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THE KINETICS OF CATALYTIC HYDROGENATION
OF METHYL-SUBSTITUTED BENZALDEHYDES

A THESIS

Presented to

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Alvaro Abidaud

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THE KINETICS OF CATALYTIC HYDROGENATION
OF METHYL-SUBSTITUTED BENZALDEHYDES

Approved:

A. L. ...

Chairman

[Signature]

[Signature]

Date approved by Chairman:

Dec. 4, 1967

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SUMMARY

A study of the rate of the hydrogenation of 14 methyl-substituted benzaldehydes was made, using 10 per cent palladium-on-carbon as catalyst and a solvent of absolute alcohol under an initial pressure of approximately 64 psia. The standard mixtures were prepared from 1.00 ml. of aldehyde, 0.20 g. of catalyst, and 50 ml. of absolute alcohol. A standard Parr Hydrogenation Apparatus was used.

The hydrogenation was found to be first order with respect to the hydrogen pressure for the small range of pressure drop of a single run.

The reaction rate constant and the weight of catalyst used were in direct proportion over the range of catalyst weight from 0.050 g. to 0.300 g.

An Arrhenius-type temperature dependence of the reaction rate with temperature was found, and activation energies were calculated from the slope of the $\log K$ versus $1/T$ plots (see Table 9).

In mono-methylbenzaldehydes a methyl group *ortho* to the aldehyde increased the rate of hydrogenation of the aldehyde to the alcohol, whereas a *meta* or a *para* methyl group decreased the rate of hydrogenation of the aldehyde. This was explained in terms of hyperconjugation theory in which a formal negative charge could be supported on the carbonyl-oxygen, thus enabling it to be attracted more readily to the catalyst surface. In higher substituted aldehydes the influence of an

ortho methyl group was also noted to be significant.

The products of hydrogenation were identified by using gas chromatography. In all cases only four peaks appeared in the chromatograph. These were identified as the solvent, the benzenoid hydrocarbon, the unreacted aldehyde, and the alcohol. Most of the aldehydes hydrogenated to the corresponding alcohol and gave maximum amounts of alcohol at about 60 to 70 per cent consumption of aldehyde. The amount of the corresponding benzenoid hydrocarbon began to increase significantly after this point.

No trend was found relating the structure of the methylbenzaldehydes to the amount of alcohol or of hydrocarbon produced.

Table 1. The Hydrogenation of Methyl-substituted Benzaldehydes
Over 10 Per Cent Palladium Supported on Carbon

Aldehyde	Activation Energy Calories per Mole	$K_{25^{\circ}\text{C}}$ $\text{min.}^{-1} \text{g.}^{-1}$
Benzaldehyde	3,520	0.0077
2-Methylbenzaldehyde	12,600	0.0088
3-Methylbenzaldehyde	7,300	0.0029
4-Methylbenzaldehyde	14,400	0.0038
2,3-Dimethylbenzaldehyde	6,100	0.0060
2,4-Dimethylbenzaldehyde	8,000	0.0059
2,5-Dimethylbenzaldehyde	10,800	0.0057
2,6-Dimethylbenzaldehyde	6,950	0.0052
3,4-Dimethylbenzaldehyde	10,700	0.0039
3,5-Dimethylbenzaldehyde	8,700	0.0043
2,3,4-Trimethylbenzaldehyde	8,840	0.0044
2,4,5-Trimethylbenzaldehyde	7,000	0.0078
2,4,6-Trimethylbenzaldehyde	7,960	0.0044
2,3,5,6-Tetramethylbenzaldehyde	6,850	0.0047

CHAPTER I

INTRODUCTION

The purpose of this research was to determine the reaction rate constants for the hydrogenation of a series of methyl-substituted benzaldehydes in the presence of a catalyst composed of 10 per cent palladium supported on carbon. From these data it was hoped that a relationship between structure of acceptor and the rate could be realized.

Equilibrium is a thermodynamically controlled state which depends only on the difference in the free energies of the reactants and products. Thus, a catalyst can not influence the position of an equilibrium. For this reason a catalyst has been defined as "a substance which, by its presence in a medium where a reaction takes place, either increases or decreases the reaction velocity without being changed itself or appearing in the products resulting from the reaction."¹ The manner in which the catalyst takes part in the reaction, however, is not so easily explained.

Heterogeneous catalytic reactions are those in which gaseous or liquid reactions take place in the presence of a solid catalyst. The solid responsible for these effects is termed a *contact mass*. The contact masses employed in heterogeneous catalytic reactions are

¹H. M. Lohse, "Catalytic Chemistry," Chemical Publishing Co., New York, 1945, p. 1.

frequently metallic in character.

The discussion of interest might then be confined to metallic masses. These can be classified into three categories:² (a) macroscopic forms of metals such as gauzes, wires, or foils which may be catalytically active; (b) microscopic forms of metals as catalysts containing no other component, such as colloidal metals, powdered metals, or evaporated metal films; and (c) microscopic forms of metals serving as catalysts containing one or more other components. The last category, of wide use in chemical industry, may be further divided into (1) supported metal catalyst, (2) promoted metals, and (3) bi-functional catalysts.

The supported metal catalyst consists of the metal dispersed over another material called a *carrier*. The carrier has no catalytic activity itself, but when a metal is supported on its surface, the physical and mechanical properties of the metal may be changed to such a degree that the supported metal may be more active as a catalyst than the unsupported metal. Since the supported metals usually consist of more than 80 per cent by weight of carrier, their surface areas are effectively increased. This is one significant purpose of the support. In general, one will find that the reactivity of a solid catalyst needs not necessarily be directly proportional to the surface area. As Wheeler³ has pointed out, the rate of reaction may be directly propor-

²M. Prettre, "Catalysis and Catalysts," Dover Publications, Inc., New York, 1963, p. 5.

³P. H. Emmett, Editor, "Catalysis," Reinhold Publishing Corp., New York, 1955, Vol. II, Chap. 2.

tional to the surface area, directly proportional to the square root of the surface area, or completely independent of the surface area, depending on the pore distribution within the catalyst and the reaction kinetics of the particular reaction system.

In promoted metal catalysts, the promotor may or may not have catalytic activity of itself. A promoted metal, however, will exhibit at some composition (usually less than 10 per cent by weight of promoter) an activity greater than that expected if both components were acting individually. In some instances it has been observed that there may exist chemical interaction between the promoter and the metal.⁴

A substance having more than 50 per cent by weight of the catalyst may be defined as a carrier and if less than 50 per cent, may be defined as a promoter.

In bi-functional catalysts, the component which supports the metal catalyst may play a significant part in the overall reaction. A good example of the bi-functional catalyst is platinum supported on silica-alumina which is very selective for isomerization, cyclization, and dehydrogenation of straight-chain paraffins. The hydrocarbon is adsorbed on the metal and then may migrate to the oxide surface where isomerization or other reaction occurs.

If one considers a system composed of a catalyst, a hydrogen acceptor in a solvent, and an atmosphere of hydrogen, one can visu-

⁴G. C. Bond, "Catalysts by Metals," Academic Press, London and New York, 1962, Chap. 3.

alize several distinct problems. First, the hydrogen must dissolve in the solvent. This is usually facilitated by some sort of agitation which in some measure may exert control on the rate of the reaction. Second, the hydrogen and the acceptor must reach the catalyst surface and be adsorbed on it in a position favorable for reaction. Third, after the reaction has taken place, it is necessary that the products of the reaction be removed or be desorbed from the catalyst.

Each of these steps may proceed in a variety of ways. The first is effected by exposure of the solvent to the hydrogen. The second is partially a translational problem which is effected by the viscosity of the solvent and partially a problem of adsorption which is effected by the surface area of the catalyst, the nature of the catalyst surface, and other factors which will be discussed in greater detail below. The last step is necessary because the catalyst must be able to react with many starting molecules in successive steps unless sufficient catalyst is present to allow simultaneous reaction of all of the molecules of acceptor and hydrogen.

Adsorption on the catalyst surface appears to be the primary difference in a catalytic and a noncatalytic reaction. Two types of adsorption occur: physical adsorption and chemisorption.

Physical adsorption is a relatively weak adsorption, being due to van der Waals' forces. It is essentially nonspecific with respect to adsorbent and adsorbate, easily reversible, and involves relatively small heats of adsorption similar in magnitude to heats of liquifaction.⁵

⁵P. H. Emmett, Editor, "Catalysis," Vol. I, Reinhold Publishing Corp., New York, 1954, p. 2.

This heat of adsorption is frequently found to be of the order of a few hundred calories per mole and thus physical adsorption is deemed to have little importance in heterogeneous catalytic reactions.

Chemisorption, or activated adsorption as it is sometimes called, is the result of binding by valence forces of the same nature as those which bind atoms together in molecules.⁶ These forces are much stronger than those involved in physical adsorption and the heats involved are of the same order of magnitude as the heats of chemical reactions. Values of 10 to 100 kcal. per mole are common. For example, the energy of adsorption of hydrogen molecules on tungsten is known to be of the order of 45 kcal. per mole at 25°C.⁷ Chemisorption is irreversible or is reversible only with difficulty.

The large forces and high degree of selectivity encountered in chemisorption may preclude the desired reaction. Thus, a variety of substances may interfere with the reaction by being strongly and preferentially adsorbed on the catalyst surface, thereby excluding the adsorption of the reactants; the apparatus then must be kept free of materials which are known to be poisons.

Palladium is exceptionally useful in catalytic hydrogenation reactions involving not only carbon-to-carbon unsaturated bonds of olefins and acetylenes, but also a number of other functional groups including nitro, nitroso, oximino, nitriles, acid chlorides, and various aromatic systems. Many of these reactions proceed under mild

⁶*Ibid.*, p. 75.

⁷O. Beeck, *Rev. Modern Phy.*, 17, 61 (1945).

conditions, palladium supported on high surface carbon being the most commonly used catalyst form.

For reduction reactions with reagents other than hydrogen, such as sodium borohydride and hydrazine, palladium is also an effective catalyst.^{8,9}

The carbon-carbon double bond is, in general, very easily reduced over palladium catalysts and a great number of such reductions have been recorded. Both straight-chain and cyclic olefins such as maleic acid, fumaric acid, cinnamic acid, cyclohexene, isoprene, and phellandrene are readily hydrogenated. Palladium is an excellent catalyst for the reduction of unsaturated aldehydes to saturated aldehydes such as crotonaldehyde to butyraldehyde.¹⁰

Palladium is particularly useful for the selective hydrogenation of functional groups on aromatic rings since it has only a very slight tendency to cause ring saturation under mild conditions.

Since the work involved in this research was primarily of a kinetic nature, it seems advisable to discuss the equations and terminology which will be used in later chapters of this thesis.

Some reactions proceed with a greater velocity than others. There are situations where it is desirable to know the relative rates of several reactions. It may be sufficient to say that reaction A is faster than reaction B, but often a more precise definition of the

⁸R. T. Coutts, *J. Chem. Soc.*, 4610 (1963).

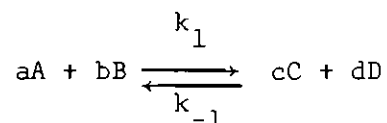
⁹A. Furst, *Chem. Rev.* 65, 51 (1965).

¹⁰P. N. Rylander, *Englehard Inds. Tech. Bul.*, IV, 49 (1963).

relationship is needed. The study of kinetics has developed general equations which can be applied to most reactions.

It has been observed that many reactions occur at a rate proportional to the concentration of one of the reactants present. Since the reactant is being used up, the reaction rate constantly changes. Thus, when one-half of the original reactant is used up, the reaction rate is one-half the original rate. Other reactions may have a rate proportional to some power of the reactant concentration other than one. For the purpose of definition, the reaction rate may be considered to be the rate of change of that substance involved in the reaction. A negative sign indicates disappearance of that substance.

For a typical mechanistic equation



where a , b , c , and d represent the number of times A, B, C, and D, respectively, enter the reaction before or during the rate-determining step, and k_1 , k_{-1} are the rate constants for the forward and reverse reactions, respectively, the rate may be expressed as the rate of disappearance of A:

$$\frac{-d[A]}{dt} = k_1[A]^a [B]^b - k_{-1}[C]^c [D]^d . \quad (1)$$

The terms in brackets, $[]$, refer to molar concentration of the particular substance. A derivative is used because the concentrations

are constantly changing with time. Similar rate equations may be set up for B, C, and D; the k_1 and k_{-1} 's for these equations will be identical in value to those of Equation (1).

If the reverse reaction can be neglected (i.e., if k_{-1} can be set equal to zero) Equation (1) becomes

$$\frac{-d[A]}{dt} = k_1[A]^a [B]^b \quad (2)$$

The exponent "a" is defined as the order of the reaction with respect to A. Similarly, "b" is defined as the order of the reaction with respect to B. The overall order of the reaction, n, is defined as the sum of the exponents to which the concentrations of the reacting species are raised:

$$n = a + b . \quad (3)$$

Consider the case where a hydrogenation reaction is first order in hydrogen and zero order in acceptor. Since the hydrogen pressure and not concentration is measured as a function of time, it is desirable to express the rate equation in terms of pressure. From the general gas law it can be stated that

$$[H_2] = ZP_H \quad (4)$$

where P_H represents the absolute pressure of hydrogen and Z is a pro-

portionality constant dependent on the volume of the system, the temperature of the gas, etc. Substituting $[H_2]$ for $[A]$ in Equation (2) and setting $a = 1$ and $b = 0$ there is obtained

$$\frac{-d[H_2]}{dt} = k_1[H_2]^1 [B]^0 \quad (5)$$

which reduces to

$$\frac{-d[H_2]}{dt} = k_1[H_2] \quad (6)$$

Substitution of Equation (4) in Equation (6) gives

$$\frac{-d(P_H Z)}{dt} = k_1 P_H Z \quad (7)$$

which, upon rearrangement, yields

$$\frac{-d(P_H Z)}{P_H} = k_1 dt Z \quad (8)$$

Integration of this equation between the limits of $P_H = P_0$ at $t = 0$ and $P_H = P$ at $t = t$ gives

$$\log \frac{P_0}{P} = \frac{k_1 t Z}{2.303} \quad (10)$$

Thus, a plot of $\log P_0/P$ versus time yields a straight line, the slope of which equals $Z K_1/2.303$. The apparent rate constant, $K_1 Z$, therefore, may be obtained by multiplying the slope of the line by 2.303. The apparent rate constant must be converted to actual rate constants if comparisons of rates of reactions, carried out in different physical systems, are desired. If the system remains essentially the same with the exception of the volume of the hydrogen supply system, the apparent rate constants may be compared by multiplying them by the volume of the hydrogen to which the pressure measurements apply.¹¹ Thus, a reaction having a total volume of one liter of hydrogen present would appear to react at twice the rate of a similar system having a two liter hydrogen volume. Conversion to a true rate constant is much more difficult and requires a knowledge of the solubility of hydrogen in the solution being studied.

Heterogeneous catalytic reactions, like most chemical reactions, demonstrate a dependence of rate upon the reaction temperature. Therefore, before the reaction rate constants of reactions can be compared they must be converted to the same temperature. To make this correction the activation energy of the reaction must be known. This is found from the reaction rate constants for the reaction at different temperatures.

Quite often the temperature dependence will be such that a plot of $\log k$ versus $1/T$ will be linear. This result is that predicted by

¹¹H. A. Smith, W. Bedoit, Jr., and J. Fuzek, *J. Am. Chem. Soc.* 71, 3769 (1949).

the Arrhenius equation:

$$\frac{d(\ln k)}{dt} = \frac{E_a}{RT^2} \quad (11)$$

where R is the general gas law constant, T is the absolute temperature, k is the reaction rate constant, and E_a is called the Arrhenius activation energy. The activation energy bears no relationship to the free energy of the reactants and products, just as there is no relationship between the height of two mountains and the depth of the valley between them. It is best considered as an energy barrier over which the reactants must pass before they can be transformed into product.

The Arrhenius Equation (11) can be transformed through integration to

$$\ln K = \frac{-E_a}{RT} + \text{constant} \quad (12)$$

which is equivalent to

$$K = e^{-E_a/RT} \quad (13)$$

Integration of Equation (11) between the limits k_1 and T_1 and k_2 at T_2 and conversion of the resulting equation to log to the base 10 yields:

$$\log \frac{k_2}{k_1} = \frac{E_a (T_2 - T_1)}{2.303 R (T_1 T_2)} \quad (14)$$

A plot of K versus T according to Equation (13) is an "S" shaped curve having a reasonably straight portion which curves toward a horizontal at both ends. At higher temperatures, K approaches a constant value asymptotically. At low temperatures the slope of the line decreases with temperature until $K = 0$ at $T = 0^\circ \text{K}$.¹²

The plot of $\log k$ versus $1/T$ may have a break with two linear portions of differing slopes on each side of the break. This is usually attributed to a change in the mechanism of the reaction at the temperature at which the break occurs.¹³

While an Arrhenius type of temperature dependence is the most typical, other relationships may be observed. If the $\log k$ versus $1/T$ plot is not linear and the curvature can not be attributed to a transition between two linear portions of the curve, additional terms may be added to the Arrhenius equation to form a new expression which will give a linear plot. Explosions, enzyme reactions, and oxidations of carbon are known to follow other relationships.

¹²A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Second edition, John Wiley and Sons, Inc., New York, 1961, p. 23.

¹³*Ibid.*, p. 24.

CHAPTER II

EXPERIMENTAL

All boiling points, melting points, and reaction temperatures reported herein are uncorrected.

ApparatusThe Parr Hydrogenation Apparatus

A series 3901 shaker-type hydrogenation apparatus, purchased from Parr Instrument Company, of Moline, Illinois, was used in this work. This apparatus consisted of a shaker assembly and a hydrogen tank connected by suitable valves and tubing. The shaker assembly was composed of a bottle holder mounted so that it could rock back and forth about a point approximately one inch above the top of the bottle and a connecting rod attached to a drive wheel. The bottle was caused to oscillate through a 30-degree arc at a frequency of 220 cycles per minute, thus imparting a sloshing motion to any liquid in the bottle.

A hydrogen tank of approximately four liters volume was connected to the reaction bottle through a two-way valve and a section of high pressure rubber tubing. This valve was arranged so that one position connected the bottle to a tank and another position exposed the bottle to a vacuum pump. Either or both of these positions could be activated to allow evacuation of the bottle, evacuation of the tank, or admission of hydrogen to the bottle. The hydrogen tank was connected to a cylinder of commercial hydrogen through another valve and

suitable tubing. A gauge was provided to measure the hydrogen pressure within the system. This gauge was a six-inch Ashcroft Laboratory Test Gauge graduated in 0.25 psi units.

The bottles used were standard 500 ml. Parr pressure reaction bottles.

The Manometer

The variation of reaction rate with the initial hydrogen pressure was studied during this work. At gauge pressures of 2 psi the accuracy of the pressure readings afforded by the pressure gauge became questionable. This was overcome through the use of a manometer.

The manometer consisted of a mercury-filled U-tube of 6 mm. glass tubing and a meter stick so arranged that the difference in the levels of mercury in the two legs of the tube could be measured. A rubber tube led from one leg of the U-tube to the reaction apparatus while the other leg was open to the atmosphere. The entire apparatus was mounted on a suitable stand which held the U-tube vertical.

The Distillation Columns

Distillation of the aldehydes was accomplished in a Todd Precision Distillation Assembly manufactured by the Todd Scientific Company, Springfield, Pennsylvania. This column was 42 inches in length and 1/2-inch in diameter. Also, an Annular Teflon Spinning Band Distillation Column made by Nester/Faust Manufacturing Corporation, Newark, Delaware was used. This column was 24 inches in length and 1/4-inch in diameter.

Temperature Control Equipment

This system consisted of an electric stirrer, a circulating pump, a large water bath, and a water jacket for the reaction bottle.

The metal water jacket had a water inlet just above the bottom and an outlet just below the opened top. A rubber ring of suitable outside and inside diameters was used to seal the jacket and the bottle.

Water from the large water bath was circulated through the jacket by means of a conventional circulating pump. The desired temperatures could be obtained within 0.5°C by addition of hot water or of ice water to the water bath.

Gas Chromatograph

The purity of reagents and the analyses of the products of hydrogenation were obtained using a Dual Column Programmed Temperature Gas Chromatograph, Model 720, made by the F & M Scientific Corporation, Avondale, Pennsylvania.

The stainless steel columns used were 6 feet in length, 10 per cent Carbowax 20 M, on 60-80 mesh Diatoport S. The gas chromatograph was used under the following conditions: injection port temperature 275°C, detector temperature 355°C, oven temperature 200°C, helium flow 10 ml/12 sec., chart speed set at one, attenuation set at four. Samples of two microliters were injected by means of a 10 microliter syringe.

Miscellaneous Equipment

The reactions were timed by a Cleco stopwatch.

Reagents

Solvent

Ethanol. Absolute ethanol (99+ per cent) was obtained from U. S. Industrial Chemicals and used without any further treatment.

Hydrogen

Hydrogen was obtained from American Cryogenics, Inc., and was used without further purification.

Catalyst

The catalyst used in all experiments consisted of 10 per cent palladium supported on carbon, and was prepared in this laboratory according to procedure in Appendix M of this thesis.

Aldehydes

Benzaldehyde, 3-methylbenzaldehyde, and 4-methylbenzaldehyde were obtained from Columbia Organic Chemicals Company, Inc., Columbia, South Carolina.

2-methylbenzaldehyde, 2,3-dimethylbenzaldehyde, 2,4-dimethylbenzaldehyde, 2,5-dimethylbenzaldehyde, 2,6-dimethylbenzaldehyde, 3,4-dimethylbenzaldehyde, 3,5-dimethylbenzaldehyde, 2,3,4-trimethylbenzaldehyde, 2,4,5-trimethylbenzaldehyde, 2,4,6-trimethylbenzaldehyde, and 2,3,5,6-tetramethylbenzaldehyde were prepared in this laboratory according to procedures given in the Appendices.

Since most of the aldehydes oxidized rapidly in air it was necessary to store them under a nitrogen atmosphere in small bottles with tight rubber caps, and to keep them in the dark.

Procedure

Preparation for Hydrogenation

The ability of small amounts of foreign materials to poison the catalyst system used was found to be quite significant. Extreme precautions were taken to insure cleanliness of the system.

The tank of the hydrogenation apparatus was washed with water and then with methanol, and, after a drainage period, was placed in a drying oven at 110°C to remove all traces of methanol and water.

The bottles, pipettes, syringes, and graduated cylinders were scrubbed in a detergent solution and rinsed in tap water. This was followed by chromic acid cleaning solution and a final triple rinse in distilled water. After all glassware was dried in an oven at 110°C, it was allowed to cool and capped with aluminum foil until needed.

All rubber stoppers and the rubber tubing used for hydrogenation apparatus were boiled in 20 per cent sodium hydroxide solution for at least half an hour to remove sulfur containing materials, then rinsed, boiled in tap water, and finally rinsed in distilled water.

Catalyst Pretreatment

In order to prevent an induction period and to obtain maximum activity of the catalyst, it was found necessary to pretreat each catalyst sample immediately prior to its use.

A given amount of catalyst was weighed to 0.1 milligram on a tared watch glass and was transferred to the reaction bottle by aid of a camel hair brush. Fifty ml. of absolute alcohol was measured with a graduated cylinder and added into the reaction bottle.

Table 2. Boiling Points and Densities of Aldehydes

Aldehyde	Observed Boiling Point °C/mm. Hg	Density g./ml.
Benzaldehyde	176.2/741	1.07
2-Methylbenzaldehyde	88.0/16	1.04
3-Methylbenzaldehyde	60.0/5	1.01
4-Methylbenzaldehyde	53.8/2	1.02
2,3-Dimethylbenzaldehyde	98.0-100.0/12	1.03
2,4-Dimethylbenzaldehyde	93.0/2	1.02
2,5-Dimethylbenzaldehyde	110.0/10	1.00
2,6-Dimethylbenzaldehyde	94.0-96.0/3	1.20
3,4-Dimethylbenzaldehyde	85.0-87.0/5	1.02
3,5-Dimethylbenzaldehyde	75.0/5	1.00
2,3,4-Trimethylbenzaldehyde	110.0-115.0/18	0.99
2,4,5-Trimethylbenzaldehyde ^a	95.0-97.0/5	-
2,4,6-Trimethylbenzaldehyde	97.0-99.0/5	1.10
2,3,5,6-Tetramethylbenzaldehyde ^b	130.0-132.0/10	-

^aMelting point 42.0°C.

^bMelting point 38.5°C.

The reaction bottle with mixture in it was placed on the shaker and clamped tightly in place. By proper use of the valve system, the reaction bottle was opened to the vacuum pump and was evacuated until the solvent began to boil. Hydrogen was then introduced into the bottle after which the latter was again evacuated in order to insure complete removal of air from the reaction bottle. The hydrogen pressure was then adjusted to 50 psig and the shaker started. After 20 minutes of shaking, the catalyst surface was deemed to be cleaned and saturated with hydrogen. The shaker was stopped and, using the valve and pump system, the hydrogen was removed. Air could then be admitted safely into the bottle and the bottle removed from the shaker assembly.

Hydrogenation Procedure

After pretreatment of the catalyst, the given volume of substrate was immediately introduced into the reaction bottle by means of a 2 ml. or 5 ml. hypodermic syringe. The reaction bottle and its contents were placed and clamped tightly on the shaker. Following the same treatment described above to expel the air, the pressure was adjusted to the desired value. The shaker and a stop watch were then started simultaneously and the pressure was observed and recorded. At regular time intervals pressure readings were taken and recorded.

At the completion of the reaction, the residual hydrogen in the reaction bottle was expelled and the bottle removed from the shaker. After filtering the reaction mixture, the spent catalyst was preserved and the filtrate was retained in air tight bottles.

Hydrogenation Procedures at Various Temperatures

Hydrogenation studies at various temperatures were subjected to

the usual procedures with the exception that water at the desired temperature of reaction was circulated around the bottle by means of the metal jacket and the circulating pump described above.

Before starting the shaker mechanism, it was necessary that the temperature of the reaction mixture be the same as that of the water bath. At least ten minutes of water circulation was found necessary for this.

Product Isolation and Identification

The catalyst was removed from the reaction mixture by filtration through a fritted glass disc. The products were identified by using the gas chromatograph described previously. Samples ranging from 1 to 4 microliters were analyzed. The various peaks which appeared on the chromatogram were identified by using the retention time of known compounds. Areas were integrated by means of a planimeter and finally plots of the number of moles of each compound versus the amount of hydrogen taken up were made.

CHAPTER III

DISCUSSION OF EXPERIMENTAL RESULTS

Benzaldehyde was chosen as a standard hydrogen acceptor and was, therefore, investigated extensively. The remaining aldehydes studied were chosen for their structural characteristics which would make a relationship of aldehyde structure to hydrogenation performance most likely to appear. The products of reaction were shown to be mainly the corresponding alcohols, at least for about 60 to 70 per cent reaction.

The work was divided into seven broad categories:

- a. The kinetics of the reaction;
- b. The relationship between the reaction rate constant and the initial concentration of aldehyde;
- c. The relationship between the reaction rate constant and the initial hydrogen pressure;
- d. The relationship between the reaction rate constant and the amount of catalyst used;
- e. The relationship between the reaction rate constant and the reaction temperature;
- f. The relationship between the reaction rate constant and the structure of the aldehyde; and
- g. The analysis of the reaction products.

No attempt was made to study each aldehyde for its behavior in all categories. Table 3 will illustrate the studies made and the aldehydes upon which they were made.

The Kinetics of the Reaction

Benzaldehyde

Reaction mixtures consisting of 50 ml. of absolute ethanol, 0.200 g. of catalyst, and 0.0106 moles (1.00 ml.) of benzaldehyde were prepared and hydrogenated according to the procedure discussed in Chapter II. The reaction data were processed and a plot of $\log P_0/P$ versus time was prepared. Plotting this the data in this manner would give a straight line if the reaction was first order in hydrogen pressure. As can be observed by an inspection of Figure 1, a typical plot of such data, the linear relation is observed. The reaction is, therefore, first order in hydrogen pressure.

Aldehydes Other Than Benzaldehyde

The hydrogenation data from all of the methyl-substituted benzaldehydes studied were plotted as $\log P_0/P$ versus t , and a linear relationship was observed in each instance. This indicated that all of the aldehydes studied followed a kinetic relationship representing a reaction first order in hydrogen pressure. The experimental conditions for these hydrogenations were identical to those for the reduction of benzaldehyde.

Table 3. Aldehydes and Parameters Studied

Aldehyde	EFFECT OF VARYING THE:			
	Catalyst Amount	Aldehyde Concentration	Hydrogen Pressure	Reaction Temperature
Benzaldehyde	X	X	X	X
2-Methylbenzaldehyde				X
3-Methylbenzaldehyde		X	X	X
4-Methylbenzaldehyde	X			X
2,3-Dimethylbenzaldehyde				X
2,4-Dimethylbenzaldehyde				X
2,5-Dimethylbenzaldehyde				X
2,6-Dimethylbenzaldehyde				X
3,4-Dimethylbenzaldehyde				X
3,5-Dimethylbenzaldehyde	X			X
2,3,4-Trimethylbenzaldehyde				X
2,4,5-Trimethylbenzaldehyde				X
2,4,6-Trimethylbenzaldehyde				X
2,3,5,6-Tetramethylbenzaldehyde				X

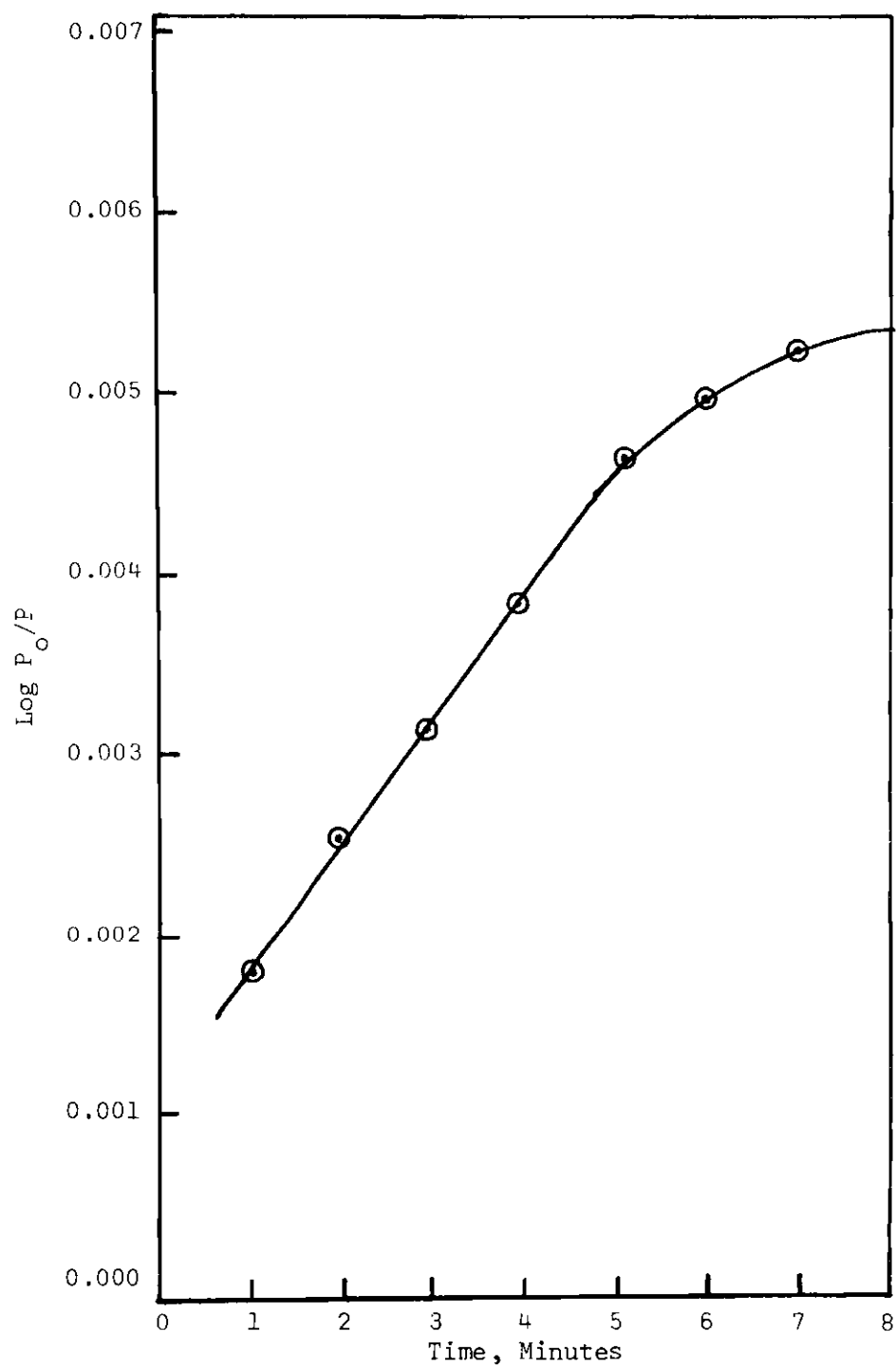


Figure 1. Hydrogenation of Benzaldehyde Plotted as First Order in Hydrogen Pressure

Table 4. First Order Rate Constants for
the Hydrogenation of Aldehydes

Aldehyde	$K_{25^{\circ}\text{C}}$ min. ⁻¹ g. ⁻¹
Benzaldehyde	0.0077
2-Methylbenzaldehyde	0.0088
3-Methylbenzaldehyde	0.0029
4-Methylbenzaldehyde	0.0038
2,3-Dimethylbenzaldehyde	0.0060
2,4-Dimethylbenzaldehyde	0.0059
2,5-Dimethylbenzaldehyde	0.0057
2,6-Dimethylbenzaldehyde	0.0052
3,4-Dimethylbenzaldehyde	0.0039
3,5-Dimethylbenzaldehyde	0.0043
2,3,4-Trimethylbenzaldehyde	0.0044
2,4,5-Trimethylbenzaldehyde	0.0078
2,4,6-Trimethylbenzaldehyde	0.0044
2,3,5,6-Tetramethylbenzaldehyde	0.0047

The Relationship Between the Reaction Rate Constant
and the Initial Concentration of Aldehyde

Benzaldehyde

A series of hydrogenation was made using three different initial amounts of benzaldehyde. Table 5 shows that the rate constant did not vary as the initial benzaldehyde concentration changed; indeed, a two-fold and a fourfold increase in the aldehyde concentration produced no change in the reaction rate constant. From this data, the reaction of benzaldehyde and hydrogen was shown to obey a kinetic equation representing zero order kinetics with respect to aldehyde concentration. The reaction rate constant was, therefore, expected to be independent of the initial amount of aldehyde used.

Table 5. Initial Aldehyde Amounts Versus
Reaction Rate Constants

Aldehyde	Moles of Aldehyde	Reaction Rate Constant	Reaction Temperature
Benzaldehyde	0.0106	$0.0077 \text{ min.}^{-1} \text{ g.}^{-1}$	25.0°C
Benzaldehyde	0.0212	$0.0076 \text{ min.}^{-1} \text{ g.}^{-1}$	25.0°C
Benzaldehyde	0.0424	$0.0076 \text{ min.}^{-1} \text{ g.}^{-1}$	25.0°C
3-Methylbenzaldehyde	0.0084	$0.0029 \text{ min.}^{-1} \text{ g.}^{-1}$	25.0°C
3-Methylbenzaldehyde	0.0168	$0.0030 \text{ min.}^{-1} \text{ g.}^{-1}$	25.0°C
3-Methylbenzaldehyde	0.0336	$0.0029 \text{ min.}^{-1} \text{ g.}^{-1}$	25.0°C

Aldehydes Other Than Benzaldehyde

The effect of varying the initial concentration of methyl-substituted benzaldehydes on the reaction rate constant was the same noted with benzaldehyde. Table 5 shows that the rate constant for the hydrogenation of 3-methylbenzaldehyde remains constant as its initial concentration is changed by a twofold and fourfold increase. This indicated that the reaction was zero order with respect to aldehyde.

The Relationship Between the Reaction Rate Constant and the Initial Hydrogen Pressure

The reaction was found to follow a linear plot when $\log P_0/P$ was plotted versus t . This indicated that the velocity of the reaction was influenced by the hydrogen pressure.

Benzaldehyde

Benzaldehyde was hydrogenated at initial pressures of 64, 32, and 16 psia. Over this wide range of hydrogen pressure, linear plots were obtained when $\log P_0/P$ was plotted versus t . The slopes of these lines were the same indicating that the reaction was first order in hydrogen.

Aldehydes Other Than Benzaldehyde

The effect of varying the initial hydrogen pressure on the reaction rate constant noted with benzaldehyde was also noted with the methyl-substituted benzaldehydes. Table 6 summarizes the data for the dependence of the rate constant on the initial hydrogen pressure. This indicates that the reaction was independent of the initial hydrogen pressure.

Table 6. Rate Constant Versus Initial Hydrogen Pressure

Aldehyde	Initial Hydrogen Pressure	Reaction Rate Constant min. ⁻¹ g. ⁻¹	Reaction Temperature Degrees C
Benzaldehyde	64.30	0.0077	25.0
Benzaldehyde	32.40	0.0078	25.0
3-Methylbenzaldehyde	16.72	0.0030	25.0
3-Methylbenzaldehyde	64.40	0.0029	25.0

The Relationship Between the Reaction Rate
Constant and the Amount of Catalyst Used

If one considers a heterolytic catalytic reaction as a reaction occurring on the surface of a catalyst, one would expect the reaction to have a rate proportional to the amount of catalyst present. This is found to be true over certain ranges of catalyst amount. Such ranges, for lack of a better term might be called "normal" or "optimum." At very large catalyst to reactant weight ratios the catalyst surface may not be utilized efficiently. In such cases it is possible that the reactants are unable to reach the catalyst surface as fast as they are adsorbed, react, and products are desorbed. This results in a depletion of reactants in the general vicinity of the catalyst and in the entire catalyst surface not being maximumly covered with reactants. Thus, a reaction rate somewhat less, proportionately, than that expected

from consideration of the rate at some lower catalyst weight results. The deviations observed at very low catalyst weights are not fully understood; however, the presence of smaller than "normal" weight ratios of catalyst to reactants may affect the equilibrium of the reaction just as the application of pressure to a reaction which proceeds with a large change in volume will change that equilibrium. Thus, the aldehyde may be adsorbed more strongly or the product may be desorbed less readily than when more ideal conditions are observed. Then, too, any poisoning effects would be much more noticeable when the relative amount of catalyst is small since a given amount of catalyst poison would affect a larger percentage of the active surface. This would result in proportionally less of the surface being available to reactants and a more significant decline in rate of reaction.

The relationship between the rate and the catalyst weight may be described by a plot in which the rate per gram of catalyst is plotted against weight of catalyst.¹⁴ Three situations may arise:

(1) the plot may take the form of a horizontal line, indicating that the catalyst is operating under equilibrium conditions;

(2) the line may have a negative slope, indicating that the surface is not being entirely used; or

(3) the line may have a positive slope, indicating that the catalyst is not present in amounts great enough to allow equilibrium to be reached. For kinetic work, the desired portion of the curve is, of

¹⁴A. Williams, Jr., "Catalytic Hydrogenation Studies Using Five Per Cent Rhodium Supported Catalyst," Unpublished Ph.D. Dissertation, Georgia Institute of Technology, 1962, p. 46.

course, that portion where $K/g.$ is constant.

Benzaldehyde

Benzaldehyde was hydrogenated using different amounts of catalyst. Table 7 shows the results of this study. The data indicated that the reaction rate was proportional to the amount of the catalyst over the range of weights used.

Table 7. $K/g.$ Benzaldehyde, 25.0°C

Catalyst Weight Grams	$K/g. \text{ min.}^{-1} \text{ g.}^{-1}$
0.050	0.0078
0.100	0.0078
0.200	0.0077
0.300	0.0078

4-Methylbenzaldehyde and 3,5-Dimethylbenzaldehyde

A similar study was made using 4-methylbenzaldehyde and 3,5-dimethylbenzaldehyde. The results of the study are given in Table 8.

To summarize, these data indicated that from 0.05 to 0.30 g. of catalyst the reaction rate was directly proportional to the weight of the catalyst used and the reaction was occurring under conditions of equilibrium between catalyst, and adsorbed reactants and reactants in solution.

Table 8. K/g. Versus Catalyst Weight

Aldehyde	Grams	K/g.
4-Methylbenzaldehyde	0.100	0.0038
4-Methylbenzaldehyde	0.200	0.0039
4-Methylbenzaldehyde	0.300	0.0039
3,5-Dimethylbenzaldehyde	0.100	0.0039
3,5-Dimethylbenzaldehyde	0.200	0.0039
3,5-Dimethylbenzaldehyde	0.300	0.0037

Activation Energy Studies: The Change of the Reaction
Rate Constant with Changing Reaction Temperature

The hydrogenations of all the aldehydes studied obeyed an Arrhenius type relationship of rate versus temperature. From a typical plot, such as is shown in Figure 2, an apparent activation energy was obtained. Table 9 records the energies obtained.

The initial temperatures of the reactions were used as the temperature for the Arrhenius plot.

The Relationship Between the Reaction Rate Constant
and the Structure of the Aldehyde

Table 4 is a tabulation of the reaction rate constants for all the aldehydes studied. These were obtained from the Arrhenius Activation Energy plots and thus are an average of all data taken.

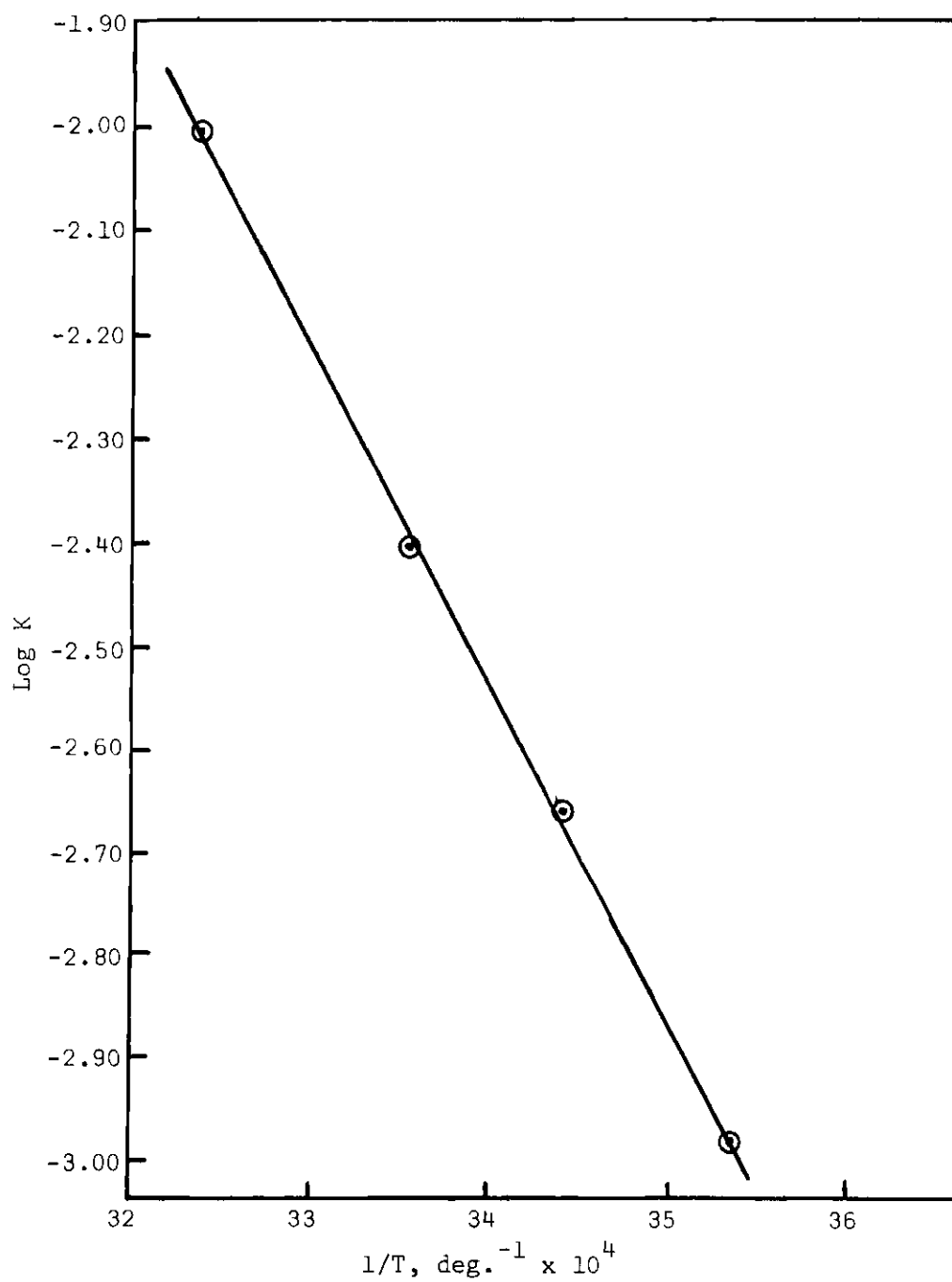


Figure 2. Activation Energy Plot for 4-Methylbenzaldehyde

Table 9. The Arrhenius Activation Energy for the Reduction of Aldehydes

Aldehyde	Activation Energy Calories Per Mole
Benzaldehyde	3,520
2-Methylbenzaldehyde	12,600
3-Methylbenzaldehyde	7,300
4-Methylbenzaldehyde	14,400
2,3-Dimethylbenzaldehyde	6,100
2,4-Dimethylbenzaldehyde	8,000
2,5-Dimethylbenzaldehyde	10,800
2,6-Dimethylbenzaldehyde	6,950
3,4-Dimethylbenzaldehyde	10,700
3,5-Dimethylbenzaldehyde	8,700
2,3,4-Trimethylbenzaldehyde	8,840
2,4,5-Trimethylbenzaldehyde	7,000
2,4,6-Trimethylbenzaldehyde	7,960
2,3,5,6-Tetramethylbenzaldehyde	6,850

If the rate of hydrogenation of benzaldehyde is taken as a standard, then it is seen from Table 4 that methyl-substituted benzaldehydes having an *ortho*-methyl-substituent react faster than those unsubstituted at this position. The data show that an *ortho*-methyl-substituent increases the rate, a *meta*-methyl-substituent decreases the rate, and a *para*-methyl-substituent decreases the rate though to a lesser extent than the *meta*.

According to Schmidt¹⁵ catalytic hydrogenation is an ionic catalysis. By the polarization of the reactants their centers of electric gravity are separated. We get dipoles, the electric field of which is much stronger than that of an undeformed organic compound.

Difference in adsorption of the carbonyl group by the catalyst could be responsible for the difference in reaction rate constants observed. Thus a formal negative charge on the oxygen atom is supported by hyperconjugation. This would make the carbonyl to be more readily attracted to and be more easily adsorbed by the catalyst surface.

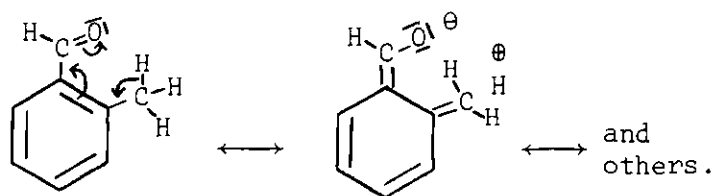


Figure 3. Hyperconjugation Structure for 2-Methylbenzaldehyde

¹⁵O. Schmidt, *Chem. Rev.*, 12, 363 (1933).

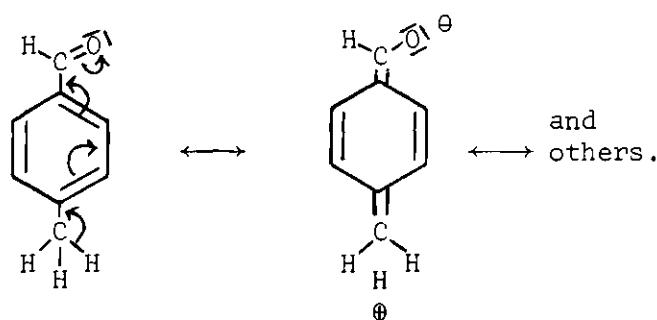


Figure 4. Hyperconjugation Structure for 4-Methylbenzaldehyde

Figures 3 and 4 show one of several possible hyperconjugation structures for 2-methylbenzaldehyde and 4-methylbenzaldehyde. The hyperconjugation structure for 2-methylbenzaldehyde is energetically more favorable than the corresponding one for 4-methylbenzaldehyde because the work necessary to separate the charges in the case of the *ortho*-methylbenzaldehyde is less than in the *para*-methylbenzaldehyde. Also intermolecular hydrogen bonding between the carbonyl-oxygen and one of the *ortho*-methyl-hydrogens is possible in the case of an *ortho*-methylbenzaldehyde, but not possible in the case of a *para*-methylbenzaldehyde.

A *meta*-methyl substituent cannot enter in hyperconjugation with the carbonyl group and thus it is unable to aid in the development of a formal negative charge on the carbonyl-oxygen atom.

It is known that in *ortho*-alkyl-substituted anilines the basicity follows the order: aniline < *ortho*-methylaniline < *ortho*-ethylaniline < *ortho*-isopropylaniline < *ortho*-*t*-butylaniline. The effect of increasing the basicity of the nitrogen atom as the *ortho*-substituent increases in size is attributed to steric inhibition of resonance

between the unshared pair of electrons on nitrogen and the aromatic ring. From this, one would anticipate that benzaldehydes having an *ortho*-methyl substituent would react slower than benzaldehydes having no *ortho*-methyl substituent. Data on Table 4 shows just the opposite effect. Every time benzaldehyde has an *ortho*-methyl substituent, it reacts faster than the unsubstituted one at that position. This shows, then, that steric factors are not so important in the case of methyl substituted benzaldehydes having an *ortho*-methyl group as in the case of the *ortho*-methyl substituted anilines.

As mentioned previously, hyperconjugation theory is helpful in this case because an *ortho*-methyl substituted benzaldehyde can have favorable hyperconjugation structures involving the carbonyl-aldehyde and the *ortho*-methyl group.

Each of the di-substituted benzaldehydes having substituent in *ortho* position is faster than those di-substituted benzaldehydes having no *ortho* substituent. Two *ortho*-methyl substituents, as in the case of 2,6-dimethylbenzaldehyde, decrease the rate of hydrogenation of the aldehyde group. This might be due to steric hindrance to the approach of hydrogen on both sides of the carbonyl group. Also, models indicate some steric inhibition of resonance by one of the *ortho*-methyl groups to the formation of hyperconjugation structures involving the other *ortho*-methyl group.

From Table 4 it can be seen that 2,4,6-trimethylbenzaldehyde, having two *ortho*-methyl groups, and 2,3,4-trimethylbenzaldehyde having only one *ortho*-methyl group, hydrogenate at the same rate. We would have expected the former to react slightly slower than the latter for

reasons discussed previously for the 2,6 isomer. The other trimethyl-substituted benzaldehyde studied was 2,4,5-trimethylbenzaldehyde. It reacts very fast compared to the other trimethyl-substituted benzaldehydes hydrogenated. The lack of a "buttressing effect" is significant, so that this compound actually is like a mono-*ortho*. Finally, 2,3,5,6-tetramethylbenzaldehyde hydrogenates at a rate comparable to other benzaldehydes having both *ortho*-positions substituted, for the reasons mentioned for the 2,6 isomer.

Analysis of the Reaction Products

The products were identified by gas chromatograph using procedures described previously. In all cases only four peaks appeared in the chromatograph. These were identified as solvent, hydrocarbon, aldehyde, and alcohol. Figures 5 through 19 show the data obtained for each aldehyde hydrogenated in this study. It can be seen that for most of the aldehydes hydrogenated, the alcohol was by far the major product at about 60 to 70 per cent completion. The corresponding hydrocarbon started to build up significantly after this point.

No trend was found relating the structure of the methylbenzaldehydes to the amount of alcohol or of hydrocarbon produced. Tables 10 and 11 summarized the data on the amounts of alcohol and hydrocarbon formed at various stages of reaction.

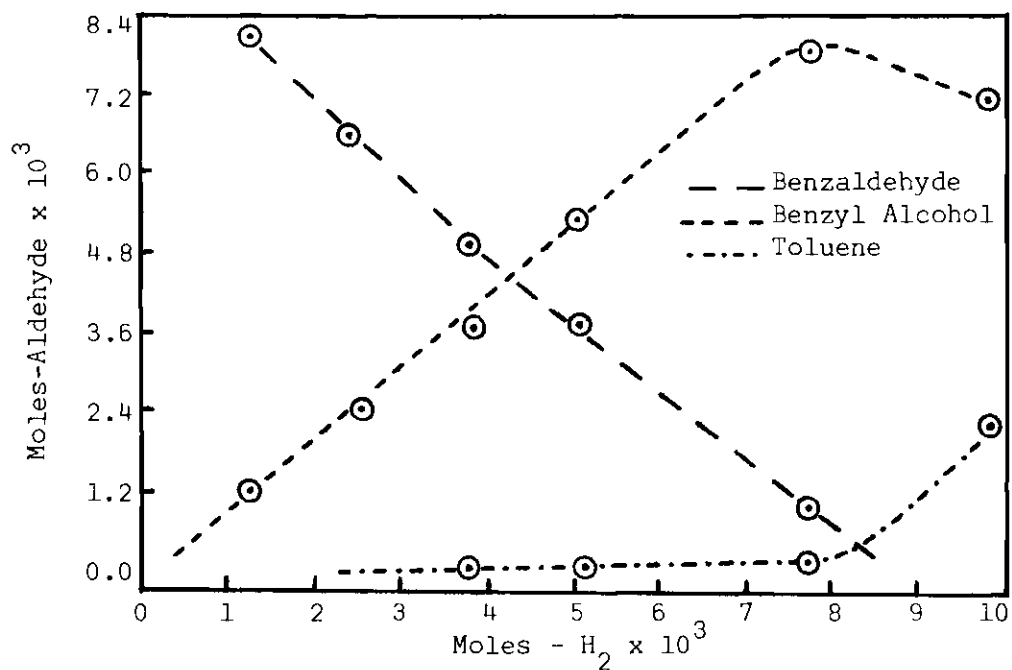


Figure 5. Product Analysis--Benzaldehyde

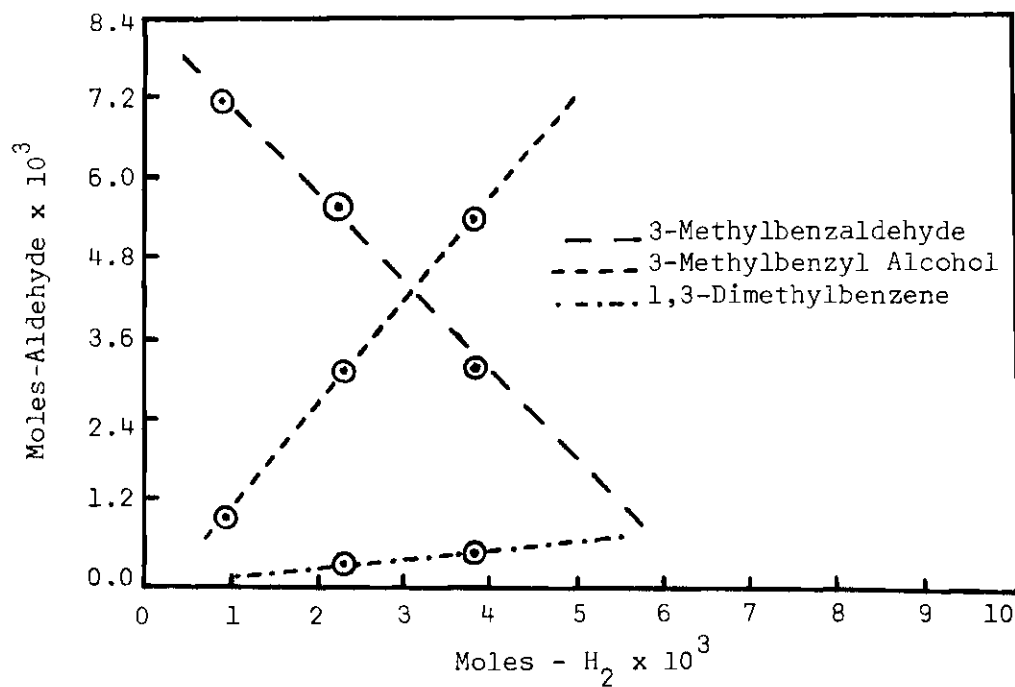


Figure 6. Product Analysis--3-Methylbenzaldehyde

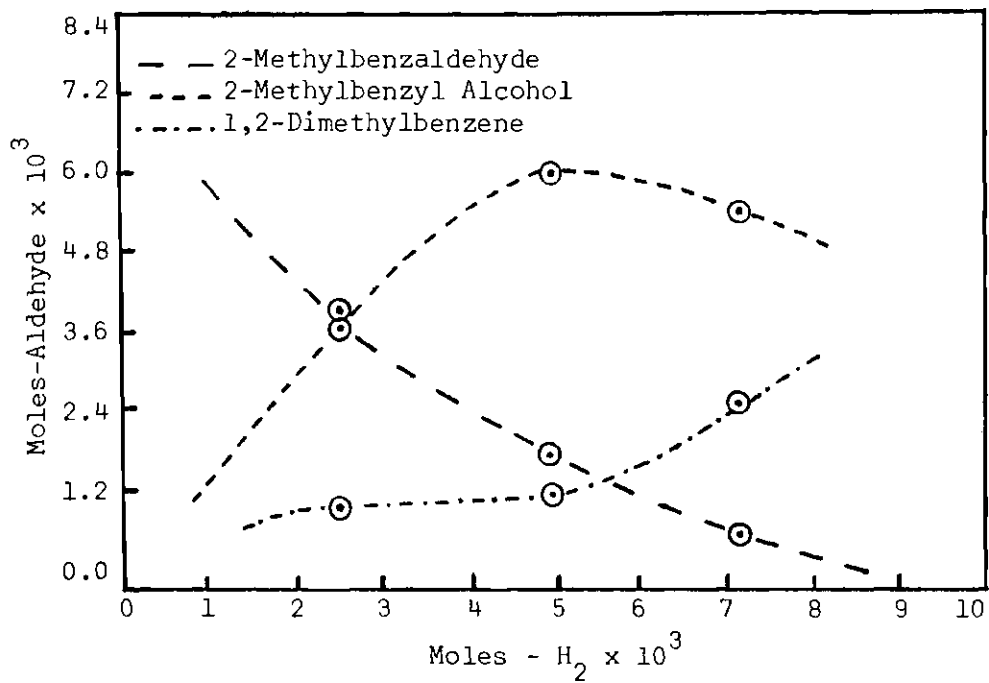


Figure 7. Product Analysis--2-Methylbenzaldehyde

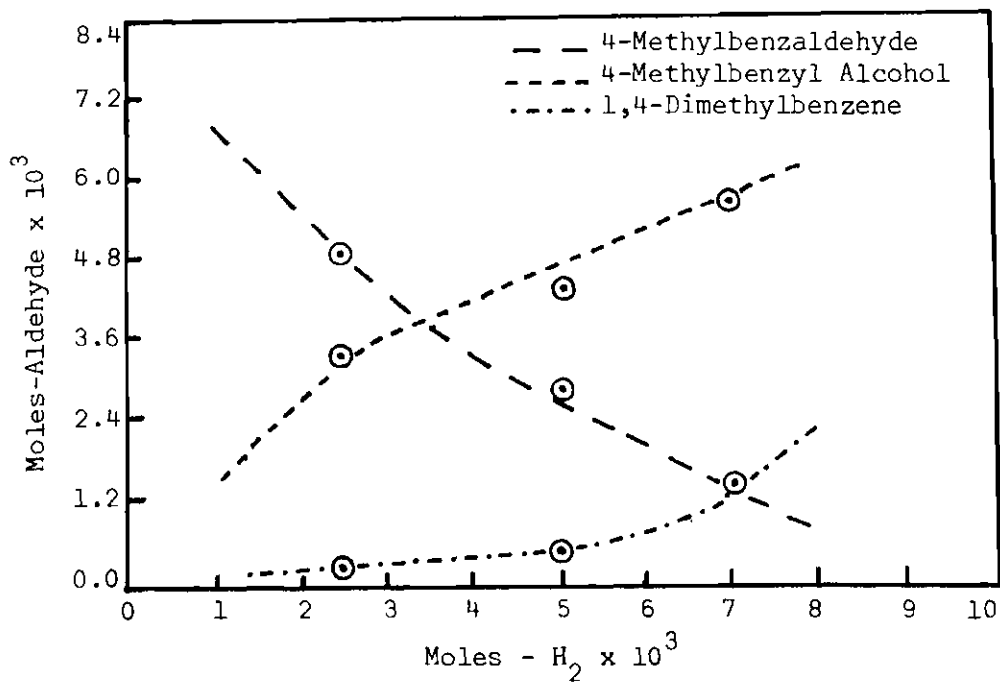


Figure 8. Product Analysis--4-Methylbenzaldehyde

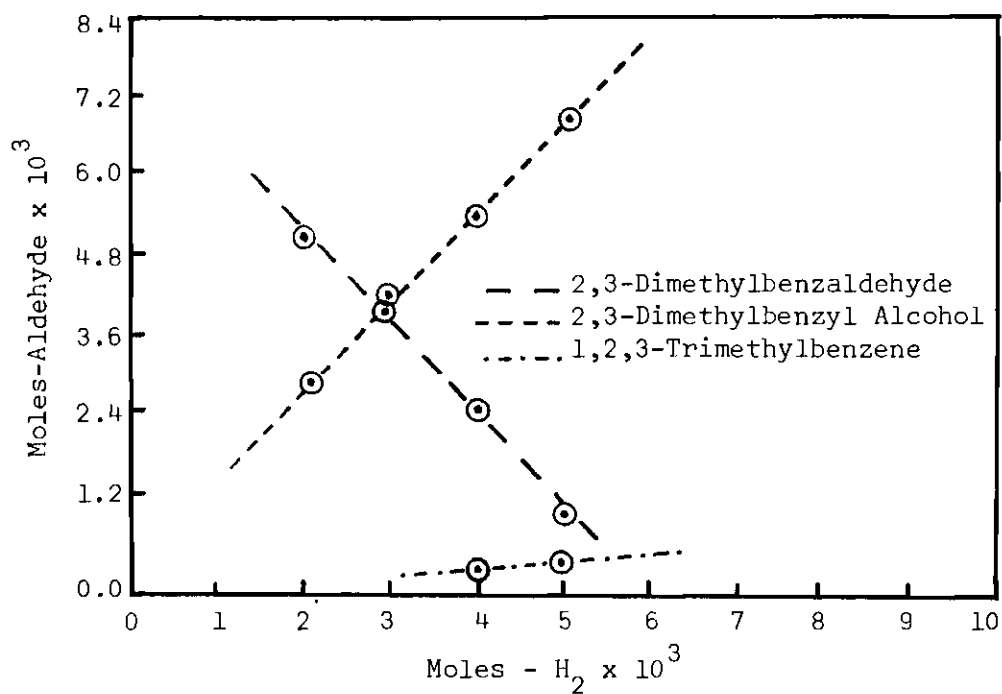


Figure 9. Product Analysis--2,3-Dimethylbenzaldehyde

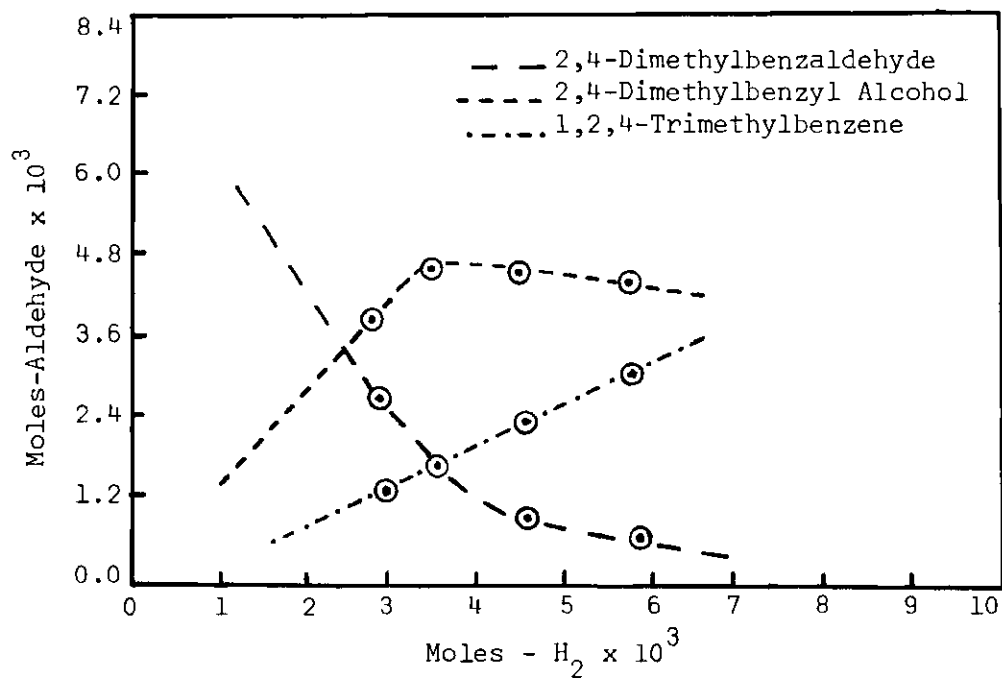


Figure 10. Product Analysis--2,4-Dimethylbenzaldehyde

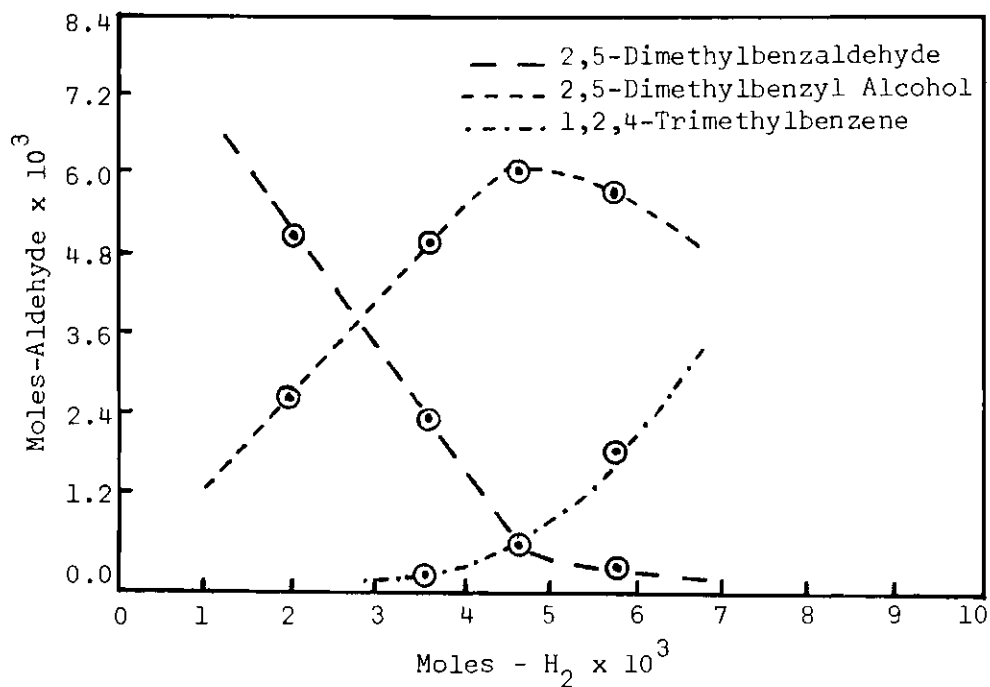


Figure 11. Product Analysis--2,5-Dimethylbenzaldehyde

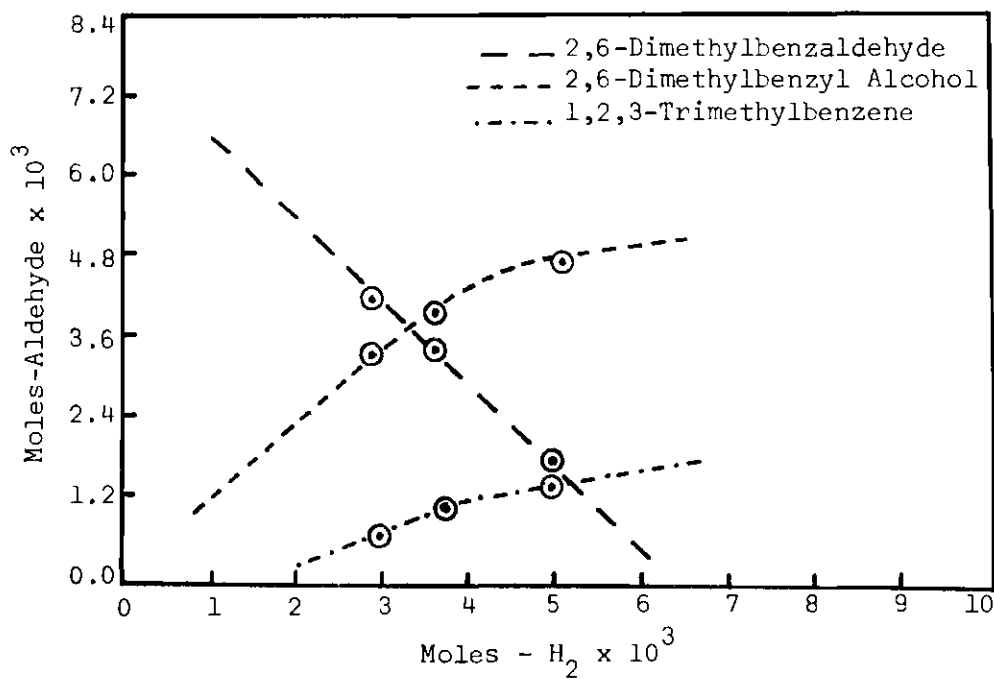


Figure 12. Product Analysis--2,6-Dimethylbenzaldehyde

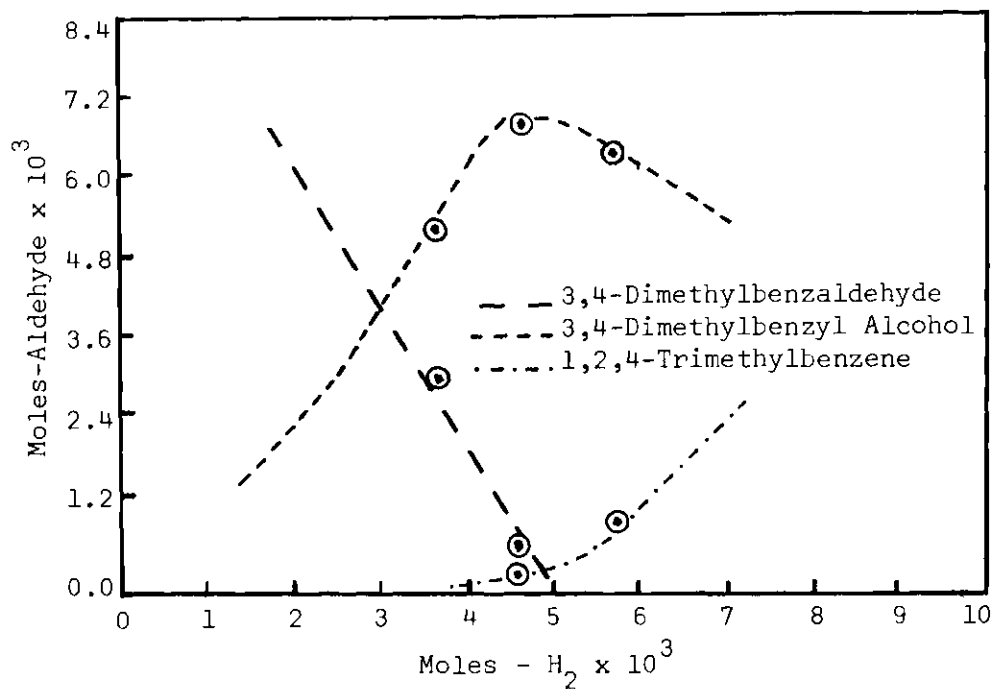


Figure 13. Product Analysis--3,4-Dimethylbenzaldehyde

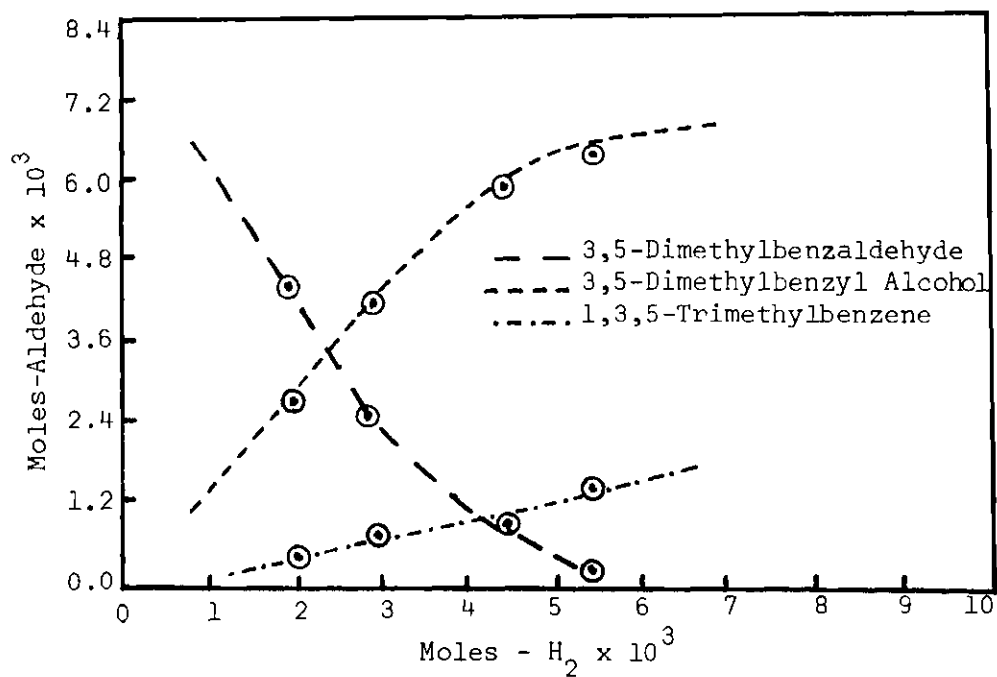


Figure 14. Product Analysis--3,5-Dimethylbenzaldehyde

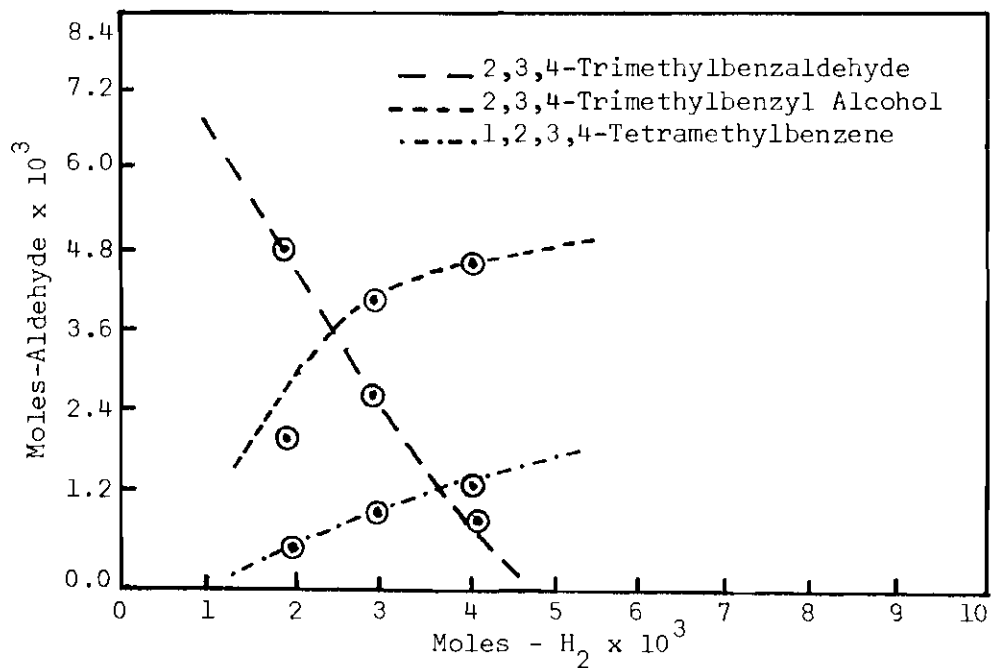


Figure 15. Product Analysis--2,3,4-Trimethylbenzaldehyde

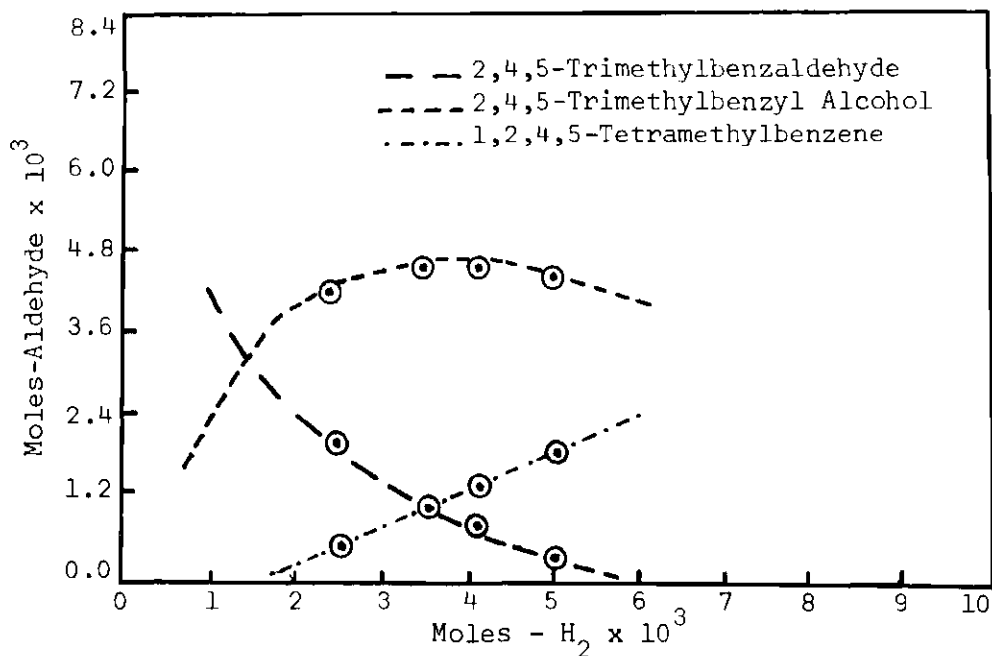


Figure 16. Product Analysis--2,4,5-Trimethylbenzaldehyde

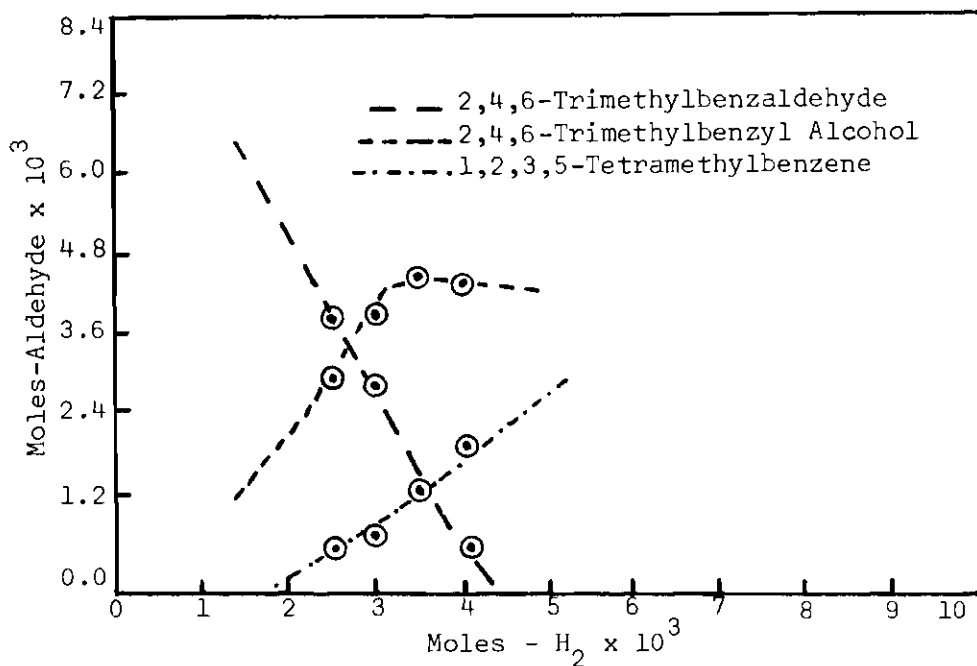


Figure 17. Product Analysis--2,4,6-Trimethylbenzaldehyde

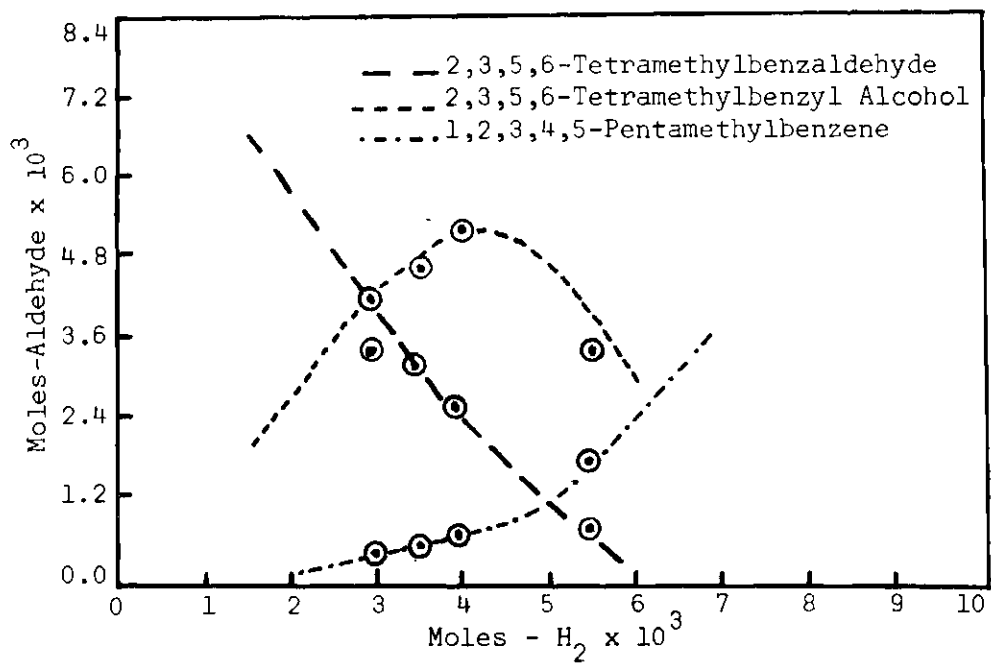


Figure 18. Product Analysis--2,3,5,6-Tetramethylbenzaldehyde

Table 10. Aldehyde Consumed, Alcohol and Hydrocarbon Produced

Position of Methyl Substituents on Benzaldehyde	Initial Amount of Aldehyde (Moles)	NUMBER OF MOLES X 10 ³					
		Aldehyde Consumed: 2.0		Aldehyde Consumed: 4.0		Aldehyde Consumed: 6.0	
		Alcohol Produced	Hydrocarbon Produced	Alcohol Produced	Hydrocarbon Produced	Alcohol Produced	Hydrocarbon Produced
None	0.01006	1.7	0.3	3.6	0.4	5.5	0.5
2	0.00866	1.3	0.7	3.2	0.8	4.9	1.1
3	0.00841	1.9	0.1	3.9	0.1	5.7	0.3
4	0.00850	1.9	0.1	3.4	0.6	4.7	1.3
2,3	0.00768	2.0	-	3.9	0.1	5.8	0.2
2,4	0.00760	1.8	0.2	3.2	0.8	4.6	1.4
2,5	0.00746	2.0	-	3.9	0.1	5.7	0.3
2,6	0.00894	1.2	0.8	2.6	1.4	4.3	1.7
3,4	0.00760	1.8	0.2	3.7	0.3	5.6	0.4
3,5	0.00746	1.9	0.1	3.6	0.4	5.4	0.6
2,3,4	0.00601	1.9	0.1	3.8	0.2	4.8	1.2
2,4,5	0.00682	1.5	0.5	3.4	0.6	4.8	1.2
2,3,5,6	0.00700	1.9	0.1	3.8	0.2	4.3	1.7

Table 11. Aldehyde Reacted (Per Cent), Alcohol and Hydrocarbon Produced

Position of Methyl Substituents on Benzaldehyde	Initial Amount of Aldehyde (Moles)	ALDEHYDE REACTED:					
		25%		50%		75%	
		MOLES OF PRODUCT X 10 ³					
		Alcohol	Hydrocarbon	Alcohol	Hydrocarbon	Alcohol	Hydrocarbon
None	0.01006	2.2	0.3	4.6	0.4	7.1	0.4
2	0.00866	1.4	0.7	3.4	0.9	5.3	1.1
3	0.00841	1.8	0.3	3.8	0.4	5.8	0.5
4	0.00850	1.9	0.2	3.5	0.7	5.1	1.2
2,3	0.00768	1.9	-	3.7	0.1	5.5	0.2
2,4	0.00760	1.6	0.3	2.9	0.9	4.3	1.4
2,5	0.00746	1.8	-	3.6	0.1	5.3	0.2
2,6	0.00894	2.0	0.2	3.4	1.0	4.9	1.8
3,4	0.00760	1.9	-	3.8	-	5.6	0.1
3,5	0.00746	1.7	0.1	3.4	0.3	5.0	0.5
2,3,4	0.00601	1.4	0.1	2.8	0.2	4.2	0.3
2,4,5	0.00682	1.5	0.2	2.9	0.5	4.5	0.6
2,4,6	0.00743	1.5	0.3	3.0	0.7	4.3	1.2
2,3,5,6	0.00700	1.6	0.1	3.2	0.3	4.7	0.5

CHAPTER IV

CONCLUSIONS

The rate of reduction of methyl-substituted benzaldehydes, using a catalyst of 10 per cent palladium supported on carbon and a solvent of absolute ethanol, was found to be first order with respect to the hydrogen pressure, independent of initial acceptor concentration, and directly proportional to the amount of catalyst used. The reactions were found to obey a straight line relationship when plotted according to an equation describing kinetics of first order in hydrogen.

The products of reaction were shown to be mainly the corresponding alcohols, at least for about 60 to 70 per cent reaction.

The temperature dependence of the rate constants of hydrogenation of the aldehydes was found to obey the Arrhenius equation, and the Arrhenius activation energies ranged from 3,520 to 14,400 calories per mole.

An *ortho*-methyl group to the carbonyl aldehyde increased the rate of hydrogenation of the aldehyde to the alcohol. This could be explained in terms of hyperconjugation theory in which a formal negative charge could be supported on the carbonyl-oxygen. This could make such compound to be more readily attracted to and be more easily adsorbed on the catalyst surface.

Meta-methyl groups decreased the rate of hydrogenation of the aldehyde to the corresponding alcohol. A *meta*-methyl substituent

cannot enter in hyperconjugation with the carbonyl group and thus it is unable to aid in supporting a formal negative charge on the carbonyl oxygen atom.

A *para*-methyl group, even though it could enter in hyperconjugation with the carbonyl group, decreased the rate of hydrogenation of the aldehyde to the alcohol. This could be due to the large separation of the charges produced by hyperconjugation, which would make such structure energetically unfavorable. Each of the di-substituted benzaldehydes having substituent in *ortho* position is faster than those di-substituted benzaldehydes having no *ortho* substituent. Two *ortho*-methyl substituents decreased the rate of hydrogenation of the aldehyde to the corresponding alcohol. This was attributed to the steric inhibition by one of the *ortho*-methyl groups to the formation of hyperconjugation structures involving the other *ortho*-methyl group.

Of the tri-substituted methylbenzaldehydes studied, the 2,4,5 isomer reacted the fastest compared to the other trimethyl-substituted benzaldehydes hydrogenated. The lack of a "buttressing effect" is significant, so that this compound actually is like a mono-*ortho*.

Finally, 2,3,5,6-tetramethylbenzaldehyde hydrogenated at a rate comparable to other benzaldehydes having both *ortho*-positions substituted, for the same reasons mentioned for the 2,6 isomer.

No trend was found relating the structure of the methylbenzaldehydes to the amount of alcohol or of hydrocarbon produced.

CHAPTER V

RECOMMENDATIONS

The discussion described in Chapter III concerning the relationship between the reaction rate constant and the structure of the aldehyde should be investigated further through studies of hydrogenation of other methyl-substituted benzaldehydes, particularly 3,4,5-trimethylbenzaldehyde. This aldehyde is the only trimethyl-substituted one that does not have *ortho*-substituents. It would be interesting to see how its rate of hydrogenation compares with the other trimethylbenzaldehydes. On the basis of the present work, one might predict it would hydrogenate more slowly than any of the trimethyl compounds studied herein.

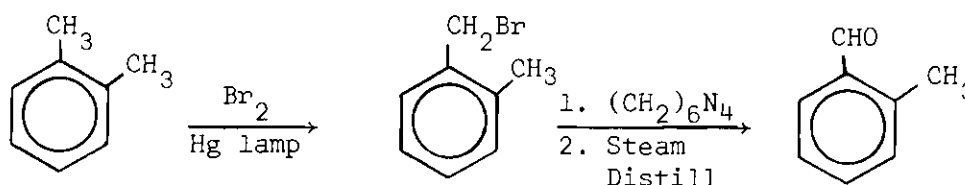
Further work on the rates of hydrogenation of methyl-substituted acetophenones might be interesting. In these compounds the hydrogen of the carbonyl group being replaced by a methyl group gives a much bulkier substituent. Steric effects of *ortho* groups would likely be more evident in their influence upon the rates of hydrogenation.

Also, work should be done on the rates of hydrogenation of hydroxybenzaldehydes and methoxybenzaldehydes. In these compounds hydrogen-bonding is possible only in the case of the *ortho*-substituted ones. Possible resonance effects may be more pronounced than in the case of the methyl benzaldehydes, and steric factors would be of less significance.

APPENDIX

APPENDIX A

SYNTHESIS OF 2-METHYLBENZALDEHYDE

Preparation of o-Xylyl Bromide

According to the procedure given by Cumming *et al.*¹⁶ 106 g. of *o*-xylene, obtained from Columbia Organic Chemicals, was reacted with bromine in carbon tetrachloride. From this 60 g. (33 per cent) of *o*-xylyl bromide was obtained. It boiled at 198 - 204°C at 742 mm. pressure.

Preparation of 2-Methylbenzaldehyde

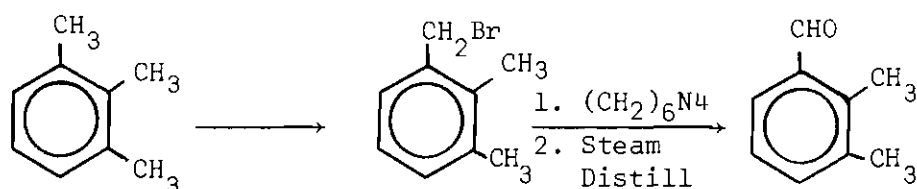
From *o*-xylyl bromide, 2-methylbenzaldehyde was prepared using the Sommelet reaction¹⁷ without the isolation of the hexaminium salt. From one mole of *o*-xylene an overall yield of 30 g. (25 per cent) of 2-methylbenzaldehyde was obtained. The pure aldehyde boiled at 88°C at 16 mm. pressure.

¹⁶W. M. Cumming, V. Hopper and T. S. Wheeler, "Systematic Organic Chemistry," Fourth Edition, Constable and Company, London, 1950, p. 351.

¹⁷C. Weygand, "Organic Preparations," Interscience Publishers Incorporated, New York, 1945, p. 156.

APPENDIX B

SYNTHESIS OF 2,3-DIMETHYLBENZALDEHYDE

Preparation of 2,3-Dimethylbenzyl Bromide

The method in Cumming¹⁸ used to prepare *o*-xylyl bromide was followed. From 120 g. (one mole) of 1,2,3-trimethylbenzene and 159 g. of bromine in 900 ml. of carbon tetrachloride, a yield of 180 g. (90 per cent) of 2,3-dimethylbenzyl bromide was obtained. The bromo compound boiled at 98°C at 15 mm. pressure.

Preparation of 2,3-Dimethylbenzaldehyde

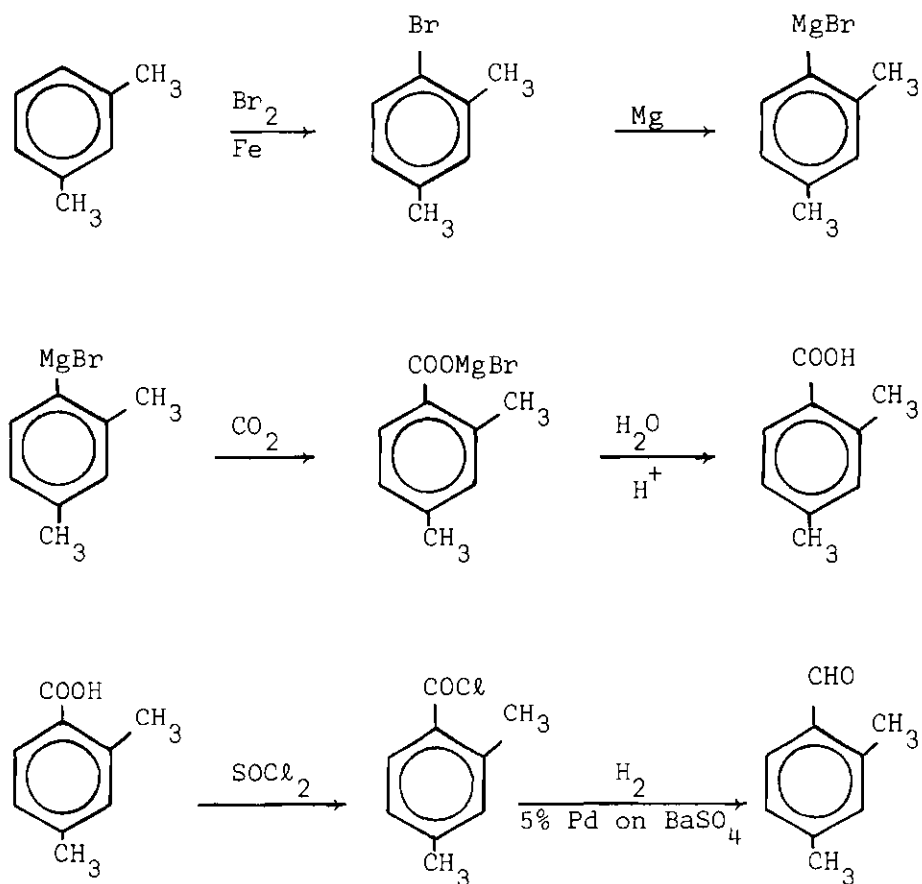
The Sommelet reaction followed in this procedure was advanced by Weygand.¹⁹ A total of 0.9 mole of the bromo compound yielded only 20 g. or 18 per cent of the 2,3-dimethylbenzaldehyde. The boiling point of the fraction collected was 98 - 100°C at 12 mm. pressure.

¹⁸W. M. Cumming, V. Hopper and T. S. Wheeler, "Systematic Organic Chemistry," Fourth Edition, Constable and Company, London, 1950, p. 351.

¹⁹C. Weygand, "Organic Preparations," Interscience Publishers Incorporated, New York, 1945, p. 156.

APPENDIX C

SYNTHESIS OF 2,4-DIMETHYLBENZALDEHYDE

Preparation of 4-Bromo-1,3-Dimethylbenzene

The method of Wisansky²⁰ was used. One mole (106 g.) of *m*-xylene was brominated and from this, 166 g. (90 per cent) of

²⁰W. A. Wisansky, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, New York, N.Y., 1955, p. 138.

4-bromo-1,3-dimethylbenzene, boiling at 90 - 92°C at 14 mm. pressure, was obtained.

Preparation of 2,4-Dimethylbenzoic Acid

Employing the Grignard reaction²¹ with 166 g. of 4-bromo-1,3-dimethylbenzene, a yield of 95 g. of the acid was prepared. This represents a yield of 57 per cent of theoretical. After recrystallization from ethanol, it melted at 123°C.

Preparation of 2,4-Dimethylbenzoyl Chloride

The procedure given by Barnes²² for the conversion of mesitoic acid into mesitoyl chloride was used here, and from 95 g. of 2,4-dimethylbenzoic acid 46 g. (36 per cent) of 2,4-dimethylbenzoyl chloride was obtained. It boiled at 105°C at 5 mm. pressure.

Preparation of 2,4-Dimethylbenzaldehyde

The acid chloride was reduced to the aldehyde using the Rosenmund reaction.²³ The preparation of the catalyst is given in Appendix L. From 45 g. of 2,4-dimethylbenzoyl chloride 13 g. (45 per cent) of 2,4-dimethylbenzaldehyde (boiling point 93°C at 2mm. pressure) was obtained.

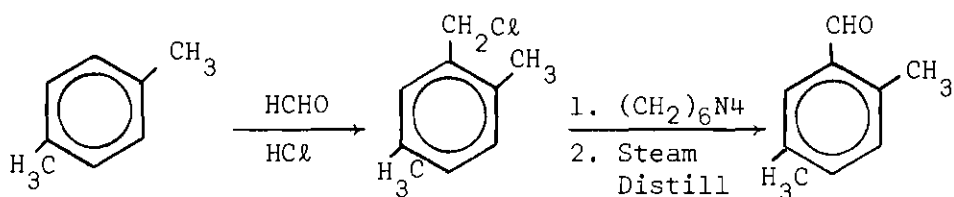
²¹R. P. Barnes, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, New York, N. Y., 1955, p. 555.

²²*Ibid.*, p. 556.

²³*Ibid.*, p. 551.

APPENDIX D

SYNTHESIS OF 2,5-DIMETHYLBENZALDEHYDE

Preparation of 2,5-Dimethylbenzyl Chloride

The chloromethylation of one mole (106 g.) of *p*-xylene, obtained from Columbia Organic Chemicals, was carried out according to the method given by Fuson²⁴ and from this 30 g. (20 per cent) of 2,5-dimethylbenzyl of chloride boiling at 102°C at 12 mm. pressure was obtained.

Preparation of 2,5-Dimethylbenzaldehyde

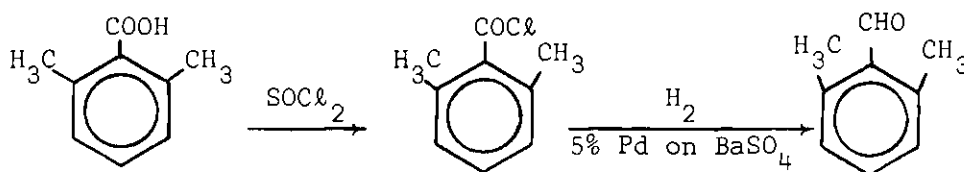
The Sommelet reaction,²⁵ effected without the isolation of the hexaminium salt, was used herein but only 4 g. (15 per cent) of 2,5-dimethylbenzaldehyde was obtained. It boiled at 110°C at 10 mm. pressure.

²⁴R. C. Fuson, "Organic Reactions," Vol. I, John Wiley and Sons, New York, N.Y., 1943, p. 63.

²⁵C. Weygand, "Organic Preparations," Interscience Publishers Incorporated, New York, 1945, p. 156.

APPENDIX E

SYNTHESIS OF 2,6-DIMETHYLBENZALDEHYDE

Preparation of 2,6-Dimethylbenzoyl Chloride

The conversion of 12 g. of 2,6-dimethylbenzoic acid, prepared by Dr. James A. Stanfield of this laboratory, into the corresponding acid chloride was effected employing the procedure described by Barnes.²⁶ A yield of 12 g. (90 per cent) of 2,6-dimethylbenzoyl chloride was obtained. The product boiled at 102°C at 5 mm. pressure.

Preparation of 2,6-Dimethylbenzaldehyde

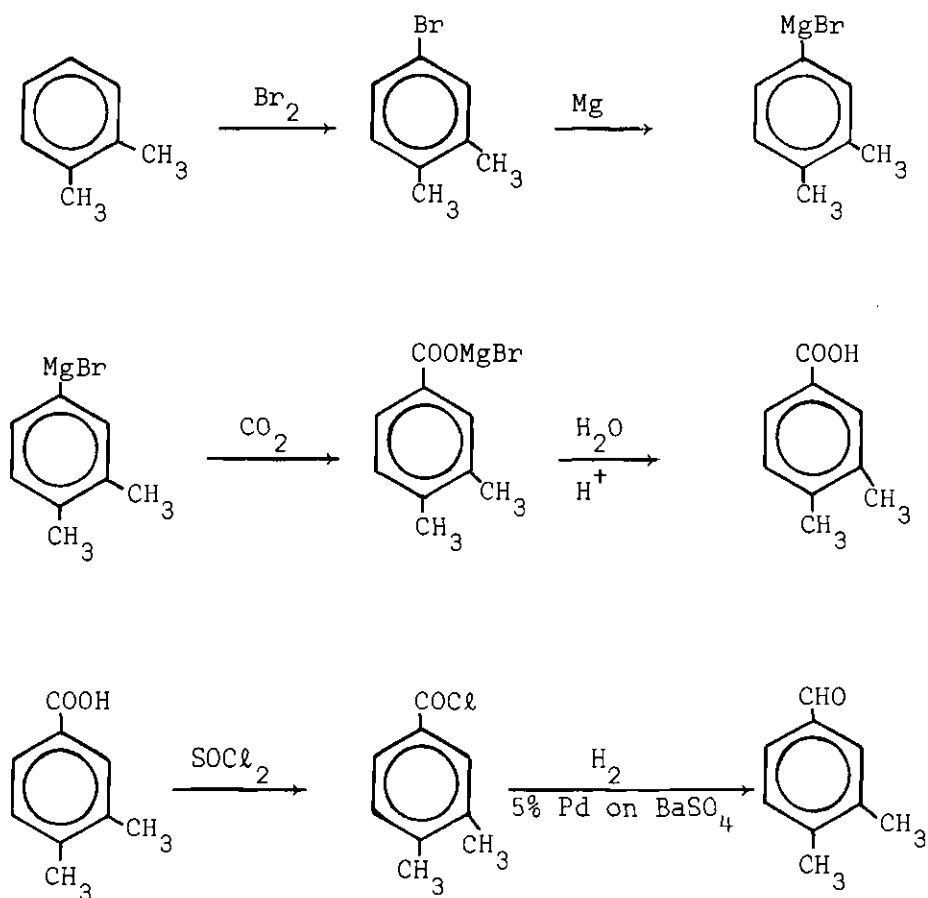
According to the procedure²⁷ given previously for the preparation of 2,4-dimethylbenzaldehyde, a yield of 3 g. (30 per cent) of 2,6-dimethylbenzaldehyde was obtained from 12 g. of 2,6-dimethylbenzoyl chloride. The boiling point of the fraction collected was 94 - 96°C at 3 mm. pressure.

²⁶R. P. Barnes, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, New York, N. Y., 1955, p. 555.

²⁷*Ibid.*, p. 551.

APPENDIX F

SYNTHESIS OF 3,4-DIMETHYLBENZALDEHYDE

Preparation of 4-Bromo-o-Xylene

The bromination of *o*-xylene was carried out according to the procedure given by Wisansky.²⁸ From one mole (106 g.) of *o*-xylene,

²⁸W. A. Wisansky, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, New York, N.Y., 1955, p. 138.

95 g. (48 per cent) of 4-bromo-*o*-xylene was obtained. It boiled at 90 - 93°C at 12 mm. pressure.

Preparation of 3,4-Dimethylbenzoic Acid

The Grignard reaction followed in this procedure was advanced by Barnes.²⁹ A total of 0.95 mole of the bromo compound yielded only 24 g. or 16 per cent of the 3,4-dimethylbenzoic acid.

Preparation of 3,4-Dimethylbenzoyl Chloride

The acid chloride was prepared using the method of Barnes.³⁰ From 24 g. of 3,4-dimethylbenzoic acid, 24 g. (90 per cent) of pure 3,4-dimethylbenzoyl chloride, boiling at 102°C at 5 mm. pressure, was obtained.

Preparation of 3,4-Dimethylbenzaldehyde

Reduction of 3,4-dimethylbenzoyl chloride to the aldehyde was accomplished through the use of the Rosenmund reaction.³¹ The yield obtained was 12 g. or 56 per cent of 3,4-dimethylbenzaldehyde. The fraction collected boiled at 85 - 87°C at 5 mm. pressure.

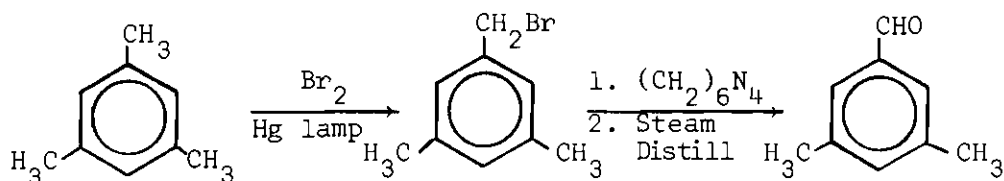
²⁹R. P. Barnes, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, New York, N.Y., 1955, p. 555.

³⁰*Ibid.*, p. 556.

³¹*Ibid.*, p. 551.

APPENDIX G

SYNTHESIS OF 3,5-DIMETHYLBENZALDEHYDE

Preparation of 3,5-Dimethylbenzyl Bromide

The method of Cumming *et al.*³² was used to brominate one mole (120 g.) of mesitylene. A 60 per cent (119 g.) yield of the bromo compound (boiling point 94 - 95°C at 11 mm. pressure) was obtained.

Preparation of 3,5-Dimethylbenzaldehyde

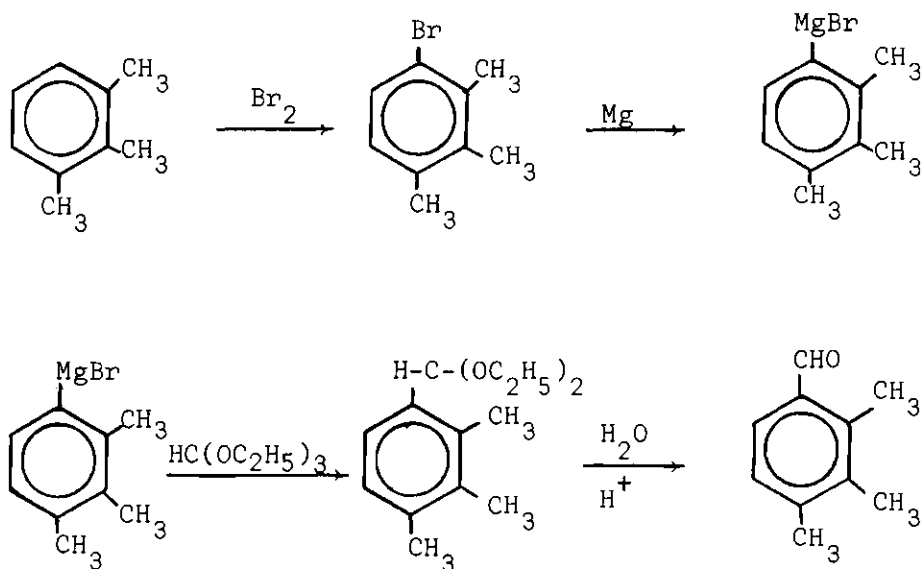
The Sommelet reaction³³ was used here without the isolation of the hexaminium salt. From one mole of mesitylene 26 g. (22 per cent) of 3,5-dimethylbenzaldehyde was obtained. The aldehyde boiled at 75°C at 5 mm. pressure.

³²W. M. Cumming, V. Hopper and T. S. Wheeler, "Systematic Organic Chemistry," Fourth Edition, Constable and Company, London, 1950, p. 351.

³³C. Weygand, "Organic Preparations," Interscience Publishers Incorporated, New York, 1945, p. 156.

APPENDIX H

SYNTHESIS OF 2,3,4-TRIMETHYLBENZALDEHYDE

Preparation of 4-Bromohemimellitene

4-Bromohemimellitene was made following the procedure given by Smith and Moyle.³⁴ From 120 g. (one mole) of hemimellitene 175 g. (89 per cent) of 4-bromohemimellitene was obtained. The bromo compound boiled at 123°C at 25 mm. pressure.

Preparation of 2,3,4-Trimethylbenzaldehyde

The procedure given by Smith and Bayliss³⁵ for the preparation of aldehydes from Grignard reagents was followed. One mole of

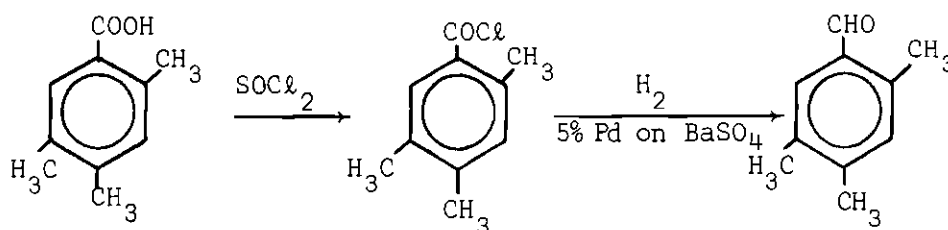
³⁴L. I. Smith and C. L. Moyle, *J. Am. Chem. Soc.*, 58, 9 (1936).

³⁵L. I. Smith and M. Bayliss, *J. Org. Chem.*, 6, 437 (1941).

hemimellitene yielded 22 g. (15 per cent) of 2,3,4-trimethylbenzaldehyde. It boiled at 110 - 115°C at 18 mm. pressure.

APPENDIX I

SYNTHESIS OF 2,4,5-TRIMETHYLBENZALDEHYDE

Preparation of 2,4,5-Trimethylbenzoyl Chloride

The conversion of 45.5 g. of 2,4,5-trimethylbenzoic acid, prepared by Dr. James A. Stanfield of this laboratory, into the corresponding acid chloride was effected employing the procedure described by Barnes.³⁶ A yield of 47.5 g. (94 per cent) of 2,4,5-trimethylbenzoyl chloride was obtained. The product boiled at 120°C at 5 mm. pressure.

Preparation of 2,4,5-Trimethylbenzaldehyde

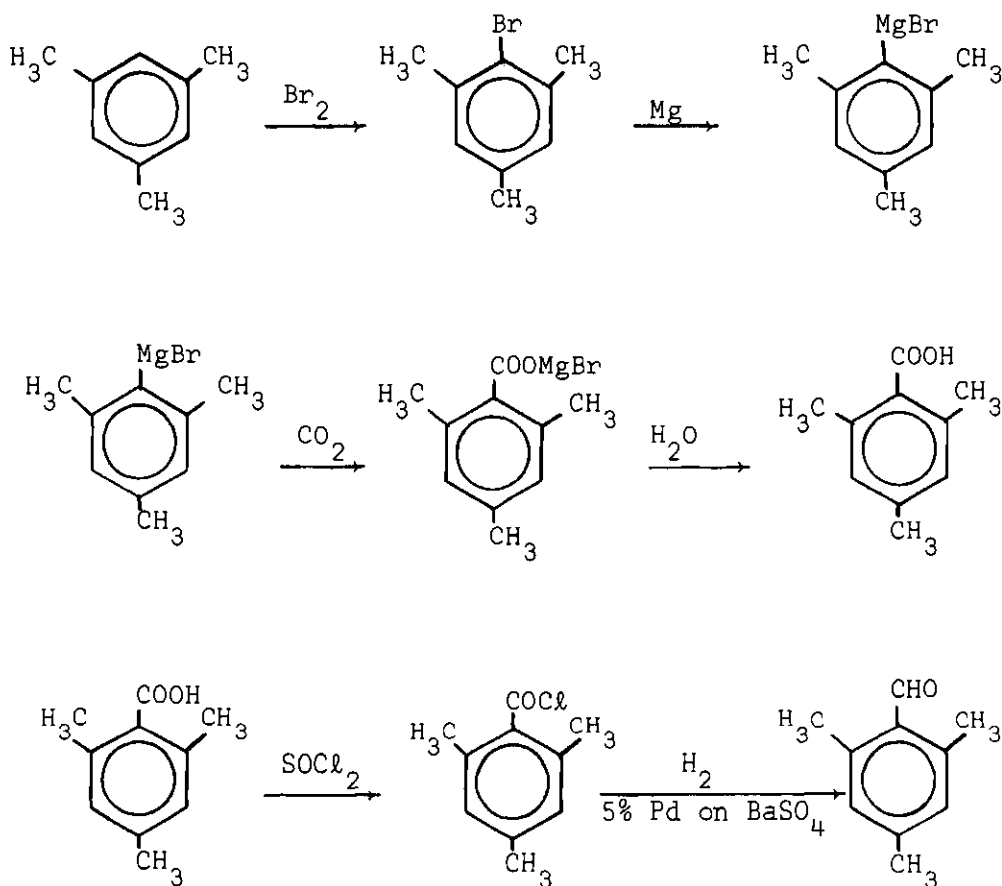
The Rosenmund reduction³⁷ of 47.5 g. of 2,4,5-trimethylbenzoyl yielded 18.5 g. (44 per cent) of 2,4,5-trimethylbenzaldehyde. It melted at 42°C after recrystallization from ethanol.

³⁶R. P. Barnes, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, New York, N.Y., 1955, p. 556.

³⁷*Ibid.*, p. 551.

APPENDIX J

SYNTHESIS OF 2,4,6-TRIMETHYLBENZALDEHYDE

Preparation of Bromomesitylene

The method of Smith³⁸ was used to brominate two moles (240 g.) of mesitylene. A yield of 75 per cent (290 g.) of bromomesitylene

³⁸L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N.Y., 1943, p. 96.

was obtained. The fraction collected boiled at 103 - 105°C at 15 mm. pressure.

Preparation of Mesitoic Acid

Employing the Grignard reaction³⁹ with 290 g. of bromomesitylene, a yield of 130 g. (40 per cent) of the acid was obtained.

Preparation of Mesitoyl Chloride

The acid chloride was obtained by the action of thionyl chloride on mesitoic acid according to the procedure described by Barnes.⁴⁰ From 130 g. of mesitoic acid 135 g. (95 per cent) of mesitoyl chloride (boiling point 108 - 110°C at 5 mm. pressure) was obtained.

Preparation of 2,4,6-Trimethylbenzaldehyde

Using the Rosenmund reduction⁴¹ on 135 g. of 2,4,6-trimethylbenzoyl chloride 6 g. (5 per cent) of 2,4,6-trimethylbenzaldehyde was obtained. The fraction collected boiled at 97 - 99°C at 5 mm. pressure.

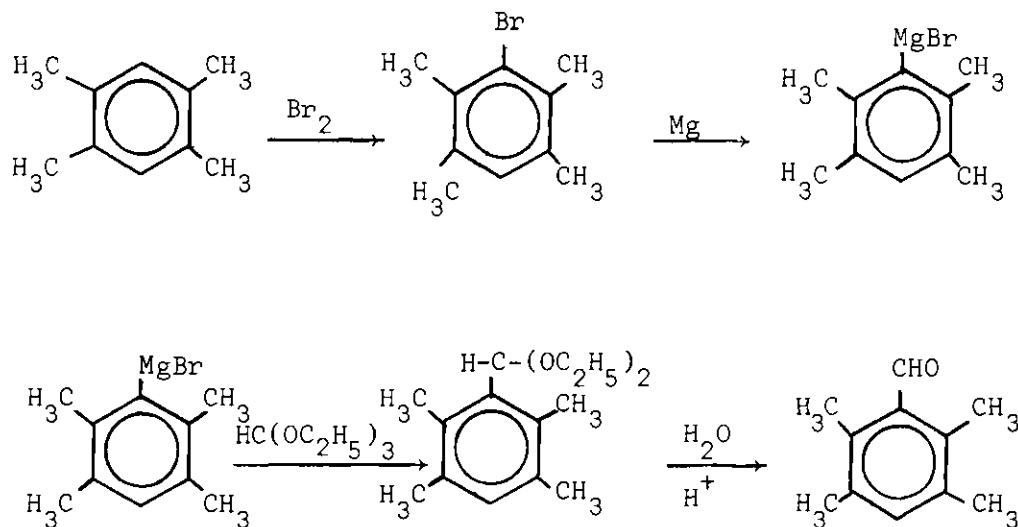
³⁹R. P. Barnes, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, New York, N.Y., 1955, p. 555.

⁴⁰*Ibid.*, p. 556.

⁴¹*Ibid.*, p. 556.

APPENDIX K

SYNTHESIS OF 2,3,5,6-TETRAMETHYLBENZALDEHYDE

Preparation of Bromodurene

Bromodurene was prepared from durene following the procedure of Smith and Moyle.⁴² A yield of 67 per cent (141 g.) of bromodurene was obtained from 134 g. (one mole) of durene. It melted at 58 - 59°C.

Preparation of 2,3,5,6-Tetramethylbenzaldehyde

The procedure followed in the preparation of 2,3,4-trimethylbenzaldehyde was used.⁴³ From one mole of durene, 16 g. (10 per cent)

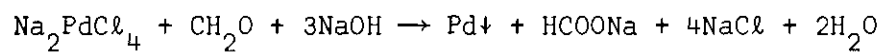
⁴²L. I. Smith and C. L. Moyle, *J. Am. Chem. Soc.*, 58, 9 (1936).

⁴³L. I. Smith and M. Bayliss, *J. Org. Chem.*, 6, 437 (1941).

of 2,3,5,6-tetramethylbenzaldehyde boiling at 130 - 132°C at 10 mm.
pressure, was obtained.

APPENDIX L

PREPARATION OF 5 PER CENT PALLADIUM ON BARIUM SULFATE



Using the method of Mozingo⁴⁴ 98.7 g. of 5 per cent Palladium on barium sulfate was prepared. It was gray in color.

⁴⁴R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, New York, N.Y., 1955, p. 685.

APPENDIX M

PREPARATION OF 10 PER CENT PALLADIUM ON CHARCOAL CATALYST

The procedure used in this preparation is given by Augustine.⁴⁵

Fifty-seven g. of the catalyst was prepared.

⁴⁵R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, Inc., New York, N.Y., 1965, p. 152.

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