dehydration."

In the work of Coussemant and Jungers, phenol was hydrogenated to various percentages of completion and the resulting mixtures analyzed for phenol, cyclohexanone, and cyclohexanol. A plot of mole fraction of cyclohexanone *versus* refractive index and amount of hydrogen consumed was constructed. The amount of ketone present in a partially hydrogenated mixture could be obtained from this plot. For example, a mixture hydrogenated to 32 per cent completion had a refractive index of 1.5197 which corresponded to 10.9 per cent ketone in the mixture.

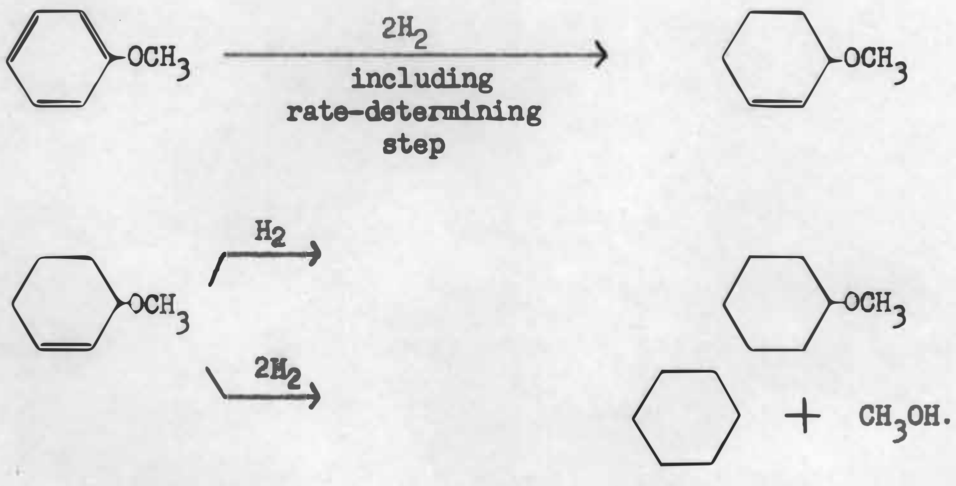
In this work, phenol was hydrogenated to 26 per cent completion using rhodium (oxide). The refractive index was 1.5165 which corresponded to 22 per cent cyclohexanone using Coussemant and Junger's plot. The presence of ketone and its amount were checked in the following manner. The hydrogenation mixture was shaken with an excess of saturated sodium bisulfite solution. Within two to three minutes the solid sodium bisulfite addition product began to separate. The reaction mixture was allowed to stand overnight for complete reaction. The precipitate was then collected on a filter and washed with aqueous sodium bisulfite, then alcohol and ether to remove all organic material. This sodium bisulfite addition product corresponded to 24 per cent ketone in the original mixture. This is in reasonable agreement with the value obtained directly from the refractive index of the mixture.

For the hydrogenation of phenol with Raney nickel, the ketone reached a maximum of 11 per cent. The accumulation of ketone with rhodium was at least 23 per cent. This difference is not surprising since the reaction rates, energies of activation and coefficients of adsorption for the various steps in the hydrogenation do not vary in a parallel manner from one catalyst to another. The reaction with rhodium offers possibilities as a means of preparing cyclic ketones by partial hydrogenation of various phenolic compounds. The ketone could be removed from the other constituents by distillation or extraction with aqueous sodium bisulfite.

CHAPTER IV

POSSIBLE CLEAVAGE MECHANISM

From the data collected on the hydrogenation and hydrogenolysis of methoxy compounds, the following mechanism is postulated. The methoxybenzene, anisole for example, is adsorbed on the catalyst surface. With the approach of hydrogen to the catalyst surface, hydrogenation takes place to give methoxycyclohexene as a short-lived intermediate. This intermediate may then either undergo cleavage to give cyclohexene and methanol or ring hydrogenation to give methoxycyclohexane. These reactions will probably occur simultaneously until the double-bonded molecules are saturated.



It has been shown that the methoxyl group is cleaved neither before the hydrogenation nor after the hydrogenation. Instead, the cleavage occurs after the rate-determining step for ring saturation and apparently before this saturation is complete. There is little question but that the first step in the reaction scheme above includes the rate-determining step. For the proposed intermediate, as written above, the carbon-oxygen bond adjacent to the ring would be expected to be labilized by the double bond involving the β - γ carbons. Such ether linkages are easily cleaved under a number of conditions. Acid would certainly be expected to promote cleavage of such a species *via* a carbonium or oxonium ion intermediate. As experimentally observed, acid did promote the cleavage.

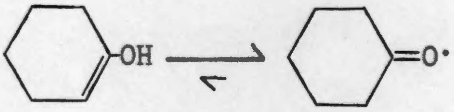
The existence of a diene as the intermediate is not feasible thermodynamically; cyclohexene is thermodynamically possible, however. In the hydrogenation of benzene it has not been possible to isolate cyclohexene as an intermediate. One of the reasons often advanced for this failure is that the molecule does not desorb from the catalyst until all the double bonds are hydrogenated. This mechanism does not require desorption of the substituted cyclohexene. Only the existence of the cyclohexene or some equivalent for a short time on the catalyst surface is necessary. From the relative rates of hydrogenation of benzene and cyclohexene over Adams platinum, the existence of cyclohexene as an intermediate seems reasonable. Cyclohexene hydrogenates only 8.1 times as rapidly as benzene.[44] Schniepp, Geller and Korff[45] found that the hydrogenation of 2-methylfuran over copper chromite gave 2-methyltetrahydrofuran when the reaction was carried out in water alone. In the presence of a small amount of acid, ring cleavage occurred during hydrogenation to give 1,4-pentanediol. This can be explained by the formation of 4,5-dihydro-2-methylfuran as a partially hydrogenated intermediate.

For the hydrogenations carried out in this work, cleavage was never 100 per cent. Two reasons are suggested which may account for this fact. A distribution of 1-methoxycyclohexene-1, 1-methoxycyclohexene-2, and 1-methoxycyclohexene-3 may be formed during the hydrogenation. For only the 1-methoxycyclohexene-2 would the carbon-oxygen bond adjacent to the ring be expected to be more labile than other aliphatic ether linkages. Second, the cleavage reaction is probably slower than the rapid hydrogenation of the cyclohexene. Thus the saturation of the double bond would be expected to be complete before all the methoxyl groups could cleave. Differences in relative rates of cleavage and ring saturation for different catalysts may explain the fact that the amount of cleavage varies from catalyst to catalyst.

It has been seen that 5 per cent rhodium on alumina gives little methoxyl cleavage. The rates of hydrogenation of benzene and cyclohexene were measured for this catalyst. These rates were 0.1627 and 3.324 l. min.$^{-1}$, respectively. Cyclohexene thus hydrogenates 20.4 times as rapidly as benzene for this catalyst; for Adams platinum, cyclohexene hydrogenates 8.1 times as rapidly as benzene.[44] Thus any cyclohexene intermediate would be expected to have a shorter life with rhodium and therefore permit less cleavage.

The activation energy for the hydrogenation of cyclohexene over platinum is 2.4 kcal. mole^{-1}.[44] Although data are not available for the activation energy of the proposed cleavage step, it is reasonable to assume that it would be higher than for the simple double bond hydrogenation. If this is true, then the increase in cleavage with temperature is in agreement with the proposed mechanism.

As shown in this work and by previous workers, the hydrogenation of phenol proceeds through the cyclohexanone intermediate. The formation of this ketone can be explained by a partial hydrogenation of the benzene ring to 1-hydroxycyclohexene-1, which is the tautomeric form of cyclohexanone:



If a statistical distribution of isomeric cyclohexenols were formed this mechanism would not account for more than one third of the phenol molecules undergoing hydrogenation <u>via</u> cyclohexanone. However, there is no basis at present for determining the distribution of isomers formed by the partial hydrogenation or subsequent tautomerization.

CHAPTER V

SUMMARY

The catalytic hydrogenation of methoxybenzenes and other aromatic methoxyl compounds has been studied. Hydrogenation of the aromatic ring was usually accompanied by some cleavage of the methoxyl groups. This cleavage occurred predominately upon the carbon-oxygen bond adjacent to the aromatic ring. The cleavage reaction was found to occur only as a part of the aromatic hydrogenation process. The amount of cleavage was found to be dependent upon the catalyst used. Platinum led to extensive methoxyl cleavage while rhodium catalyzed ring saturation with little cleavage. Also found to influence the extent of cleavage were reaction temperature and acid concentration.

A mechanism for the cleavage has been proposed. This mechanism involves the formation of a methoxycyclohexene or equivalent in which the carbon-oxygen bond of the ether is labilized by the β - γ carbon-carbon double bond.

The utility of various rhodium compounds as catalysts for the hydrogenation of the benzene nucleus has been demonstrated. With respect to catalytic activity, supported catalysts have been shown to be superior to the pure metals when the two groups are compared on the basis of percentage of active constituent.

The effect of substitution and number of substituents on the rate of hydrogenation was found to be about the same for the various methoxybenzenes as for the corresponding methyl compounds.

APPENDIX

APPENDIX

EVIDENCE FOR CARBONIUM ION FORMATION FROM CRYSTAL VIOLET IN CONCENTRATED SULFURIC ACID

This research, while not directly connected to the work on catalytic hydrogenations, was performed by the author as a part of the research requirement for the Ph.D. degree. The theory, properties, and reactions of carbonium ions in sulfuric acid have been adequately covered by the author in his M.S. thesis.[46]

A. Introduction

It has been well established that triphenylcarbinol and many substituted triphenylcarbinols ionize in sulfuric acid to give stable carbonium ions, according to the equation:

$$(C_6H_5)_3COH + 2H_2SO_4 \longrightarrow (C_6H_5)_3C^+ + 2HSO_4^- + H_3O^+.$$

The solutions are intensely colored, give <u>i</u>-factors of 4.0 by cryoscopic measurements, and undergo various reactions typical of carbonium ions. The <u>i</u>-factor is defined as the ratio of the observed freezing point depression to the depression expected if the solute were not ionized.

When the carbinol contains three dimethylamino groups, as in crystal violet (tri-<u>p</u>-dimethylaminophenylcarbinol), the ionization in sulfuric acid would be expected to be accompanied by protonation of one or more of the dimethylamino groups. Newman and Deno[47] obtained an i-factor of 6.0 for crystal violet in 100 per cent sulfuric acid. These workers observed that the solution was intensely colored (orange-brown). The ionization was assumed to be as follows:

$$((CH_3)_2NC_6H_4)_3COH + 4H_2SO_4 \longrightarrow ((CH_3)_2\overset{+}{N}HC_6H_4)_2\overset{+}{C}C_6H_4N(CH_3)_2 + H_3O^+ + 4HSO_4^-$$

(i = 6.0).

An i-factor of 6.02 and similar coloration was obtained for the analogous tri-p-aminophenylcarbinol, with the same type of ionization assumed.

Branch and Warba[48] have reported measurement of the spectrum of crystal violet in concentrated sulfuric acid (specifically, a solution of 2 parts acetic acid and 98 parts concentrated sulfuric acid). The workers reported that no absorption bands were present from 275-700 $m\mu$ a region embracing almost the entire visible spectrum. The explanation offered is that all three dimethylamino groups are protonated, thereby increasing the positive charge on the molecule to the extent that any carbonium ion, if formed, reacts with a bisulfate ion to give a benzenoidal ion:

$$((CH_3)_2NC_6H_4)_3COH + 5H_2SO_4 \longrightarrow ((CH_3)_2\overset{+}{N}HC_6H_4)_3CHSO_4 + 4HSO_4^- + H_3O^+.$$

This benzenoidal ion should possess no color. It should be noted that the formation of the benzenoidal ion in sulfuric acid also leads to an i-factor of 6.0, so that cryoscopic measurements alone cannot indicate whether a carbonium or benzenoidal ion is present.

The different interpretations of the behavior of crystal violet in sulfuric acid solution as presented by Newman and Deno on the one hand

and Branch and Warba on the other appear to stem from conflicting observations. The orange-brown color observed by the former experimenters is hardly compatible with the complete lack of bands throughout the range of 275-700 mμ as reported by the latter workers. Newman and Deno synthesized their tri-p-dimethylaminophenylcarbinol by previously described methods[49], while Branch and Warba purified commercial crystal violet by recrystallization. No melting points or analytical data are recorded in either case. It is possible that the commercial sample may have been the triphenylmethane derivative which is also known as crystal violet. In view of these possibilities it seemed advisable to obtain a sample of crystal violet identified by analytical means, and to study its behavior in sulfuric acid.

B. Results and Discussion

The spectrum of crystal violet in concentrated sulfuric acid is shown in Figure 9. The spectrum is analogous to other triphenylcarbonium spectra studied by Newman[47] and by Branch[48]; both the wave lengths of maximum absorption and the value of the extinction coefficients at maximum absorption are comparable. The color of the solution was orange-brown in agreement with Newman's observations.

A sulfuric acid solution of the methyl ether of crystal violet gave the same orange-brown color as observed for the carbinol. Methyl ethers derived from carbinols which form stable carbonium ions in

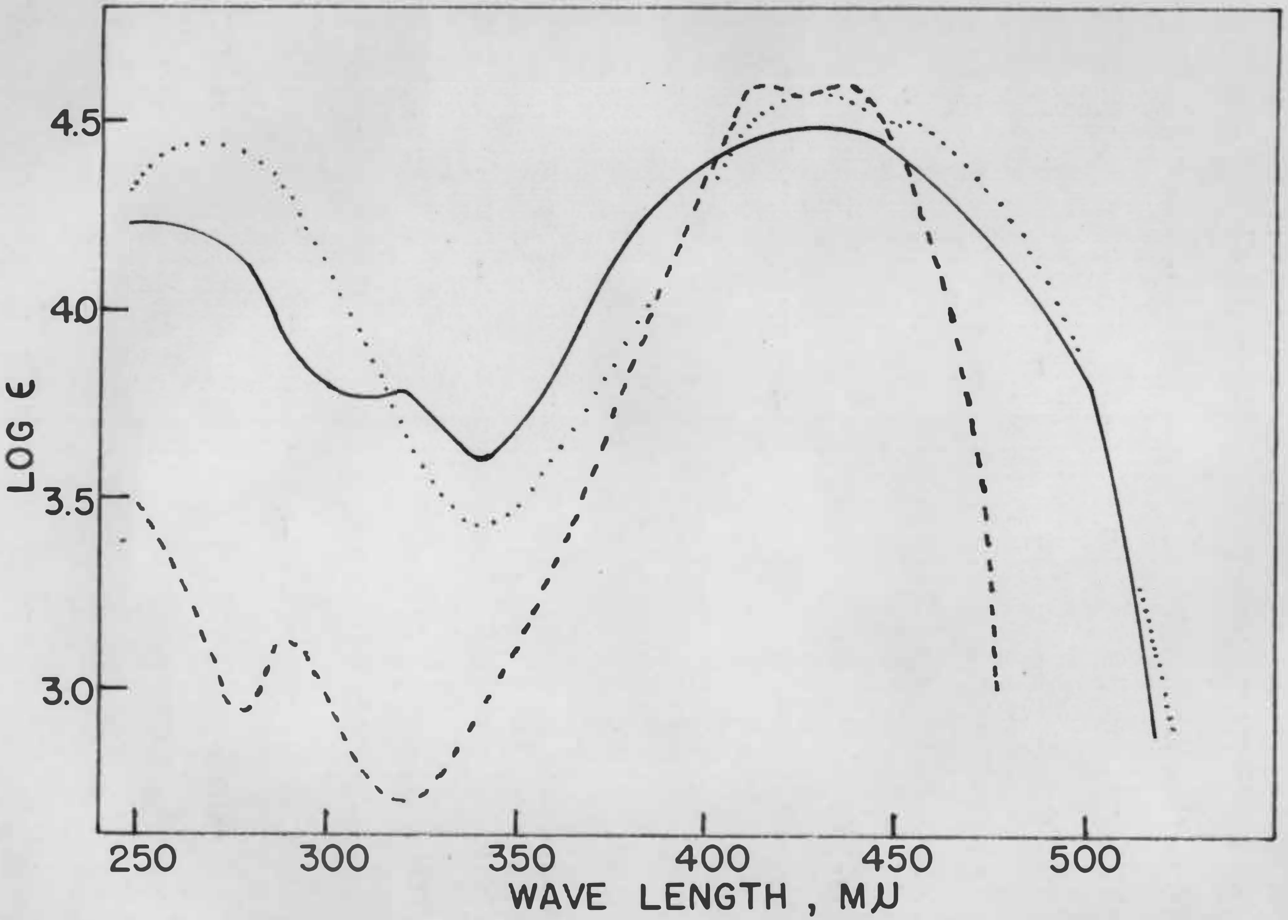


Figure 9.- Spectra of Triphenylcarbonium Ions in Concentrated Sulfuric Acid: ——, tri-p-dimethylaminophenylcarbinol; ...., tri-p-nitrophenylcarbinol;[47] ----, triphenylcarbinol.[47] Crystal Violet Solution 2.5×10^{-5} Molar.

sulfuric acid are known to ionize to give the same carbonium ions as the parent carbinols. For example:

$$(C_6H_5)_3COCH_3 + 3H_2SO_4 \longrightarrow (C_6H_5)_3\overset{+}{C} + CH_3HSO_4 + H_3O^+ + 2HSO_4^-.$$

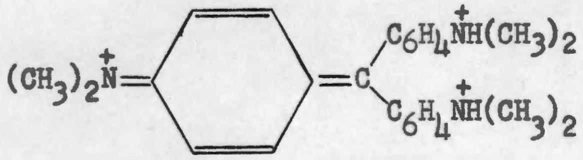
It has been shown[50] that a solution of triphenylcarbonium ions in sulfuric acid reacts immediately with methanol to form the corresponding methyl ether, according to the following equations:

$$(C_6H_5)_3C^+ + CH_3OH \longrightarrow (C_6H_5)_3\overset{+}{C}HOCH_3$$

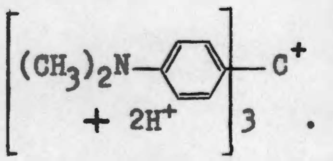
$$(C_6H_5)_3\overset{+}{C}HOCH_3 + H_2O \longrightarrow (C_6H_5)_3COCH_3 + H_3O^+.$$

The ordinary acid-catalyzed etherification of triphenylcarbinol or similar hindered alcohols, as well as bisulfates of the type proposed by Branch, would be expected to give practically no ether in a short reaction time. A solution of crystal violet in concentrated sulfuric acid gave the methyl ether in approximately 50 per cent yield for a reaction time of not more than 5 minutes. This is an excellent confirmation of the assumption that the solution contained carbonium ions.

The above data support the original conclusion of Newman that only two dimethylamino groups of crystal violet are protonated in sulfuric acid, and the resulting species is a carbonium ion. Newman also suggested that the electron distribution in this ion was more accurately represented by the quininoid structure:



than by the usual carbonium ion structure,



The rapid formation of the ether upon addition of a sulfuric acid solution of crystal violet to methanol suggests that the latter formulation is of considerable importance.

C. Experimental

The spectra were run on a Beckman model DU spectrophotometer; quartz cells 1 cm. thick were used.

1. Crystal Violet Preparation

The carbinol was prepared by dissolving the chloride salt of crystal violet (a product of the National Aniline Division, Allied Chemical and Dye) in water and precipitating the carbinol by addition of solid sodium hydroxide pellets. After filtration, the solid carbinol was blue in color. Attempts to purify the product by recrystallization from ligroin and benzene were futile. The method of purification was that followed by Heertjes[51], who also reported that simple recrystallization from organic solvents failed. The carbinol was dissolved in acetone and precipitated by the slow addition of an aqueous sodium hydroxide solution. The carbinol, collected by filtration, was much less colored than originally. This process was repeated several times, finally yielding a white solid. In order to remove traces of sodium hydroxide from the carbinol, it was dissolved in a small volume of anhydrous ether, and the solution filtered. The carbinol, after evaporation of the ether, was stored under vacuum since exposure to air causes the compound to turn blue slowly. The compound melted at 200° with decomposition; a melting point of 205° has been reported.[51]

Anal. Calcd. for $C_{25}H_{31}ON_3$: C, 77.08; H, 8.02. Found: C, 77.02; H, 8.11.

2. Methyl Ether Preparation

A 3 g. sample of crystal violet was dissolved in 10 ml. of concentrated sulfuric acid, giving an intense orange-brown solution. This solution was added dropwise to 50 ml. of absolute methanol which was cooled in a Dry Ice-acetone bath during the addition. The resulting solution was immediately added to 200-300 ml. of an ice-water mixture and sufficient sodium hydroxide solution added to make the solution basic. The methyl ether was extracted from this solution with two 100-ml. portions of ether. Evaporation of this solution yielded a blue solid which was purified in the same manner as that described for the carbinol. The yield of crude material was approximately 50 per cent. The purified ether melted with decomposition at 145-150°. This compound was also unstable in air.

Anal. Calcd. for $C_{26}H_{33}ON_3$: C, 77.38; H, 8.24. Found: C, 77.16; H, 8.19.

D. Summary

Evidence has been given to show that crystal violet ionizes to form a carbonium ion in concentrated sulfuric acid. The solution was an intense orange-brown and exhibited an ultra-violet and near-visible spectrum comparable with other triphenylcarbonium ions. The sulfuric acid solution reacted with methanol immediately to give the methyl ether. This behavior can be readily explained only by the presence of carbonium ions in the sulfuric acid solution.

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VITA

Robert Gene Thompson was born in Hiddenite, North Carolina, on December 23, 1931. He received his elementary and high school education in Pittsylvania County, near Danville, Virginia. After receiving a junior college diploma from Averett College, Danville, Virginia, he entered the University of North Carolina. He graduated with a Bachelor of Science degree in Chemistry in August, 1952.

The author entered the University of Tennessee in September, 1952, holding a graduate assistantship. He received his Master of Science degree from the University of Tennessee in August, 1954. Since September, 1954, the author has been working under a grant from the Petroleum Research Fund of the American Chemical Society.

The author is a member of Phi Kappa Phi, Sigma Xi, and the American Chemical Society. He is the coauthor of the following publications: "Preparation and Properties of Substituted Benzhydryl Carbonium Ions," Hilton A. Smith and R. Gene Thompson, *J. Am. Chem. Soc.*, *77*, 1778(1955); "Evidence for Carbonium Ion Formation from Crystal Violet in Concentrated Sulfuric Acid," R. Gene Thompson and Hilton A. Smith, *J. Am. Chem. Soc.*, *77*, 4432(1955); "A Study of the Catalytic Hydrogenation of Methoxybenzenes over Platinum and Rhodium Catalysts," in "Advances in Catalysis," Vol. 8, New York, Academic Press, Inc., in press.