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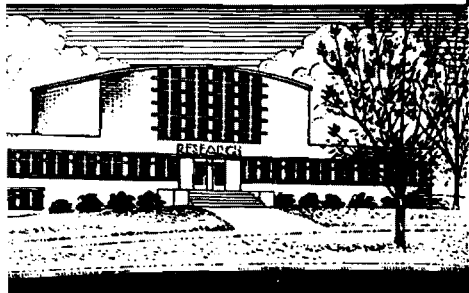
THE USE OF RADIOISOTOPES IN THE STUDY OF
MODIFICATIONS OF PLATINUM CATALYSTS



by
James A. Stanfield

Prepared for
THE DIVISION OF ISOTOPE DEVELOPMENT
UNITED STATES ATOMIC ENERGY COMMISSION

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Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

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THE USE OF RADIOISOTOPES IN THE STUDY OF
MODIFICATIONS OF PLATINUM CATALYSTS

By

JAMES A. STANFIELD

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ABSTRACT

It has been found that in the presence of Adams' platinum catalyst acid, mesityl oxide is first hydrogenated to the saturated ketone at a rate of $627 \times 10^{-4} \text{ min}^{-1} \text{ g}^{-1}$ and is then hydrogenated to the saturated alcohol at a rate of $17.7 \times 10^{-4} \text{ min}^{-1} \text{ g}^{-1}$. In ethanol as a solvent, only the first step was observed, occurring at a rate of 504×10^{-4} .

The addition of ferrous chloride to the acetic acid-hydrogenation mixture led to a rate increase of about 17 per cent for the hydrogenation of the olefin bond. There appeared to be no trend or relationship between the amount of ferrous chloride added over the range of from 1 to 25×10^{-5} moles and the rate constant for the reaction. The hydrogenation rates of the carbonyl function decreased only slightly at lower amounts of added salt, but increased to a maximum of 37.7×10^{-4} when 4×10^{-5} moles of ferrous chloride had been added. In ethanol solvent, the rate of olefinic bond reduction was decreased about 8 per cent with no observable trend being noted.

When the reaction was effected in the presence of zinc acetate, the rate of the first step increased to a maximum of 769×10^{-4} at 4×10^{-5} moles of added zinc acetate, but showed a decrease to 383×10^{-5} by the time that 25×10^{-5} moles had been added. The rate of the second step was noted to decrease over the entire range of added zinc salts. Similar effects for the first step were noted in ethanol solvent.

Studies were also made using cinnamaldehyde as the acceptor, freshly distilled aldehyde being hydrogenated at a rate of 297×10^{-4} in acetic acid and at a rate of 233×10^{-4} in ethanol. Addition of zinc acetate to the acetic acid-hydrogenation mixture yielded a slight increase in rate (to a

value of 334×10^{-4} when 0.05×10^{-3} millimoles were added); however, continued larger additions of the salt resulted in a continued decrease in observed rate. On the other hand, in ethanol as solvent, a rate increase of about 33 per cent was noted even when only 10×10^{-5} moles of salt had been added.

The only technique adaptable to the determination of the very small amounts of metal ions adsorbed on the catalyst is that employing radioactive zinc-65 solutions. First, in order to determine the exact amount of zinc present in a sample of Zn-65 chloride of known radioactivity, techniques were devised using ethylenediaminetetraacetic acid (EDTA) as a titrant with Erio-T as an indicator. Having determined the exact amount of zinc present in the radioactive sample, standard solutions were prepared from it and portions of these were used to impregnate a known weight of catalyst. Careful evaporation of the solvent gave a standard catalyst sample containing a known amount of adhering zinc salt. The extent of radioactivity of the sample was also determined using conventional counting techniques adapted to the situation at hand.

Hydrogenations were effected in which varying amounts of the standard radioactive zinc solution had been added to the reaction mixture. The rates of these reactions were determined and were found to be comparable to those reaction mixtures to which zinc acetate was added. At the conclusion of the reaction, the catalyst, now having some radioactive and nonradioactive zinc adsorbed on its surface, was carefully removed from the mixture, washed, and dried. The catalysts were then analyzed for the amount of zinc salt adsorbed on the surface using the same counting techniques as were used for the standard catalyst sample. These comparison studies indicated that the adsorption

of the zinc on the catalyst surface was related in an asymptotic way to the amount of salt added to the reaction mixture. While the greater per cent adsorption was noted at lowest added amounts, the actual amount of material adsorbed increased until 15×10^{-3} millimoles were adsorbed for 250×10^{-3} millimoles of salt added.

Surface area measurements of the catalyst were made and found to have a value of $8.3 \text{ m}^2/\text{g}$. Calculations using the maximum amounts of zinc adsorbed indicated that about 11.7 per cent of the surface of the catalyst was covered by the zinc ions. On the other hand, for each zinc ion adsorbed there must be two acetate ions held nearby, thus presenting a shielding effect. From this picture, it is believed that at least 76 per cent of the catalyst surface is covered or shielded by catalytically inactive materials. No evidence was found which would lead to the conclusion of multilayer adsorption.

Factors influencing the adsorption, such as hydrogen (presence or absence), acceptor, isolation time, and air (presence or absence) were studied. Once the zinc salts had been adsorbed, it was not found possible to remove them by extensive washing with either alcohol, acetic acid, or water.

Methods for the chromatographic analyses of the products of the hydrogenation were studied and developed. From these it was found at 50 per cent hydrogenation the product consisted of 25 per cent of 3-phenylpropanal and 37.5 per cent each of the starting compound (cinnamaldehyde) and 3-phenyl-1-propanol.

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I. INTRODUCTION

This report summarizes work performed during the period of the subject contract ending June 30, 1961. The purpose of work under this contract was (1) to study, by means of radioactive isotopes, the role that salts of certain metals have upon the activity of Adams' platinum catalyst when this catalyst is used in the hydrogenation of organic molecules; (2) to determine the extent to which these salts are attracted to and held on the catalyst surface; (3) to attempt to correlate the extent to which the salts are associated on the catalyst surface with effects the salt has upon the hydrogenation characteristics of the catalyst; and (4) to devise means by which the salts or metal ions may be removed from the catalyst and thus restore the catalyst to its original activity and behavior.

The director of this task was Dr. James A. Stanfield, Professor of Chemistry. Mr. Earl Gorton, a graduate student in the School of Chemistry, assisted the project on a part-time basis during the months of July, August, and September 1959. Mr. James D. Brown became associated with the project on a half-time basis beginning September 1, 1959, and continued until the end of the project. Mr. Brown devoted half time to the project and half time to his studies in the Graduate Division of the School of Chemistry.

Minute traces of foreign substances present during the preparation or use of a catalyst may exert tremendous effects upon the behavior of that catalyst. If the substance has little activity in itself but imparts to the catalyst a greater activity, stability, or selectivity, it is termed a promotor. On the other hand, if the substance can have an adverse effect upon the behavior of the catalyst, it is termed a catalyst poison. In some cases, however, poisoning of a catalyst may be quite beneficial. Effects such as these are quite common

in catalytic work. For example, with Adams' platinum catalyst it has been found that the action of ferrous and zinc salts render it possible to reduce the carbonyl function of certain α - β -unsaturated carbonyl compounds without obtaining reduction of the olefin bond.¹ The quantities of salts used in these reactions were on the order of 0.0002 to 0.00004 mole in 50 ml of alcohol solvent.

In our own laboratories it has been observed that ferric salts in amounts up to 0.01 millimole per 0.20 g of catalyst do not noticeably affect the rate of hydrogenation of the benzene nucleus in the presence of platinum oxide. When the amount of iron salts was increased to 0.05 millimole, the activity of the catalyst was greatly affected. Other salts such as nickel nitrate, cobalt nitrate, and cobalt chloride showed similar effects. Palladium chloride, however, did not decrease the activity of the catalyst even in amounts up to 0.1 millimole of the salt per 0.20 g of catalyst.

Earle² has shown that extremely minute quantities of certain metals, when incorporated in the Adams' catalyst during its preparation (even in amounts as low as 0.0005 millimole), enhance the activity of the catalyst. With larger amounts of these metals, however, the activity of Adams' catalyst for the hydrogenation of benzene in acetic acid was greatly decreased.

The exact manner in which these salts are able to exert their effects is inexplicable within a single concept. These impurities may (1) alter the surface area of the active catalyst component; (2) exert a dual action, that is, provide additional active centers on the catalyst so that one of several reactions is more favored than others; (3) alter the electronic characteristics

¹Tuley and Adams, J. Am. Chem. Soc. 47, 3061 (1925); Adams and Garvey, ibid., 48, 477 (1926).

²Earle, Master's Thesis, Georgia Institute of Technology, 1950.

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of the catalyst; (4) exert a very large effect on the number of lattice defects, thus altering greatly the activity of the catalyst; or (5) cause the promotion or creation of the number of active interfaces that exist at the boundary zones between phases of crystals of the catalyst.

It is the hope that through the incorporation of radioactive isotopes of certain metals in the added salts it will be possible to determine the manner in which these metals' ions are able to manifest their promotor and/or poison-action.

II. GENERAL EXPERIMENTAL DETAILS

A. Literature

The early period of the project was devoted to conducting a literature survey over the area of promotor and poisoning action of metals and salts on platinum catalysts when these catalysts are used for hydrogenation reactions. Approximately 100 references were obtained in this area and in very closely related areas. In addition, general literature references were studied by the graduate assistants.

B. Materials and Apparatus

1. Acetic Acid

Distillation of CP glacial acetic acid was effected using a Todd precision fractionating column having a height of 90 cm and a diameter of 22 mm. The column was packed with 1/8-inch, single-turn glass helices. It had approximately 30 theoretical plates. The fraction of acetic acid boiling at the constant temperature of 117° C at 743 mm pressure was collected and used as the solvent for the hydrogenation experiments.

2. Benzoic Acid

CP benzoic acid was found to be satisfactory for use in hydrogenations.

3. Mesityl Oxide

Distillation Products' white label grade of mesityl oxide was carefully fractionated using the Todd column, and that fraction boiling at 126.0° to 127.0° C at 743 mm pressure was collected and stored in a nitrogen atmosphere.

4. Platinum Oxide Catalyst

Three different samples of platinum catalyst were used, all of which were obtained from Baker and Company. The samples were designated as Baker 8380-3, Baker 8412, and Baker 8. Baker 8412 was used in experiments with mesityl oxide whereas Baker 8 was used with cinnamaldehyde.

5. Ferrous Chloride

CP ferrous chloride was used without further purification. A 0.005M solution was prepared by dissolving 0.4971 g of the tetrahydrate in 5 ml of pure methanol and then adding sufficient glacial acetic acid to form 500 ml of solution.

6. Zinc Acetate

The zinc acetate used was CP material. A solution of 0.5487 g of the dihydrate was prepared with 25 ml of methanol. This was diluted to 500 ml with glacial acetic acid to give a 0.005M solution.

7. Zinc Chloride

Radioactive zinc-65 chloride was obtained from the Oak Ridge Laboratories and was used without further purification. It was obtained as a solution of zinc chloride in hydrochloric acid (appr. 1N).

8. Ethylenediamine Tetraacetic Acid, Disodium Salt

This material was obtained from Distillation Products Industries and was used without further purification.

9. Erio-T

This indicator was obtained from Dr. H. Flaschka of these laboratories. The sample consisted of a fine powdered mixture of 0.1 g of Erio-T and 10 g of

sodium chloride.

10. Methanol

Synthetic methanol, CP, was used without further purification.

11. Ethanol

For solvent purposes, 95 per cent ethanol, CP, was used as obtained.

12. Cinnamaldehyde

Distillation Products Industries' white label cinnamaldehyde was used as obtained for some experiments, but for others the material was fractionally distilled under reduced pressure and stored under nitrogen. Results of the fractionation are given in Table I.

TABLE I
DISTILLATION OF CINNAMALDEHYDE

<u>Fraction</u>	<u>Volume (Ml)</u>	<u>Distillation Temperature (°C)</u>	<u>Pressure (Mm Hg)</u>	<u>n_D at 20°C</u>
1	0-40	120.2 - 129.8	24	-
2	41-120	129.8 - 131.4	27	-
3	121-190	131.4 - 132.2	27	-
4	191-290	132.2 - 132.7	27	1.6210 at 22
5	291-390	130.6	15	1.6212 at 22
6	391-430	130.6	15	1.6216 at 22
7	431-510	130.4	15	1.6217 at 21
8	511-550	130.0 - 129.0	15-14	1.6217 at 21

C. Hydrogenation Apparatus

A standard low pressure reaction apparatus, manufactured by the Parr Instrument Company of Moline, Illinois, was used. Briefly, this apparatus consisted of a hydrogen storage cylinder of about 4 liters capacity which was equipped

with an Ashcroft test gauge, graduated in 1/4-pound intervals over the range of 0 to 60 pounds. The storage tank was connected by means of suitable valves to a glass reaction bottle, which, in turn, was affixed to a stand connected by means of an eccentric shaft to an electric motor. This enabled the reaction bottle to be shaken during the hydrogenation.

All reaction bottles were thoroughly washed with soap and water before use, rinsed well with tap water, and then filled with dichromate cleaning solution. After standing at least one-half hour, the bottles were again rinsed with tap water (three times) and then rinsed with distilled water (three times). The cleaned bottles were dried in an electric drying oven.

D. Hydrogenation Procedure

In conducting the hydrogenation experiments, 50 ml of distilled glacial acetic acid were placed in the reaction vessel and the desired amount of a sample to be hydrogenated was added. The weighed quantity of catalyst, usually 0.200 g, was then introduced. In those instances in which a salt was to be included, the quantity of salt solution was pipetted into the acetic acid prior to its measurements so that in each case a total of 50 ml of solvent was being used. The bottle and its contents were then affixed to the apparatus and the system tightly sealed. Air was removed from the bottle by means of a vacuum system, and when the acetic acid began to boil, hydrogen was permitted to fill the system. The evacuation of the bottle and rinsing with hydrogen was repeated twice more. The hydrogen pressure was then adjusted to an initial gauge pressure of approximately 50.0 psi, after which the shaking mechanism was set in motion. At this instant, the pressure on the test apparatus gauge, as well as the time, was noted. At regular time intervals, usually 2 to 4 minutes, the pressure and elapsed time were noted and recorded. The temperature of the

system was also noted at various intervals. At the conclusion of the hydrogenation, the excess hydrogen was removed from the reaction vessel and the bottle disassembled from the shaker. The contents were filtered to remove the catalyst, and the acetic acid solution was either saved for product determination or discarded.

E. Treatment of Data

It has been established that the hydrogenation of benzene, benzoic acids, and many olefinic and carbonyl materials may be expressed in terms of first order kinetics with respect to hydrogen. Mathematically this may be stated as:

$$-\frac{dc}{dt} = kc,$$

where c is the concentration of the reactant, t is the time, and k is a proportionality constant.

Integrating this equation between the limits of c_1 at t_1 , and c_2 at t_2 , converting to base 10 logarithms, and rearranging, gives:

$$\log \frac{c_1}{c_2} = \frac{k(t_2 - t_1)}{2.303} .$$

This may be simplified by considering c_1 to be the initial concentration of material, c_0 ; c_2 then becomes c , the concentration at time t ; and t_1 becomes 0. Also, since the concentration of a gas is directly proportional to its pressure (volume being constant in this case), the concentration terms may be replaced by pressure terms. Under these conditions, the following equation is obtained:

$$\log \frac{p_0}{p} = \frac{k}{2.303} t .$$

According to this equation, a plot of $\log p_0/p$ against t will give a straight line, the slope of which will be $k/2.303$. Thus, the rate constant for the reaction may be calculated by multiplying the slope by 2.303. This constant will be for the quantity of catalyst used, and if it is divided by the grams of catalyst used, its units are reciprocal minutes per gram when t is in minutes.

In order for the constants from one run to another to be fully comparable, the temperature variations must be considered. The integrated form of the Arrhenius equation was employed to correct all results to 30° C. This equation is:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) .$$

E_a is the energy of activation for the process, and is taken to be on the order of 8000 calories per mole, the average value for a great number of catalytic hydrogenations.

F. Counting Apparatus

The counting work was done by using a lead shielded sample holder, commonly called a "pig," Nuclear Chicago Model 3037B, in conjunction with a "scaler," Nuclear Chicago Model 182. The "scaler" is essentially the recording device for the count rate in given periods of time. During the course of the work, two different "scalers" and "pigs" were used due to mechanical failure at one time and tie-up in other work at another occasion. However, these instruments were the same in type and were treated according to the methods cited below for each combination used. This scintillation counter device was used to determine the activity of catalyst standards and samples on which was adsorbed Zn-65 which emits gamma radiation of 1.12 Mev.

G. Handling of the Radioactive Materials

In order to determine the amount of zinc present in a one-millicurie sample of the radioactive zinc chloride, a method of analysis for the small amount of zinc in this sample had to be obtained. After considerable attempts, a method in which EDTA was used was found to be most satisfactory. This method is described below.

A standard solution of ethylenediamine tetraacetic acid (EDTA) was prepared by dissolving 3.722 g of the dried disodium salt in water and diluting to 200 ml. This formed a 0.0500M EDTA solution. Distilled water was used in preparing the solution. A buffer solution (pH = 10) was prepared by dissolving 7.00 g of ammonium chloride in 57.0 ml of ammonium hydroxide (sp. gr. 0.90) and diluting with distilled water to 100 ml. Both the EDTA and the buffer solutions were kept in polyethylene bottles. A standard zinc acetate solution was made by dissolving an accurately weighed sample of the CP salt in sufficient distilled water to make a 0.028M solution. A zinc chloride solution of similar strength was also prepared.

Titrations of these samples and the radioactive solution samples were carried out in a similar manner whether one used 5 to 6 ml of the standard or only 0.10 ml of the standard. The procedure was to add the zinc solution to about 50 to 75 ml of distilled water and 5.0 ml of the buffer solution. Then sufficient Erio-T indicator was added to give a deep blue color. The sample was then titrated with the EDTA solution until the color changed from blue to red. In the case of larger samples, ordinary 5 ml burettes were used. For the very small amounts, hypodermic syringes of suitable size were used. The endpoints were observed very readily and no difficulty was encountered in detecting the change of color so long as sufficient indicator was used; otherwise,

the end points were less readily observed and reproduced, particularly when very small amounts of zinc salts were being determined.

After determining the actual amount of zinc salt present in the radioactive sample of zinc chloride, calculations were made to determine what weight of material would be needed to form 250 ml of 0.005M and of 0.00005M solutions. These solutions were then used for the preparation of the "standard radioactive catalyst" or else were used for the hydrogenation purposes.

For example, a 0.00005M zinc chloride solution, containing zinc-65, was prepared and 1.0 ml of this solution was carefully placed on 0.200 g of platinum oxide catalyst contained in a plastic counting tube. Very careful evaporation of the solvent yielded a catalyst sample impregnated with radioactive zinc. It was found that a count corrected for background radiations of 13×10^3 cpm was obtained. This sample of catalyst was prepared to serve as a standard of comparison for other catalyst samples for which the extent of adsorption was to be determined.

Before experimental counting could be done with the counting apparatus previously described, it was necessary to make a determination of the voltage area in which the count rate did not change appreciably. A plot was made of the count rate as a function of the "working voltage" using the standard sample of radioactive catalyst just described. It had been observed that the count rate of a given sample was influenced by the voltage over a rather wide range, except for a plateau region where the count rate was essentially independent of the voltage. The plateau region was therefore determined for each "scaler" and "pig" combination. This plateau region generally covered a range of about 200 volts and was usually in the region of 900 to 1200 volts. Once the plateau region had been determined for the apparatus to be used, the working voltage on the scaler was set at a value near the lower voltage end of the

plateau. Presumably there was enough fluctuation in the D.C. current supplied to cause the voltage fluctuation and the resultant variation in count rate.

Once the working voltage had been determined (usually 1000 to 1100 volts was used), the experimental counting could be carried out. This was done as follows. At the start and at the end of a counting session, the relative constancy of the "background" count was taken as evidence that no extraneous radiation sources had been introduced and that the "scaler-pig" combination was functioning properly. The material to be counted, contained in a plastic counting tube, was then introduced into the apparatus being used. First the standard catalyst containing a known amount of Zn-Zn-65 on a known weight of catalyst was counted. This established a relationship between the amount of zinc adsorbed and the number of counts per minute obtained. The experimental samples were then introduced in the apparatus and a count obtained. It was assumed that the same relationship between amount of material adsorbed and count rate existed as it did for the standard sample. A standard sample was prepared for each concentration of Zn-Zn-65 used in the experimental work.

The actual count rate, in counts per minute, was determined by taking the average of at least three readings, each reading being over a period of from 3 to 10 minutes. In a few cases, time intervals of 2 minutes were used, but these were checked later using longer counting period. Statistically speaking, it was determined that the accuracy of a count had reached a maximum in a 3 to 5 minute interval using the instruments described above. There were a few cases in which the count rate was so high that the scaler did not record fast enough, but these were rechecked after decay had reduced the radioactivity and more reliable results were then obtained.

H. Vapor Phase Chromatography Materials and Techniques

The materials obtained from the hydrogenation experiments were, for the most part, analyzed with a Perkin Elmer Vapor Fractometer, Model 154. With this apparatus, several columns were prepared and used in the work. Among these, four were of major interest. One was a Perkin Elmer "O" column, a 3-ft stainless steel column packed with Chromosorb coated with a silicone grease. The second was a Perkin Elmer "R" column, a 3-ft stainless steel column packed with Chromosorb which had been impregnated previously with polypropyleneglycol, "UCON". The third column was prepared according to the following procedures.

Approximately 100 g of Chromosorb P, 30-60 mesh, non-acid washed material was treated with 360 ml of concentrated reagent grade hydrochloric acid for a period of 3.5 hours. During the washing, the mixture was stirred mechanically. The acid solution was decanted, and the solid material was washed with distilled water until the washings were neutral to pH paper and then filtered. After oven drying the wet material at 100° to 110° C, the Chromosorb was kept for 3 hours under 500 ml of 0.5N methanolic potassium hydroxide solution. The base solution was then decanted and the adsorbent washed with distilled water until the washings were neutral to pH paper. When the solid had been dried in an oven at 110° C for several hours, it was resieved using 28- and 60-mesh sieves. That portion passing the 28-mesh sieve but retained by the 60-mesh sieve was saved for further treatment. A 3-per-cent solution of silicone gum SE-30 in toluene was prepared, and 100 ml of this solution was used to treat each 25 g of resieved material. The Chromosorb was stirred in contact with the silicone gum solution for 5 minutes and then filtered with water aspirator vacuum. Air was pulled through the solid for an additional 10 minutes, after which the solid was transferred to a small casserole and dried at 110° C for 4 hours.

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The adsorbent was then used to pack a 9-ft length of copper tubing, 4 mm OD. While a column of this type is able to be used at temperatures of 220° to 270° C, it was employed in this work at somewhat lower temperatures.

The fourth column, designated B-132-A, was a 6-ft column made of the usual copper tubing. It was packed with Chromosorb P, a 60/80 --- 70/170 mesh material. This was coated with a silicone gum, SE-30. It was prepared similarly to the previous column.

In using these columns, the apparatus, with the column in place, was heated to the desired temperature for 4 to 6 hours in order to insure column equilibrium. The sample, usually from 0.6 to 1.0 μ l, was then introduced. Helium served as the flow gas.

III. RESULTS AND DISCUSSION

A. Standardization of Catalyst and Apparatus

Table II gives the data obtained in the determination of the activity of the catalysts to be used in this work.

TABLE II
STANDARDIZATION OF CATALYSTS

Conditions: 0.020 mole benzoic acid; 50 ml glacial acetic acid; 0.200 g catalyst; 64.4 psi initial hydrogen pressure.

<u>Run No.</u>	<u>Catalyst</u>	<u>$k \times 10^4 \text{ Min}^{-1}\text{G}^{-1}$ at 30°</u>	<u>Total Drop in Pressure</u> (PSI)
1	8380-3	264	5.05
2	8380-3	285	5.10
3	8412	200	5.15
4	8412	186	5.00
5	8412	209	5.15
6	8	179	5.15
7	8	170	5.25
8	8	174	5.20

From Table II it can be seen that the catalysts were of somewhat different activity. The first, 8380-3, hydrogenated benzoic acid at a rate of $274 \times 10^{-4} \text{ min}^{-1}/\text{g}$ of catalyst at 30° C . The second, 8412, less effective, yielded a rate of $198 \times 10^{-4} \text{ min}^{-1}/\text{g}$. The third, sample 8, was still less effective, yielding a rate of $174 \times 10^{-4} \text{ min}^{-1}/\text{g}$. Such variations in commercial catalysts are not unusual.

The reaction, in going to completion, showed an average drop in pressure of 5.15 psi. Making an allowance of 0.05 psi for catalyst reduction and using the fact that 0.02 mole of benzoic acid would consume 0.06 mole of hydrogen, a 5.1-psi pressure drop would be equivalent to a drop of 85.0 psi per mole of hydrogen. Usage of this value permits determination of the extent of hydrogenation at any particular time. It also enables one to stop any reaction at any desired interval.

B. Hydrogenation of Mesityl Oxide

1. Standardization

Standard conditions for the hydrogenation of mesityl oxide were 2.00 ml of the acceptor, 0.200 g of catalyst 8412, 50 ml of glacial acetic acid as solvent, and 64.4 psi initial hydrogen pressure. Several typical runs are recorded in Table III.

TABLE III
HYDROGENATION OF MESITYL OXIDE

Conditions: 2.00 ml mesityl oxide; 50 ml acetic acid; 0.200 g catalyst 8412; 64.4 psi initial hydrogen pressure.

<u>Run No.</u>	<u>$k \times 10^4 \text{ Min}^{-1} \text{ g}^{-1} \text{ at } 30^\circ \text{ C}$</u>	
	<u>k_I</u>	<u>k_{II}</u>
1	630	17.9
2	618	18.5
3	628	16.7

It is interesting to note that the take-up of hydrogen initially proceeds much more rapidly than in the case of benzoic acid, an average rate of $625 \times 10^{-4} \text{ min}^{-1} / \text{g}$ of catalyst being obtained. This rate, noted over the first 2 to 3 minutes, was consistently obtained. After this, the rate at which hydrogen was

consumed was considerably less. Plots of the data obtained gave two straight lines intersecting at about 2.5 minutes in each case. Extrapolation from this time indicated that only half of the theoretical amount of hydrogen was taken up by this time interval. The two rate constants, k_I and k_{II} , given in Table III represent the first and the second straight lines obtained. The hydrogenation of mesityl oxide, therefore, proceeds stepwise.

There exist two possible ways in which the molecule could be hydrogenated and these are indicated in Figure 1. In this figure, the paths labeled "a" represent a hydrogenation of a carbonyl group while the paths labeled "b" represent hydrogenation of the ethylenic bond.

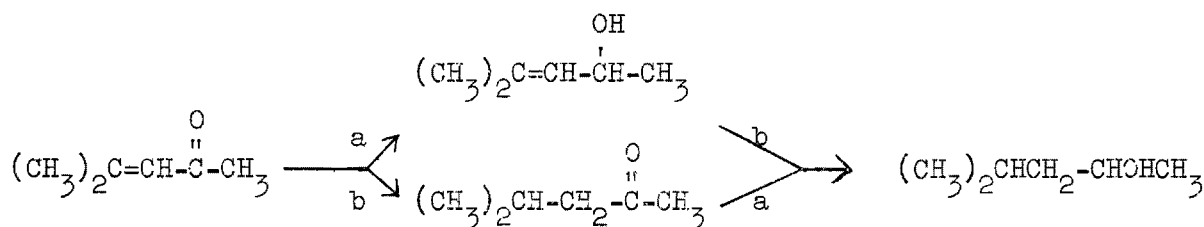


Figure 1. Reaction Paths

Studies were undertaken to determine which of these two paths was the first and which the second. A sample of mesityl oxide dissolved in 50 ml of acetic acid was hydrogenated until the hydrogen uptake indicated half-hydrogenation. After removal of the catalyst, samples of the product were titrated with a solution of 5 per cent bromine in acetic acid. Only three to four drops of the bromine solution were required to impart a permanent yellow-orange color to the half-hydrogenated product in acetic acid. On the other hand, a total of 47 ml was required to react with an acetic acid solution of mesityl oxide of equivalent concentration. Similar experiments were attempted in ethanolic

solutions, but the results were not conclusive since ethanol was a poor solvent for the titration with bromine.

Separation of the half-hydrogenation products was also attempted by distillation. Solutions of mesityl oxide in ethanol were half-hydrogenated in the usual manner, and, after removal of the catalyst, were subjected to fractional distillation. A small Vigreux column, 30 cm in length and 15 mm in diameter, was used. A yield of only one-third the theoretical amount was obtained. A considerable portion of the product formed an azeotrope with ethanol and could not be recovered pure. In attempts to remove the ethanol, distillation was effected in presence of excess benzene. In this case, the benzene-ethanol-water ternary azeotrope distilled first followed by a benzene-ethanol binary azeotrope. A mixture of benzene and product was left. This mixture was not separable, however, and an azeotrope of benzene and product (presumably methyl isobutyl ketone) was obtained.

A third method consisted of hydrogenation of a 2.0-ml sample of mesityl oxide to the half-hydrogenation stage, removal of the catalyst, and dilution of the resulting ethanolic solution with water to 250 ml. Aliquot portions of this diluted solution were reacted with 2,4-dinitrophenylhydrazine. A yield of the 2,4-dinitrophenylhydrazone of methyl isobutyl ketone amounting to 53 per cent of theoretical was obtained. In similar experiments conducted with a known quantity of methyl isobutyl ketone, there was obtained an average of 69 per cent yield of the hydrazone. On this basis, therefore, it is indicated that the half-hydrogenation mixture contains at least 77 per cent of the saturated ketone.

These results indicate that, contrary to the previous report of Adams

and co-workers³ in the cases of citral and cinnamaldehyde wherein reaction of the carbonyl was first observed, the ethylenic bond is reduced first in the case of mesityl oxide. Thus, the value of k_I represents hydrogenation of the ethylenic bond and k_{II} hydrogenation of the carbonyl. It is surprising that the two rates are so vastly different and particularly that the rate of the carbonyl hydrogenation is so slow. Generally, the simple carbonyl compounds are hydrogenated at a somewhat greater rate. For example, when 2.0 ml of 4-methylpentanone-2 was hydrogenated under conditions identical to those in Table III, a rate of $9.9 \times 10^{-4} \text{ min}^{-1}/\text{g}$ at 30°C was obtained.

2. Comparison of Solvents

From the studies in acetic acid and ethanol solvents, it appears that the hydrogenation process is more rapid in acetic acid than in ethanol. By the use of acetic acid, with no added salts, for the first step of the process, a rate constant of $625 \times 10^{-4} \text{ min}^{-1}/\text{g}$ at 30°C was obtained. Under identical conditions but using ethanol as a solvent, in the same units the constant was 504. Actually the second step of the process was either zero or almost this in every instance in which ethanol was used with mesityl oxide. The uptake of hydrogen was so slow over a 5-minute period that a pressure drop of only a few hundredths of a pound could sometimes be detected. Readings of changes of this order of magnitude are hardly significant and may very well be due to external conditions. Thus, any rate constant obtained from using these values is highly questionable. On the other hand, with acetic acid, rates on the order of $17.7 \times 10^{-4} \text{ min}^{-1}/\text{g}$ at 30°C were obtained.

³Tuley and Adams, loc cit.; Adams and Garvey, loc cit.

It would appear, therefore, that successful hydrogenation of the mesityl oxide to the half-hydrogenated product may well be achieved in either solvent, although acetic acid is more effective by a factor of 1.24. In the second step of the process, ethanolic solutions are not satisfactory since the hydrogenation process is not observed to occur in most cases.

Explanations of the lack of hydrogenation of the carbonyl group are not clear. Even when freshly distilled 4-methylpentanone-2 was used, the initial rate was only one-half that obtained when acetic acid was used with mesityl oxide. The results of hydrogenating this ketone in ethanolic solution were only fair. The uptake of hydrogen decreased considerably after about 2 minutes and continued to decrease until the reaction essentially stopped. From such data, it was difficult to select with accuracy a straight line from which the rate constant would be obtained. The exact cause of this unusual behavior is not known. It should be pointed out that excellent data are noted when acetic acid is used even though the rate of the hydrogenation is only twice as rapid in this solvent. In the acetic acid experiments, a regular change of pressure with time was noted for as long as 30 minutes.

3. In the Presence of Ferrous Chloride

Typical runs in which varying amounts of ferrous chloride were added to the reaction mixture are summarized in Table IV.

From these data, it appears that the presence of ferrous chloride will accelerate the hydrogenation of the ethylenic bond by about 16 per cent. There does not appear to be any trend over the ranges of ferrous salt added, and thus, 1×10^{-5} moles is just as effective as 25×10^{-5} moles. However, there does appear to be some difference in the behavior of the second step of the process,

TABLE IV

HYDROGENATION OF MESITYL OXIDE IN THE PRESENCE OF FERROUS CHLORIDE

Conditions: 2.00 ml mesityl oxide; 50 ml glacial acetic acid; 0.200 g catalyst 8412; 64.4 psi initial hydrogen pressure.

Run No.	Ml of FeCl ₂ 0.005M Solution	k x 10 ⁴ Min ⁻¹ G ⁻¹ at 30° C	
		k _I	k _{II}
1	2.00	730	14.3
2	2.00	700	12.9
3	4.00	750	12.9
4	8.00	738	37.7
5	16.00	703	29.0
6	50.00	755	20.0

that is, hydrogenation of the carbonyl group. At lower concentrations, the rate of the process is decreased almost 25 per cent. On the other hand, at concentrations of 4×10^{-5} the rate may be increased 100 per cent. It appears that concentrations greater than this again decrease the rate until at amounts of 25×10^{-5} moles of ferrous chloride, the rate is essentially that of the cases wherein no salt at all has been added.

All of the aforementioned runs were made in glacial acetic acid. A summary of the data obtained when 95 per cent alcohol (ethanol) was substituted as the solvent and when ethanol was used as a solvent for the ferrous chloride is presented in Table V.

In each of these cases, the presence of ferrous chloride decreased the activity of the catalyst. Toward hydrogenation of the ethylenic bond, the activity of the catalyst decreased from a rate of 504×10^{-5} to an average of 461×10^{-5} . Again, as in the case of acetic acid, the amount of salt does not seem to be a factor. However, a pronounced effect is noted on the second step of the process, the hydrogenation of the carbonyl group. In all cases in

ethanol, the reaction stopped after one mole equivalent of hydrogen had been added. The value of less than 2 reported for runs in which 4.0 ml of solution were added is very much open to question since rates of this order of magnitude are impossible to obtain with any degree of accuracy with the present equipment.

TABLE V

HYDROGENATION OF MESITYL OXIDE IN THE PRESENCE OF
FERROUS CHLORIDE IN 95 PER CENT ETHANOL AS SOLVENT

Conditions: 2.00 ml mesityl oxide; 50 ml total volume of ethanol and 0.005M ferrous chloride solution; 0.200 g of catalyst 8412; 64.4 psi initial hydrogen pressure.

<u>Run No.</u>	<u>Ml of FeCl₂, Ethanolic 0.005M Solution</u>	<u>k x 10⁴ Min⁻¹G⁻¹ at 30°C</u>	
		<u>k_I</u>	<u>k_{II}</u>
1	4.00	477	<2
2	8.00	433	0
3	50.00	474	0

4. In the Presence of Zinc Acetate

The second salt to be investigated in this project was zinc acetate. The results of typical runs in which this salt was added to an acetic acid solution of the acceptor are given in Table VI.

Considering the first step, the hydrogenation of the ethylenic bond, zinc acetate depressed the rate constant when used in amounts of 8×10^{-5} to 25×10^{-5} moles in the 50 ml of solution. On the other hand, at low amounts of salt added (1×10^{-5} moles), a slight acceleration in rate was noted. The rate continued to increase at least to the point where the amount of zinc acetate was 4×10^{-5} moles and where the value of the rate constant was 769×10^{-4} min⁻¹/g. When the behavior of the second step of the process was examined,

however, the zinc acetate had slowed the rate constant considerably, with the greatest effects being observed at higher quantities of zinc ions present. Actually, the reaction almost stopped at these upper amounts of zinc ions.

TABLE VI
HYDROGENATION OF MESITYL OXIDE IN THE PRESENCE OF
ZINC ACETATE IN GLACIAL ACETIC ACID AS SOLVENT

Conditions: 2.00 ml mesityl oxide; 50 ml total volume of acetic acid and zinc acetate solution; 0.200 g catalyst 8412; 64.4 psi initial hydrogen pressure.

<u>Run No.</u>	<u>Ml of Zn(C₂H₃O₂)₂ 0.005M Solution</u>	<u>k x 10⁴ G⁻¹ Min⁻¹ at 30° C</u>	
		<u>k_I</u>	<u>k_{II}</u>
1	4.00	697	5.2
2	8.00	769	6.6
3	16.00	473	2.0
4	50.00	383	2.4

With ethanol as a solvent, the same general pattern of greatest effect at highest amounts of zinc ions, reaching a minimum effect in the region around 4×10^{-5} moles of zinc and then once again showing a rising effect at very low concentrations, was noted. However, in each case in ethanol, the rate constant was decreased as compared with runs wherein no salts were present. The hydrogenation of the carbonyl group did not occur. These data have been tabulated in Table VII.

TABLE VII

HYDROGENATION OF MESITYL OXIDE IN PRESENCE OF ZINC ACETATE
IN 95 PER CENT ETHANOL SOLVENT

Conditions: 2.00 ml mesityl oxide; 50 ml total volume of ethanol and 0.005M zinc acetate solution in ethanol; 0.200 g catalyst 8412; 64.4 psi initial hydrogen pressure.

Run No.	Ml of $Zn(C_2H_3O_2)_2$ 0.005M Ethanolic Solution	$k \times 10^4 \text{ Min}^{-1} \text{ G}^{-1}$ at 30° C	
		k_I	k_{II}
1	4.00	581	0
2	8.00	602	0
3	16.00	561	0
4	50.00	288	0

C. Determination of Surface Area of the Catalyst

It was considered to be of some interest to determine the surface area of the platinum oxide being used. A sample of the oxide was found, by the BET method, to have a surface area of 34.9 m²/g. The gas adsorbed on the oxide surface was nitrogen.

The surface area of the reduced catalyst was also determined. The reduced catalyst was prepared by subjecting a 2.00-g sample of the oxide, suspended in glacial acetic acid, to hydrogen gas at an absolute pressure of 64 psi, using the Parr apparatus. After reduction, the acetic acid was removed by decantation and the catalyst resuspended in ethanol. The suspended catalyst was then filtered using a medium porosity fritted glass filter. As the catalyst began to approach dryness, considerable heat was evolved as air came in contact with the catalyst. The sample thus prepared was found to have a surface area of only 8.3 m²/g. Again, the BET method was used with nitrogen serving as the gas for adsorption.

The surface area measurements of platinum oxide and of reduced platinum catalyst yielded unusual results. The oxide surface was greater by a factor of four as compared with the reduced metal. One would have expected the metal surface to have been greater since it was formed by the removal of oxygen from the oxide. While it could be possible that the obtained results are real, it should be pointed out that it is probable that the value of the reduced metal surface, while correct for the surface measured, does not reflect the area of the reduced metal surface as is used during the hydrogenations. The reason for this being likely is the observation that during the isolation of the reduced material from the ethanol washes, the material became quite warm. This was possibly caused by the catalytic reaction of adsorbed hydrogen with the air taking place on the catalyst surface and by oxidation of ethanol with the air, also taking place on the catalyst surface. In these instances, the energy liberated as heat was likely sufficient to bring about softening of the tiny catalyst particles with a resultant fusion effecting a decrease in the surface area of the catalyst.

D. Analysis of Zinc Solutions

The results of the determinations of the amount of zinc present in various solutions are tabulated in Table VIII. The results of these analyses indicate that the method of EDTA titration can easily be adapted to those instances of very small quantities of zinc present in the solution. Although the accuracy in using the very small amounts of solutions is not as great as when larger amounts are used, nevertheless, the agreement from determination to determination is acceptable as is the agreement between calculated and actual amounts of material present. Therefore, the solution prepared from the radioactive zinc chloride had a molarity of 0.033. The remaining 9.45 ml of the solution contained, therefore, 0.0422 g of zinc chloride.

TABLE VIII
ANALYSIS OF ZINC-CONTAINING SOLUTIONS

Sample No.	Standard Zinc Solutions		Calc M of Zinc Solution
	Ml 0.028M Solution	Ml EDTA Soln.	
1	0.25 zinc chloride	0.144	0.029
2	0.25 zinc chloride	0.157	0.031
3	0.13 zinc chloride	0.080	0.031
4	0.25 zinc chloride	0.152	0.030
5	0.25 zinc chloride	0.152	0.030
6	10.00 zinc chloride	5.69	0.029
7	10.00 zinc chloride	5.68	0.029
8	10.00 zinc chloride	5.69	0.029
9	10.00 zinc acetate	5.67	0.029
10	10.00 zinc acetate	5.69	0.029
11	0.10 unknown active zinc	0.070	0.035
12	0.14 unknown active zinc	0.085	0.032
13	0.13 unknown active zinc	0.080	0.030
14	0.18 unknown active zinc	0.120	0.033

E. Hydrogenation of Cinnamaldehyde

1. Undistilled Cinnamaldehyde

Initial experiments were carried out using cinnamaldehyde as obtained from the previously mentioned supplier. A summary of the results of these is given in Table IX.

TABLE IX
HYDROGENATION OF UNDISTILLED CINNAMALDEHYDE

Conditions: 1.5 ml (0.012 mole) cinnamaldehyde; 50 ml of solvent; 0.200 g PtO₂ catalyst (Baker 8); 64.3 psi initial pressure.

Solvent	$k \times 10^4 \text{ Min}^{-1} \text{ G}^{-1}$ at 30° C	Moles of Hydrogen Absorbed
Acetic Acid	180	0.018
Ethanol, 95%	190	0.020

In these runs, the rates given are not truly indicative of the nature of hydrogenation. In each case the reaction proceeded only about 3.0 to 3.5 minutes before it stopped completely. Thus, only a very few points for the hydrogenation curve were obtained. These points are not always indicative of the true rate for the process and involve also the reduction of the catalyst and the adsorption of hydrogen on the surface of the newly reduced catalyst. It is also somewhat surprising that the rate in ethanol solvent is slightly greater than that in acetic acid. Generally, Adams' catalyst is more active in the presence of acid.

2. Distilled Cinnamaldehyde

Since the undistilled material could not be hydrogenated completely and the uptake of hydrogen slowed considerably even before the half-way point was reached, it was decided to hydrogenate freshly distilled material. A summary of this work is given in Table X.

TABLE X
HYDROGENATION OF DISTILLED CINNAMALDEHYDE

Conditions: 1.5 ml (0.012 mole) cinnamaldehyde; 50 ml solvent; 0.200 g PtO₂ catalyst; 64.3 psi initial pressure.

<u>Solvent</u>	<u>$k \times 10^4 \text{ Min}^{-1} \text{ G}^{-1}$ at 30° C</u>	<u>Moles of Hydrogen Absorbed</u>
Acetic Acid	297	0.021
Ethanol, 95%	233	0.021

Generally, these runs proceeded more smoothly than those when undistilled acceptor was used, although after the uptake of slightly more than one equivalent of hydrogen, the reaction slowed down considerably and eventually stopped.

Inasmuch as the presence of alkali in various hydrogenations has been shown on occasions to be beneficial, small quantities, 0.50 ml, of 3N sodium hydroxide were added to the reaction mixture. It was found that the rate constant, k , at 30° C for reactions thus effected was $315 \times 10^{-4} \text{ min}^{-1} \text{ g}^{-1}$. In every case, however, an initial induction period of about 3.5 to 4.5 minutes was noted before a regular, more rapid uptake of hydrogen occurred. The reaction, while proceeding rapidly, slowed down and stopped within 14 minutes, with a maximum uptake of hydrogen of 0.018 mole. As was the case in all previously reported runs with cinnamaldehyde, 0.012 mole of acceptor was used.

This acceleration caused by the use of sodium hydroxide was not unusual. Similar instances were observed in this laboratory when a Raney copper catalyst was used to hydrogenate certain aldehydes and olefinic compounds.⁴ The induction period had not been previously noted, however. In cases where sodium hydroxide was added to the reaction mixture, there was an initial pressure drop in the system of usually 0.1 pound within the first half-minute. There was then little (0.05 psi) or no change of pressure for the next 3 to 4 minutes, after which, for a period of about 6 minutes there was a fairly regular drop in pressure. At this point, the reaction stopped abruptly, with only 0.018 mole of hydrogen being consumed. The effect may be due to the base (as has been suggested by Adams⁵) or it could be due to only the sodium ions.

3. In the Presence of Ferrous Chloride

Varying quantities of ferrous chloride ethanolic solutions were also added to distilled cinnamaldehyde prior to hydrogenation. The summary of these

⁴P. E. Robbins, Ph.D. Dissertation, Georgia Institute of Technology, 1955.

⁵R. Adams and W. H. Carothers, J. Am. Chem. Soc., 46, 1675 (1924).

experiments is presented in Table XI. From these data it appears that the presence of ferrous chloride will accelerate the hydrogenation of the molecule, and that the extent of acceleration is related to the quantity of salt present. At the smaller quantities of salt, 2.0 ml of 0.005M solution, there was probably no specific evidence of an effect since the values of the rate constant obtained were within the experimental error of the method used. On the other hand, at amounts of salt on the order of 50 to 100 millimoles, the rate was increased considerably.

TABLE XI
HYDROGENATION OF DISTILLED CINNAMALDEHYDE
IN THE PRESENCE OF FERROUS CHLORIDE

Conditions: 1.5 ml (0.012 mole) cinnamaldehyde; 50.0 ml of solvent and solution (ethanol); 0.200 g PtO₂ catalyst; 64.4 psi initial pressure.

<u>Ml of 0.005M Ferrous Chloride</u>	<u>M Mcles of Ferrous Chloride x 10³</u>	<u>k x 10⁴ Min⁻¹G⁻¹ at 30° C</u>	<u>Moles of Hydro- gen Absorbed</u>
2.0	10.0	216	0.026
5.0	25.0	279	0.028
10.0	50.0	315	0.028
20.0	100.0	311	0.029

Also of interest in these experiments was the amount of hydrogen that was absorbed. The reaction proceeded beyond the point experienced when no salt was present until approximately 0.028 equivalent of hydrogen had been taken up. The initial take-up of hydrogen was reasonably regular for a period of several minutes, after which the amount absorbed per unit time gradually decreased and then finally stopped. The absorption of from 0.002 to 0.005 moles of hydrogen beyond that required to hydrogenate fully the aldehyde was not too significant.

It was probably due to either (1) extra hydrogen used to reduce ferric ions to ferrous ions or (2) slight error in the psi:moles of hydrogen reported above.

4. In the Presence of Zinc Salts in Ethanolic Solution

Quantities of zinc acetate, ethanolic solution, have been added to the hydrogenation mixture. These results have been summarized in Table XII. It appears in this case that the quantity of salt present does not influence the extent of change in rate constant and that 5×10^{-6} moles produce as great

TABLE XII

HYDROGENATION OF DISTILLED CINNAMALDEHYDE
IN THE PRESENCE OF ZINC ACETATE

Conditions: 1.5 ml (0.012 mole) cinnamaldehyde; 50.0 ml of ethanol and ethanolic zinc acetate solution; 0.200 g PtO₂ catalyst; 64.4 psi initial pressure.

<u>Ml of 0.005M Zinc Acetate Solution</u>	<u>M Moles of Zinc Acetate x 10³</u>	<u>k x 10⁴ Min⁻¹G⁻¹ at 30° C</u>	<u>Moles of Hydro- gen Absorbed</u>
1.0	5.0	222	0.021
2.0	10.0	211	0.026
4.0	20.0	211	0.026

an acceleration as do 2×10^{-5} moles of zinc acetate. In all cases, of course, the rate was increased by a factor of slightly more than 3. Again, as was the case with ferrous salts, the hydrogenation continued beyond the usual uptake of hydrogen. This time, however, the amount of hydrogen absorbed before the reaction stopped completely was less than in the cases of ferrous chloride. The general characteristics of the process were a rather rapid and steady absorption of hydrogen for an initial several minutes, after which the absorption of hydrogen steadily decreased per unit of time and finally stopped completely. No

satisfactory rate data could be obtained for the second step of the process in any of the cases studied. It appears that the same process that is operative in the cases of ferrous chloride is operative in the case of zinc acetate.

The hydrogenations in which a spiked zinc ion solution was added to the reaction mixture have not shown any detectable difference in rates from those shown in Table XII.

5. In the Presence of Zinc Salts in Acetic Acid Solution

From the data in Table XII it has been pointed out that the addition of zinc salts was not of great significance in the hydrogenation of the acceptor molecule when ethanol was the solvent. Such was not the case, however, when acetic acid was used as the solvent. Table XIII shows the effect of the amount of zinc acetate added to the reaction mixture when acetic acid was used as the solvent. It also indicated the per cent of the salt which is found to remain on the catalyst. Table XIV indicates the relationship between the actual amount of material which is adsorbed and the rate constant for the reaction. In these cases, one can note that extremely small amounts of salt appear to have an accelerating effect upon the rate of the hydrogenation. Larger amounts of the salt and subsequently larger amounts of material adsorbed show a somewhat opposite effect, that is a decrease in the activity of the catalyst. Similar effects have been observed previously in this laboratory.² While the relationships indicated in the tables are quite apparent, there does not seem to be any specific mathematical relationship that exists between either the amount added or the amount adsorbed and the rate constant for the hydrogenation. One can only indicate at this point the qualitative results that may exist.

TABLE XIII

COMPARISON OF SALT CONCENTRATION AND RATE CONSTANT

Conditions: 0.200 g PtO₂ catalyst Baker 8; 0.012 moles cinnamaldehyde; initial pressure 64.3 psi; 50 ml acetic acid solvent.

M Moles of Zn(C ₂ H ₃ O ₂) ₂ x 10 ³	Rate Constant x 10 ⁴	Per cent Zn ⁺²
	Min ⁻¹ G ⁻¹	Adsorbed
0.05	334	52
0.25	225	40
1.25	252	36
2.50	276	31
5.0	260	22
10.	221	16
25.	186	11
50.	163	8+
100.	138	8-
250.	39	6

TABLE XIV

EFFECT OF ADSORBED ZINC ON RATE CONSTANT

Conditions: 0.200 g PtO₂ catalyst; 0.012 mole cinnamaldehyde; initial pressure 64.3 psi; 50 ml solvent, acetic acid.

M Moles of Zn ⁺² Adsorbed, x 10 ³	Rate Constant x 10 ⁴ Min ⁻¹ G ⁻¹
0.026	334
0.10	225
0.44	252
0.775	276
1.20	260
1.60	221
2.75	186
4.0	163
8.0	138
15.	39

F. Adsorption Studies

1. Relationship of Addition of Salt to Adsorption of Salt

Rather interesting results were observed when one considered the amount of zinc salt added to the reaction mixture and the amount of zinc adsorbed. A plot of the former against the latter indicated that the amount adsorbed does not increase in a linear manner with the amount added, but rather the relationship is an asymptotic one. This is shown in Figure 2. This would appear to indicate that either the surface becomes completely covered by the salt or the surface possesses only a specific number of "active" sites which are capable of adsorbing the metal ion.

In order to obtain a solution as to which of these two postulates is true, surface area determinations of the catalyst surface were made. The method used was the conventional BET method in which the adsorbed gas was nitrogen. The area of the Adams' catalyst as furnished was found to be $34.9 \text{ m}^2/\text{g}$. After reduction of the catalyst, followed by its isolation, the area of the catalyst was somewhat less, being $8.3 \text{ m}^2/\text{g}$. The maximum adsorption realized was the 6 per cent adsorption obtained when 250×10^{-3} millimoles of salt were added. This was equivalent to an actual adsorption of 15×10^3 millimoles of zinc ions. If one uses the value of 0.83 \AA for the radius of the Zn^{+2} ion, the actual number of zinc ions adsorbed could account for only about 11.7 per cent of the total surface of the reduced catalyst.

While this appears to be only a very small portion of the surface, it should be pointed out that this is not too far from the maximum amount of zinc ions that could be accommodated on the immediate surface. It should be remembered that each zinc ion which is adsorbed on the catalyst and which is isolated

with the solid catalyst must carry with it two negative ions. By assuming a picture of a zinc ion being adsorbed on the catalyst with two negative ions above it, it would appear that the zinc ions on the catalyst could not be tangential in all instances (and thus cover completely the catalyst surface). Calculations of the area the negative ions held by the zinc ions would cover (for the case of 15×10^{-3} millimoles of adsorbed zinc ions) reveals that about 76 per cent of the catalyst surface would be shielded by the negative ions. This is based on a value of 1.5 Å for the negative ion. Thus, when the catalyst is isolated one might suppose that amounts of zinc ions much greater than the above amount reported adsorbed would not be obtained unless the concept of multilayer adsorption was applied. From the nature of Figure 2, a multilayer concept does not appear evident.

While it might be supposed that the maximum amount of metal ions one could find on the catalyst as isolated would be very near the value thus far found, it does not follow that these are all the zinc ions that may be adsorbed during the hydrogenation process or that this number of zinc ions is uniformly distributed over the catalyst surface. During the hydrogenation it is not necessary that two negative ions be held in a more or less "rigid" layer by each zinc ion. In fact, it is most probably that they are not held to the catalyst surface. Thus, during the hydrogenation there may be more zinc ions on the surface than are to be found there when the catalyst is isolated. This could account for the lack of an exact quantitative relationship being evident between the rate constant and the amount of adsorbed substance.

2. Factors Influencing Adsorption of the Salts

Several other variables were observed to be operative with regard to the amount of zinc ions adsorbed on the isolated catalyst. One of these was

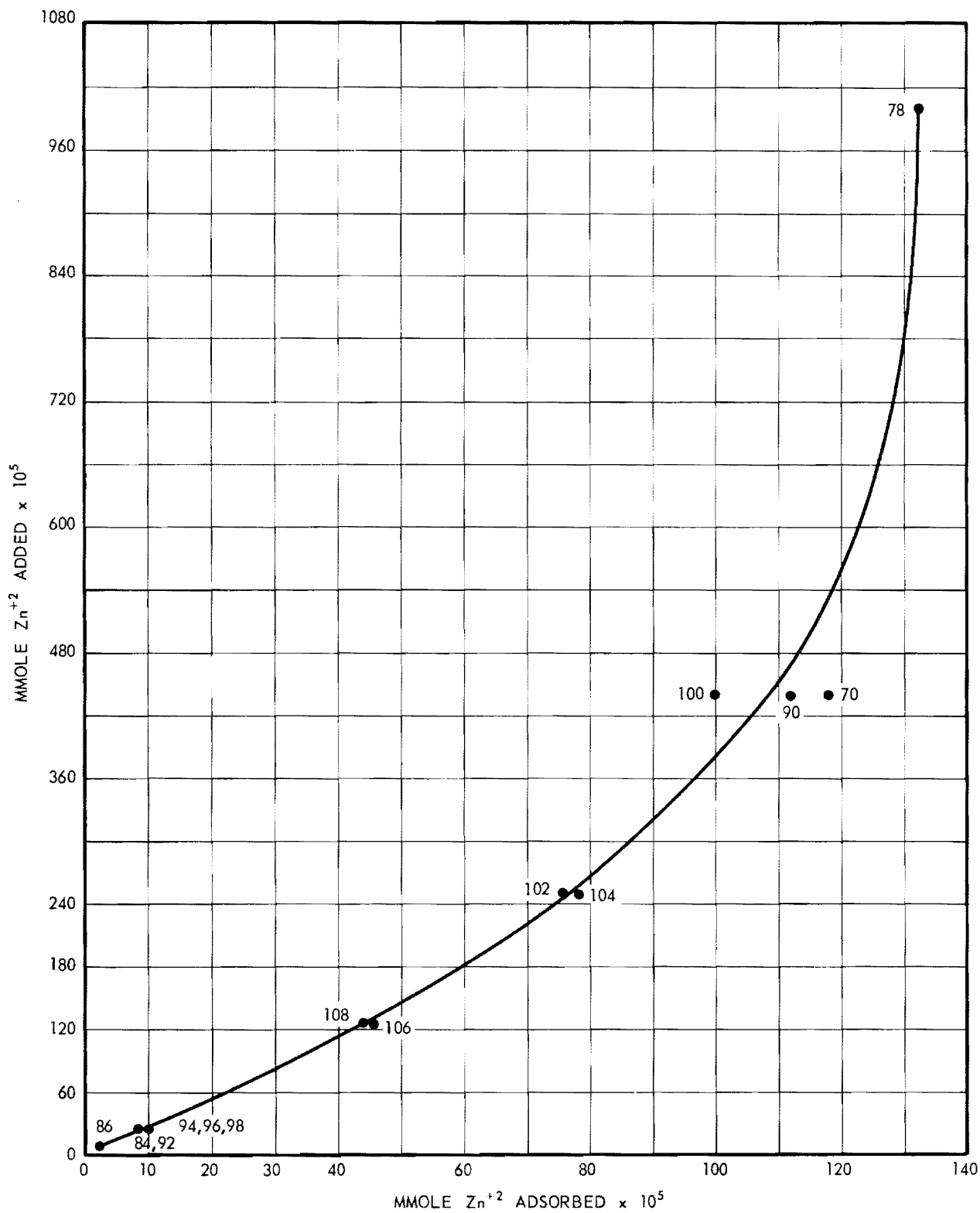


Figure 2. mmole Added Vs. mmole Adsorbed. (See Table XIII for Data)

the components of the hydrogenation system, e.g., the cinnamaldehyde, the oxide, the reduced catalyst, and the atmosphere (either hydrogen or air). Using a standard amount of platinum oxide (0.200 g), it was found that when 5×10^{-3} millimoles of salt were added to acetic acid and shaken in the absence of acceptor and hydrogen molecules, only 16 per cent (0.82×10^{-3} millimoles) of the zinc ions were adsorbed on the oxide surface. In an identical experiment in which the acceptor molecule was present, but hydrogen was absent, only 9 per cent of the zinc ions were adsorbed on the oxide surface. Thus, it appears that the presence of acceptor would decrease metal ion adsorption. This was further investigated by comparing cases in which the acceptor molecule was absent but hydrogen was present with cases in which the acceptor and hydrogen were both absent. In these latter instances, 16 per cent of the added zinc ions were adsorbed, whereas in the former instances, 22 per cent of the added zinc ions were adsorbed. Thus, a second conclusion would lead to the importance of hydrogen to the adsorption process. Of course, this is not unexpected since the presence of hydrogen likely changes the nature of the oxide surface when it effects the reduction of the oxide to the platinum metal. It would appear that when hydrogen is present, the effect of the acceptor is questionable. In cases where both acceptor and hydrogen were present (all other variables being held constant) the per cent adsorption was 22.

A second rather interesting variable of the extent of adsorption of the metal ion on the catalyst is the influence air has upon the process. In these cases, hydrogenations were effected as usual. At the end of the reaction, different treatments were made. When hydrogen was removed from the system and replaced by air and then the reaction mixture shaken for one hour in the presence of air, the usual 21 to 22 per cent adsorption was obtained. If, on the

other hand, hydrogen was removed from the system and the system shaken in the absence of both hydrogen and air, 26 per cent of the zinc ions were adsorbed on the catalyst. In the third case, at the conclusion of the reaction the hydrogen was removed and replaced with more hydrogen, but at atmospheric pressure. After shaking for the additional hour as had been done in previous cases, isolation of the catalyst revealed that 29 per cent of the zinc ions were adsorbed on the catalyst.

The exact reason why these conditions should influence the adsorption of hydrogen is obscure. As was pointed out above, the presence of hydrogen does, apparently, facilitate the adsorption of the metal ion. It may be that if hydrogen is present, it may be adsorbed on certain active centers of the catalyst (centers which are not susceptible to adsorption of zinc ions) and thus make available to other centers a greater availability of electrons for attracting zinc ions. This effect is similar to the well-known inductive effects observed so frequently in organic chemistry.

It was also noted during these studies that differences in amount of zinc absorbed were obtained that depended on the time lapse between completion of the reaction and isolation of the solid catalyst from the reaction mixture. Table XV cites some data obtained in this regard.

From these and other similar studies, it appears that the observed per cent adsorption decreases with time up to about 24 hours, after which there is no longer any change. It seems that there is an initial rapid but random adsorption of zinc ions on the catalyst. Perhaps due, however, to the repulsion of one zinc ion for another, plus the attraction of the zinc ion for two negative ions in a second monolayer above the zinc, these originally adsorbed, randomly distributed zinc ions must rearrange themselves to accommodate the negative

ions and to minimize repulsive forces. This undoubtedly results in a crowding out of some of the zinc ions until a stable arrangement is reached and equilibrium is attained.

TABLE XV
ISOLATION TIME AND PER CENT ADSORPTION

<u>M Moles of Salt Added x 10³</u>	<u>Time Elapsed</u>	<u>Per cent Zn⁺² Adsorbed</u>
10	0.00	30
10	0.09	25
10	5.8	22
10	9.5	19
10	36.	15
10	42.	15
10	90.	15

There was some concern with regard to the manner of treatment of the catalyst at the conclusion of the reaction, and prior to the counting of radioactivity of the catalyst. The initial procedure used called for isolation of the catalyst in the usual manner and then washing it with a 10.0-ml portion of glacial acetic acid. In order to determine if washing would remove a portion of the adsorbed material, three runs, identical in all respects except washing, were made. In the first trial, the usual washing procedure was followed, i.e., when the reaction solution had been removed from the catalyst by filtration under suction, a 10.0-ml portion of glacial acetic acid was added to the catalyst on the funnel, the whole stirred, the solvent permitted to remain on the catalyst a few minutes and then removed by suction filtration. In the second trial, a second wash was used, and in the third trial, a third wash was used. In each case, the amount of Zn⁺² found adsorbed was 40 per cent.

G. Chromatographic Studies1. Preliminary Studies

In order to determine whether or not a given column would likely be satisfactory with the four possible components of a partially hydrogenated cinnamaldehyde, samples of each were necessary. These substances shown in Table XVI were generally commercially available materials and were carefully distilled under reduced pressure; however, compound IV was prepared by fully hydrogenating a sample of I. The reaction product of this hydrogenation mixture was carefully distilled at reduced pressure to yield IV.

TABLE XVI
COMPOUNDS USED IN VAPOR PHASE CHROMATOGRAPHY STUDIES

<u>Compound Designation</u>	<u>Compound</u>	<u>Formula</u>
I	Cinnamaldehyde	$C_6H_5CH = CHCHO$
II	Cinnamyl Alcohol	$C_6H_5CH = CHCH_2OH$
III	3-Phenylpropanal	$C_6H_5CH_2CH_2CHO$
IV	3-Phenyl-1-propanol	$C_6H_5CH_2CH_2CH_2OH$

Table XVII summarizes the results of pure compounds in Table XVI with three of the columns found to be most successful. The known compounds were introduced separately onto the column and the time necessary for the component to come off the column was determined from the chart obtained from the apparatus. It is these times that are recorded in Table XVII. In duplicate experiments the time-intervals under identical conditions could be reproduced usually without any detectable variations. In a very few cases, variations on the order of only 0.1 min were noted. In each case, also, the ethanol used as carrying

solvent was found to come off the column in 1.0 to 1.1 min.

TABLE XVII
VAPOR PHASE CHROMATOGRAPHY RESULTS (KNOWN SAMPLES)

Column Type	Temperature (°C)	Time Taken for Elution of Various Pure Components (Minutes)			
		I	II	III	IV
"O" Perkin Elmer	176	4.4	4.8	2.7	4.2
"O" Perkin Elmer	199	2.7	2.9	1.8	2.6
"R" Perkin Elmer	176	28.7	798.	14.2	31.2
B 132A, 6 Ft.	100	Nothing apparently came off in 45 min			
B 132A, 6 Ft.	126	11.0	13.6	6.3	9.1
B 132A, 6 Ft.	148	5.3	6.1	3.4	4.6

From these data it was decided that column B 132A might be useful. Accordingly, four hydrogenations of cinnamaldehyde in ethanol were effected to the 83 per cent stage and the product isolated by first filtering off the catalyst. The solvent was then removed and a small portion of the hydrogenation product was used. (See Table XVIII for the results.)

From evidence shown in Tables XVII and XVIII it appears that the presence of any of the components has some influence on the adsorption of each of the others. This occurs to such an extent that only shoulders were observable (see codes E and J, Table XVIII) for three of the components. The order of desorption from the column is $C_6H_5CH_2CH_2CHO$, $C_6H_5CH_2CH_2CH_2OH$, $C_6H_5CH=CHCHO$, $C_6H_5CH=CHCH_2OH$, (see Table XVII). In code E, it would appear to show that the peak at 1.0 is due to solvent (ethanol), with other slight peaks close by due to benzene and water present in small amounts. The peak at 3.4 is undoubtedly

TABLE XVIII
 VAPOR PHASE CHROMATOGRAPHY RESULTS
 (COLUMN B 132A)

Code	Sample Number	Temperature, °C	Descriptive Results
A	51	151	Sharp peak at 1.0 min; 2 small peaks 1.6, 1.9 min; large peak 3.4 min; broad peak 4.7-5.8 min.
B	53	151	Same fore peaks; sharp, large peak 3.4 min; broad peak 4.7-5.6 min; with slight shoulder detectable at 4.9 min; moderate peak, small in size at 10.1-10.6 min.
C	54	151	Same fore peaks and sharp peak at 3.4 min; relatively broad peak at 4.7-5.7 min with no observable shoulder.
D	56	151	Same peaks as for sample 54.
E	I, II, III, IV Mix	151	Sharp peak at 1.0; relatively sharp at 3.4 min; broad peak with shoulders at 4.9-6.2 min.
F	51	174	Sharp peaks 0.9 min, 1.4 min, 1.6 min (due to ethanol, benzene, water) Sharp peak at 2.3 min; relatively sharp peak 2.9-3.3 min; with shoulders.
G	53	174	Same sharp peaks; sharp peak at 2.3 min; relatively sharp peak at 3.0 to 3.3 min; a third peak 5.4-5.7 min.
H	54	174	Same peaks as for sample 51.
I	56	174	Same peaks as for sample 51.
J	I, II, III, IV Mix	174	Same fore peaks as for sample 51 but with additional shoulders at 3.4 and 4.3 min.

due to $C_6H_5CH_2CH_2CHO$ and the broad peak with its two shoulders would be the other components, in the order of which the compounds are removed from the column in the absence of each other. From the nature of the curves, quantitative estimates of the relative amounts of each component are not possible--greater separation of components was needed. It did appear, however, that at the hydrogenation stage, 83 per cent of theory (see codes A through D), the reaction mixture contains more of $C_6H_5CH_2CH_2CHO$ than of any other component.

In the case of code B, the detection of a slight shoulder at 4.9 min plus an additional peak (10.1 - 10.6 area) seemed to substantiate these thoughts.

A similar interpretation also seems probable for code F-J, Table XVIII.

2. Later Qualitative Experiments

Since the use of the 6-foot column left much to be desired, a longer 9-foot column was tried. Several hydrogenations were effected and the conditions of these tabulated in Table XIX. Some of these mixtures were used with the 9-foot column and the results are given in Tables XX and XXI.

The results which are presented in Table XX and XXI were rather disappointing. It had been anticipated that the special column would prove to be much more satisfactory for the separation of the four possible products present in the half-hydrogenated mixture: cinnamaldehyde, I, $C_6H_5CH=CHCHO$; cinnamyl alcohol, II, $C_6H_5CH=CHCH_2OH$; 3-phenylpropanal, III, $C_6H_5CH_2CH_2CHO$; and 3-phenyl-1-propanol, IV, $C_6H_5CH_2CH_2CH_2OH$. For example, compounds I and IV were unresolved at 174° C although slight improvement was noticed at 156° C in terms of the time of peak height. In the latter case, however, considerable tailing--that is, a spreading of the time during which fractions would come off the

column--was observed. Such tailings rendered it most difficult to determine precisely when a new component was coming off the column and made it impossible to determine quantitatively the relative amount of each fraction.

TABLE XIX
HYDROGENATION DATA AND TREATMENT
(for Chromatographic Studies, Tables XX-XXV)

Conditions for Hydrogenations: Total initial pressures: 64.6 psi; Ethanol solvent: Enough to make 100 ml of solution; Temperature: 22°-26° C; Weight of catalyst: 0.400 g; Amount of $\phi\text{CH}=\text{CHCHO}$ used: 0.025 mole; Reaction stopped when 0.04 mole of hydrogen had been consumed.

Isolation of Product: At conclusion of reaction, mixture was filtered through a sintered glass funnel, fine porosity, under vacuum. Solvent was evaporated on a steam bath, under water-aspirator vacuum, using a Rinco Rotatory film evaporator.

<u>Sample</u>	<u>Amount of Added Salt Solution</u>
62	None
64	0.2 ml of 0.010M Zn^{++}
66	2.0 ml of 0.010M Zn^{++}
70	2.0 ml of 0.010M Fe^{++}
71	2.0 ml of 0.010M Fe^{++}

Qualitatively, however, some reasonable interpretations can be made regarding the relative amounts of these components. This may be done by considering the height of the peak top. In each instance, from runs 62, 64, 66, compound III appears to be a major component present at the 83 per cent hydrogenation stage. In Table XXII, for example, in run 62, it appears that compound IV is likely present in the larger amount of the two. But it is especially

TABLE XX

CHROMATOGRAPHIC DATA, 9-FT COLUMN, 174° C
(For Runs listed in Table XIX)

Sample	μ l of Sample	Description of Chromatogram*
62	1.0	Sharp peak at 1.6 min, shoulder on far side of peak; two small "humps" poorly resolved at 2.5 and 2.8 min.
64	1.0	Large sharp peak at 1.6 min, shoulder on tail side at 1.9 min, very small peak at 2.1 min, larger peak at 2.2 min.
66	1.0	Sharp peak at 1.6 min; very small peak at 2.1 min on tail side previous peak; larger peak at 2.2 min; tailings to 9.0 min.
ϕ CH=CHCHO	0.8	Sharp peak at 2.2 min with some tailing.
ϕ CH ₂ CH ₂ CHO	0.8	Very sharp peak at 1.6 min, no tailing.
ϕ CH ₂ CH ₂ CH ₂ OH	0.8	Sharp peak at 2.0 min, some tailing.
Mixture**	0.6	Small, sharp peaks at 0.6 and 1.6 min; poor resolution otherwise.

* In each chromatogram any solvent present was noted to come off very rapidly after introduction of the sample.

** The mixture was equivalent amount of the three compounds given in this table and cinnamyl alcohol, ϕ CH=CHCH₂OH.

significant to note that there is not indicated any appreciable amounts of compound II among the products, even when no Zn⁺⁺ was present. It should, though, be mentioned that in the absence of Zn⁺⁺ (run 62), the chromatogram shows a slight "hump" on the far side of the peak of compound III. It may be that this "hump" is due to the presence of small amounts of compound II, C₆H₅CH=CHCH₂OH.

TABLE XXI

CHROMATOGRAPHIC DATA, 9-FT COLUMN, 156° C
(For Runs Listed in Table XIX)

Sample	μ l of Sample	Description of Chromatogram
62	1.0	Large, sharp peak at 2.2 min, shoulder at 2.9 min; medium peak at 3.5 and 3.8 min with considerable tailing.
64	1.0	Large sharp peak at 2.2 min, single, slight hump at 3.0 min; medium peak at 3.6 and 4.2 min.
66	1.0	Large peak at 2.2 min with some tailing; medium peaks at 3.5 and 4.0 min.
ϕ CH=CHCHO	0.6	Peak at 4.0 min with considerable tailing.
ϕ CH=CHCH ₂ OH	0.8	Two humps at 1.8 and 4.6 min, both small and poorly resolved.
ϕ CH ₂ CH ₂ CHO	0.6	Medium peak at 2.2 min with some tailing.
ϕ CH ₂ CH ₂ CH ₂ OH	0.6	Medium peak at 3.5 min with considerable tailing.
Mixture	1.0	Peak at 3.5 min, some tailing; humps at 2.7, 5.4 and 6.1 min; generally poor resolution.

The data from the use of column "O" in Tables XXII and XXIII are also only suitable for qualitative interpretations. It also appears that the quantities of III likely present are more significant whenever Fe⁺⁺ ions are present. This larger amount of III seems to be obtained at the expense of both I and IV, that is, III accumulates both because of conversion of I to III and because of III being converted to IV at a much slower rate. Again, however, there seems little evidence that III is a significant component.

TABLE XXII

CHROMATOGRAPHIC DATA, "O" COLUMN, 175° C
(For Runs Listed in Table XIX)

<u>Sample</u>	<u>μl of Sample</u>	<u>Description of Chromatogram</u>
62	1.0	Large, sharp peak at 2.9 min; small peak at 4.0 min; another small peak at 4.5 min; medium broad peak at 4.8 min, 5.3 min with considerable tailing.
64	1.0	Large sharp peak at 2.8 min; a small peak at 4.1 min; a broad "fused" peak at 4.9 and 5.2 min with tailing.
66	1.0	Large sharp peak at 2.8 min; a slight peak at 4.0 min; a broad "fused" peak starting at 4.3 min and peaking at 4.6 and 4.9 min.
70	1.0	Small peak at 2.9 and 3.1 min; large, sharp peak at 3.8 min with slight shoulder at 4.5 min, medium peak at 4.8 min; small broad shoulder at 5.8 min on this latter peak.
71	1.0	Sharp, medium peak at 2.9 min; large, sharp peak at 3.8 min; medium large peak at 4.5 with small shoulder at 5.8 min; some tailing.
øCH=CHCHO	0.6	Large, sharp peak at 4.3-4.4 min.
øCH ₂ CH ₂ CHO	0.6	Large sharp peak at 2.8 min.
øCH ₂ CH ₂ CH ₂ OH	0.6	Medium peak at 4.2-4.3 min with considerable tailing.
Mixture	1.0	Large sharp peak at 2.8 min, small peak at 4.0 min; large peak at 4.4 min; shoulder peak at 5.6-5.8 min.

3. Qualitative Experiments

The data just cited indicated the desirability to attempt to obtain semiquantitative and fully quantitative data. Of the columns used, the "O" and the "R" columns were found to be the most useful. The data cited in Tables XXIV, XXV, and XXVII were obtained using these.

TABLE XXIII

CHROMATOGRAPHIC DATA, "O" COLUMN, 152° C
(For Runs Listed in Table XIX)

Sample	μ l of Sample	Description of Chromatogram
62	1.0	Large, sharp peak at 3.4 min; small peak at 5.0 min; medium peak at 6.1 min.
66	1.0	Large, sharp peak at 3.4 min; medium large peak at 5.4 min with tailing; broad shoulder peak appears at 6.7 min.
70	1.0	Small peak at 3.6 min; large peak at 4.9 min; Small hump at 5.9 min; small peak at 6.3 min.
ϕ CH=CHCHO	0.6	Large sharp peak at 5.7 min, little tailing.
ϕ CH ₂ CH ₂ CHO	0.8	Large sharp peak at 3.5 min, little tailing.
ϕ CH ₂ CH ₂ CH ₂ OH	0.6	Medium broad peak at 5.4 min; considerable tailing.

The results indicated in Tables XXIV and XXV are indicative of the process which is occurring. First, the double peak obtained when supposedly pure IV was used (see data in Table XXV) was unusual and indicated possibly that the material was not a pure material. It is likely that the sample consisted of IV mainly, but with some of I as a contaminant (or with a reaction product of IV with I). It should be pointed out that in runs 62, 64, and 66 peaks were noted at precisely the same times as when "pure" IV was used. It is believed that the peak at 21.2 min represents some of compound I since the time this component comes off the column is very near 21.2 min.

When the results of (1) hydrogenation in the absence of metal ions (run 62) are compared to (2) hydrogenation in the presence of Zn⁺⁺ (runs 64 and 66) or to (3) hydrogenation in the presence of Fe⁺⁺ ions (runs 70 and 71), it appears that there is little difference in the nature of the 83 per cent hydrogenated

TABLE XXIV

CHROMATOGRAPHIC DATA, "R" COLUMN, 173° C
(For Runs Listed in Table XIX)

Sample	μ l of Sample	Area Under Peak	Description of Chromatogram
62	2.0	19.6 48.9 22.8 60.0	Impurity, peak at 0.7 min (solvent) 12.4 min 21.6 min 26.4 min
64	2.0	8.4 70.4 17.1 77.0	Impurity, peak at 0.7 min (solvent) 12.4 min 21.4 min 26.3 min
66	2.0	4.4 45.5 22.0 88.8	Impurity, peak at 0.7 min (solvent) 12.4 min 21.6 min 26.4 min
70	2.0	10.1 61.2 27.0 28.6	Impurity, peak at 0.7 min (solvent) 12.4 min 25.2 min 27.8 min
71	2.0	16.6 48.6 14.4 24.0	Impurity, peak at 0.7 min (solvent) 12.4 min 25.3 min 27.8 min
71	1.0	21.6 68.2 16.2 28.3	Impurity, peak at 0.7 min (solvent) 12.5 min 25.6 min 28.2 min
ϕ CH=CHCHO	1.0	96.6	25.3 min
ϕ CH ₂ CH ₂ CH ₂ OH	1.0	74.0	27.8 min
ϕ CH ₂ CH ₂ CHO	0.4	26.7	12.4 min
	0.6	48.6	12.4 min
	0.8	55.3	12.4 min
	1.0	81.4	12.4 min

TABLE XXV

CHROMATOGRAPHIC DATA, "R" COLUMN, 183° C
(For Runs Listed in Table XIX)

Sample	μ l of Sample	Area Under Peak	Description of Chromatogram
62	2.0	---- 59.7 12.0 57.4	Impurity peak at 0.7 min, off scale 10.5 min (solvent) 17.6 min 21.2 min
62	2.0	---- 55.4 12.8 53.4	Impurity peak at 0.7 min, off scale 10.5 min (solvent) 17.7 min 21.2 min
64	2.0	6.6 58.1 14.7 64.4	Impurity peak at 0.7 min (solvent) 10.5 min 17.6 min 21.2 min
66	2.0	8.2 51.0 21.6 85.1	Impurity peak, 0.7 min (solvent) 10.5 min 17.7 min 21.2 min
70	2.0	11.1 62.8 7.0 44.1	Impurity peak, 0.7 min (solvent) 10.5 min 17.7 min 20.6 min
71	2.0	19.7 64.0 6.0 39.1	Impurity peak, 0.7 min (solvent) 10.5 min 17.6 min 20.6 min
71	2.0	19.4 64.5 6.0 46.6	Impurity peak, 0.7 min (solvent) 10.5 min 17.6 min 20.6 min
ϕ CH=CHCHO	1.0	104.	20.6 min
ϕ CH ₂ CH ₂ CH ₂ OH	1.0	9.6 39.9	17.7 min 21.2 min
C ₂ H ₅ OH	0.1	18.8	0.7 min
ϕ CH ₂ CH ₂ CHO	0.2	22.2	10.5 min
	0.4	40.1	10.5 min
	0.6	58.6	10.5 min
	0.8	79.4	10.5 min
	1.0	103.	10.5 min
	1.2	122.	10.5 min

product whether or not Zn^{++} ions are present. On the other hand the presence of Fe^{++} does not seem to change the composition of the mixture and there appears to be more of III and less of IV. This may be interpreted in either of two ways. First, it may be that in the presence of Fe^{++} ions, I is reduced to III but that III is less readily converted to IV. As a result, therefore, III would accumulate and there would be less IV. The second manner in which this could happen would be that the conversion of I to II does not occur as readily and thus there would be a greater amount of III that could be formed from I. It is also necessary in this latter case to add the additional hypothesis (since there is no evidence of II being present in any sizeable amounts in the mixture) that as rapidly as II is formed it is converted to IV. This is not unreasonable since compound II possesses an isolated ethylenic bond which should be more readily attacked than would be the aldehyde carbonyl of III. By the same token, though, it might be supposed that III would be more readily formed from I than would II be formed from I. Further determinations would be needed to ascertain the path by which IV is formed in the reaction mixture. But certainly at the present, III appears to be the major partially hydrogenated component of the 83 per cent hydrogenation product with little or no II being present.

One may make some very rough approximations from the data available in Table XXV with regard to a plot of the area under the peak for compound III as a function of the number of μl sample. Comparison of this plot with the areas under the peak for the various hydrogenations carried out can give some indication as to the percentage of III in each hydrogenation mixture. When Fe^{++} ions are present, it appears that III composes about 50 per cent of the product obtained. When no metal ions are present or when Zn^{++} ions are present, it appears that III composes only about 25 to 35 per cent of the product.

Compounds I and IV make up the remainder. By considering the amount of the sample introduced into apparatus that is due to the solvent ethanol, it appears that no more than a few per cent of the product could be due to II. (It might be mentioned here that it has been previously indicated that compound II does not come off the "R" column within the span of time indicated in Tables XXIV and XXV.)

Thus, these data indicate quite strongly that III and not II is the main product obtained in the hydrogenation of cinnamaldehyde, I, to the 83-per-cent-hydrogenated state.

The data from Table XXVII again substantiate the fact that at 83 per cent hydrogenation, the reaction product is almost all substances I, III, and IV with practically no II. The peak at 10.1 min is due to 3-phenylpropanal, III. The peaks at 17.0 and 19.8 to 20.0 min represent the 3-phenyl-1-propanol (this substance continuing to show a double peak). Masking the 19.8 min-peak due to the starting cinnamaldehyde, the presence of the alcohol prevents one from determining exactly the amount of not only the starting aldehyde, but also the saturated alcohol. The areas under the peaks are related to the actual amounts of each material, as is shown in the Table XXVII. However, the amount of III present can be indicated fairly accurately and it appears to be, on the average, 25 per cent of the total material recovered. If this is true, and if one assumes little or no II (the unsaturated alcohol) is present, then the remaining 75 per cent of product material must be I and IV. From the known amount of hydrogen consumed (0.040 mole), calculations tend to show about 5 per cent of I and 70 per cent of IV is present. This is in some contrast to the results in which ethanol was a solvent and it might also be pointed out that there appears to be no significant difference in the composition of the product as to whether the added salt was Fe^{+2} or Zn^{+2} .

TABLE XXVI

HYDROGENATION DATA AND TREATMENT
(For Chromatographic Studies Table XXVII)

Conditions for Hydrogenations: Initial Pressure = 64.6 psi; solvent: Enough to make 100 ml of solution; T = 24-26° C; Weight of catalyst = 0.400 g; 0.024 mole acceptor; Hydrogen uptake = 0.09 mole.

Isolation of Product: At conclusion of reaction, mixture was filtered under vacuum through fine porosity sintered funnel: Solvent evaporated on steam bath, under water-aspirator vacuum, using a Rinco Rotatory film evaporator.

<u>Sample</u>	<u>Solvent</u>	<u>Amount of Added Salt Solution</u>
79	C ₂ H ₅ OH	0.2 ml of 0.010M Fe ⁺⁺
80	C ₂ H ₅ OH	0.5 ml of 0.010M Fe ⁺⁺
81	CH ₃ COOH	10.0 ml of 0.005M Fe ⁺⁺
83	CH ₃ COOH	10.0 ml of 0.005M Zn ⁺⁺
84	CH ₃ COOH	1.0 ml of 0.005M Fe ⁺⁺
85	CH ₃ COOH	1.0 ml of 0.005M Zn ⁺⁺

The testing of the hypothesis that there is no cinnamyl alcohol present at intermediate stages led to experiments in which the hydrogenation was stopped at the 50-per-cent stage. The conditions for effecting this were essentially the same as those indicated previously (Table XIX) except that the reaction was stopped when one equivalent (0.024 mole) of hydrogen was absorbed. The chromatographic studies were carried out using the "R" column. In all cases these showed that the product at the half-hydrogenated state consisted of almost exactly 25 per cent of the phenylpropanal (III). The remainder of 75 per cent was found to be starting material, I, and the phenylpropanol, IV. Now, to obtain a 25 per cent yield of saturated aldehyde, one would have to consume 25 per cent of 0.024 mole of starting material and a like quantity of

TABLE XXVII

CHROMATOGRAPHIC DATA, "R" COLUMN, 183° C
(For Runs Listed in Table XXVI)

Sample	μ l of Sample	Area Under Peak		Description of Chromatogram	
		and μ l represented by area			
79	2.0	20.0	0.2	Impurity peak at 0.7 min (solvent)	
		62.5	0.57		10.1 min
		14.9	0.14		17.0 min
		51.1	0.51		19.8 min
80	2.0	10.8	0.1	Impurity peak at 0.7 min (solvent)	
		33.0	0.36		10.1 min
		16.0	0.19		17.0 min
		26.4	0.28		18.3 min
		76.4	0.76		19.8 min
81	2.0	13.2	0.1	Impurity peak at 0.7 min (solvent)	
		35.5	0.33		10.0 min
		13.2	0.13		17.0 min
		95.2	0.95		19.8 min
83	2.0	10.7	0.1	Impurity peak at 0.7 min (solvent)	
		39.5	0.36		10.0 min
		17.9	0.17		17.0 min
		120.	1.20		20.0 min
84	2.0	1.5	0.0	Impurity peak at 0.7 min (solvent)	
		43.9	0.40		10.1 min
		19.8	0.19		17.0 min
		105.	1.05		19.8 min
85	2.0	1.0	0.0	Impurity peak at 0.7 min (solvent)	
		60.0	0.55		10.1 min
		15.3	0.14		17.0 min
		100.	1.00		19.8 min

hydrogen. Thus, because 0.006 mole of hydrogen was consumed in this formation of saturated aldehyde, there would be 0.018 mole of hydrogen left to be used in converting starting material to the saturated alcohol, IV. This amount of hydrogen would be able to convert 0.009 mole of starting compound to IV.

Hence the composition of the reaction product at the 50-per-cent stage of hydrogenation must consist of 0.009 mole each of I and IV, and 0.006 mole of III. This amounts in percentages to 37.5 per cent of I, 37.5 per cent of IV, and 25 per cent of III.

The results from these chromatographic studies definitely indicate no evidence whatsoever for the hydrogenation of the carbonyl group before the olefinic group.

While one cannot state whether the formation of IV from I occurs via II or III, one can state that under no conditions studied has it been found that compound II can be isolated in more than trace amounts. From the nature of the chromatographic results and the hydrogenation curves obtained, however, it appears that compound I is hydrogenated at the ethylenic bond to give III and that III is then converted to IV.

IV. SUMMARY

Three samples of Adams' platinum catalyst were standardized using benzoic acid as the hydrogen acceptor in an acetic acid solution. These catalysts gave rates of 274, 198, and 174, each times 10^{-4} . The units of these and all other rate constants are $\text{min}^{-1} \text{g}^{-1}$.

Mesityl oxide was selected as one compound for investigation and it was found to hydrogenate in two steps: (1) the reduction of the ethylenic bond which occurred first, and (2) the hydrogenation of the carbonyl group. In acetic acid, the rates of these two steps were 625×10^{-4} and 17.7×10^{-4} , respectively. In ethanol as a solvent, only the first step could be measured, and a rate of 504×10^{-4} was obtained.

When ferrous chloride was added to the acetic acid solution of mesityl oxide in amounts of from 1 to 25×10^{-5} moles, changes in rates were noted. The ethylenic bond was hydrogenated at an increased rate of 730×10^{-4} , and there appeared to be no dependence of rate on the amount of salt added. The second step of the hydrogenation was not affected in the same manner. At low concentration the rate was decreased to 13.3×10^{-4} when 1 to 2×10^{-5} moles of salt were added. Thereafter, however, the rate increased so that when 4×10^{-5} moles of salt were present, the rate was 37.7×10^{-4} . A greater amount of ferrous chloride caused a decrease in the rate.

When the hydrogenation was carried out in the presence of the same salt but using ethanol instead of acetic acid, the ethylenic bond was hydrogenated at a slightly lower rate, 461×10^{-4} . There appeared to be no definite trend or variation with the amount of salt added. The second step of the process completely stopped.

A second salt, zinc acetate, was also used in both acetic acid and ethanol solutions. It was found to increase the rate of the hydrogenation of the ethylenic group when used in amounts up to 4×10^{-5} moles. At this amount the rate was 769×10^{-4} . Larger amounts of salt decreased the rate, and at 25×10^{-5} moles of salt, the rate was 383×10^{-4} . The second step of the hydrogenation was decreased over the entire amounts of salt used.

Ethanol solutions of acceptor to which zinc acetate had been added were also studied, and effects similar to those in acetic acid were noted. The second step of the process, however, did not occur under these conditions.

Besides mesityl oxide, cinnamaldehyde was also studied as a hydrogen acceptor. Except for a few cases in which zinc acetate was present, hydrogen uptake was as expected. With ferrous chloride the hydrogen uptake did proceed beyond the theoretical amount, but this was probably due to some reduction of the ferric iron impurities present.

Both freshly distilled and ordinary, as-obtained cinnamaldehyde were tried as acceptors. In the case of undistilled material, ethanol was found to be a better solvent than acetic acid (rates were in ratio of 1.05 to 1.00). For the distilled material, rates in the two solvents were, respectively, 297 and 233 (both times 10^{-4}).

When sodium hydroxide solution (0.50 ml of 3N) was added to the distilled cinnamaldehyde in ethanol, the rate of hydrogenation increased and a rate of 315×10^{-4} was obtained. An initial induction period of 3.5 to 4.0 minutes was noted before a regular, more rapid uptake of hydrogen occurred. Again, the reaction stopped after an uptake of 1.7 equivalents of hydrogen.

When ferrous chloride was added to distilled cinnamaldehyde in ethanol, an increase in the rate constant was observed, the increase being greater when larger amounts of salt were added. A rate constant of 311×10^{-4} was obtained when 100×10^{-3} millimoles of ferrous chloride were added.

In ethanol, zinc acetate was not found to be effective in increasing the rate of hydrogenation, nor did the salt decrease the rate. Here, the uptake of hydrogen was complete and two equivalents were absorbed.

In acetic acid solution, however, slightly different results were obtained, a slight increase in rate being observed only when amounts on the order of $0.05 \text{ millimoles} \times 10^{-3}$ of zinc acetate were added. Generally, addition of zinc acetate decreased the rate of hydrogenation.

Techniques were devised whereby very small amounts of zinc ions could be determined (quantitatively) using EDTA (ethylenediaminetetraacetic acid) with Erio-T as an indicator. This was necessary since the radioactive zinc chloride solution obtained from the Oak Ridge National Laboratories contained enough Zn-65 to produce a known intensity of radioactivity and thus precise amount of zinc present in this solution was unknown. The techniques used permitted an analysis for as little as 2.8×10^{-6} moles of Zn ions in as little as 0.1 ml of solution. Then, knowing the precise zinc content of the radioactive zinc chloride solution, it was possible to prepare a standard solution containing radioactive Zn-65 ions and to use this solution to impregnate a known weight of catalyst. This standard catalyst, now containing a known amount of zinc and possessing a known amount of radioactive zinc, was used to compare with catalysts obtained from those hydrogenations in which varying amounts of zinc salt had been added to the hydrogenation mixture. From this comparison, the extent of adsorption of zinc salt on the catalyst could be

determined. The reproducibility of the methods was excellent and it was found that from 6 to 52 per cent of the added zinc acetate became adsorbed on the catalyst.

These studies also indicated that the adsorption of the salt on the catalyst surface was related in an asymptotic manner to the amount of salt added to the solution. While the greater per cent adsorption occurred at the lowest amounts added, the actual amount adsorbed increased until 15×10^{-3} millimoles of adsorbed material was found for 250×10^{-3} millimoles of salt added. Addition of more salt beyond this latter amount did not result in a significant increase in amount of adsorbed material. The detection of these very small amounts adsorbed on the surface of the catalyst was only possible through the use of radioactive techniques developed during this research.

From a determination that the reduced platinum catalyst had a surface area of $8.3 \text{ m}^2/\text{g}$, and from the maximum amount of zinc acetate found to be adsorbed on the catalyst surface, it was determined that about 11.7 per cent of the surface was covered with zinc ions. On the other hand, if one advances the idea that for each zinc ion adsorbed there must be two acetate ions held nearby (and thus presenting a shielding effect) there would be a shielding of at least 76 per cent of the surface. Thus, even though more surface would be available for zinc adsorption, not too much more zinc could be adsorbed unless one permitted multilayer adsorption of the negative ion. There was no evidence of multilayer adsorption.

Among the factors which influence the adsorption of the salt were the presence of hydrogen, or acceptor, the time of isolation, and the presence or absence of air.

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Adsorbed salts were not able to be removed by extensive treatments with water, acid (acetic) or air.

Chromatographic studies were also made to determine the nature of the product. In no case was any isolation of cinnamyl alcohol observed. When the reaction was stopped at either 83 per cent completion or at 50 per cent completion, 25 per cent of 3-phenyl-propanal was found in the product. The remainder of the product consisted of unreacted starting material and the fully hydrogenated 3-phenyl-1-propanol. In the case of 50 per cent completion, the product consisted of 25 per cent 3-phenyl-propanal, and 37.5 per cent each of cinnamaldehyde and 3-phenyl-1-propanol.

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