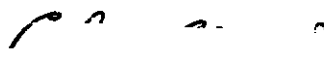


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CATALYTIC HYDROGENATION STUDIES OF SOME CYCLOALKENES
USING FIVE PER CENT RUTHENIUM SUPPORTED CATALYST

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CATALYTIC HYDROGENATION STUDIES OF SOME CYCLOALKENES
USING FIVE PER CENT RUTHENIUM SUPPORTED CATALYST

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SUMMARY

A study of the rate of the hydrogenation of eighteen cycloalkenes was made, using five per cent ruthenium-on-carbon as catalyst and a solvent of absolute alcohol under an initial hydrogen pressure of 64 psia. The standard mixtures were prepared from 2.00 ml. of cycloalkene, 0.100 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. Over a wide change in initial hydrogen pressure, however, the reaction order was calculated to be 0.98 with respect to the initial hydrogen pressure.

From conventional kinetic equations, the reaction appeared to be zero order with respect to the cycloalkene, at least for about 60 to 80 per cent reaction. When, however, the initial concentration of the acceptor was changed over wider ranges of concentration, exact zero relationships did not seem to apply in all cases. Thus for cyclohexene, the rate of hydrogenation was increased when the initial concentration of the acceptor was increased from 0.0205 to 0.0410 moles. For cycloheptene, there was noted a decrease in rate upon increase of initial acceptor concentration. Cyclooctene, on the other hand, followed zero order kinetics over the range of concentrations studied. Calculations showed that for these wider ranges of concentration the reaction generally appeared to be 0.065 order with respect to the acceptors.

The dependence of the rate constants with temperature was observed over 12 to 34°C. The rates were approximately doubled for each twenty to thirty degrees increase in temperature. Activation energies were calculated from a plot of the Arrhenius equation, that is, a plot of $\log k$ against $1/T$. Values of the activation energies and rate constants for the compounds studied are given in the table below.

It was observed that the increase in activation energy per methyl substituted group on cyclohexene was about 2100 calories per mole based on the monomethyl derivatives, and about 2900 calories per mole based on the dimethyl derivatives.

No uniform relationship seemed to exist between the size of the ring and the rate of hydrogenation of the ring alkene. Each 1-methyl-cycloalkene showed a smaller rate constant than the corresponding unsubstituted cycloalkene. This was explained by possible steric hindrance to the approach of hydrogen to the catalyst by the adsorbed reactant. The slower rate of 4-methyl-1-cyclohexene as compared to 3-methyl-1-cyclohexene might be due to the former compound having both 4-methyl-equatorial and 4-methyl-axial steric hindrances to the approach of hydrogen, but the latter compound showing only 3-methyl-equatorial steric hindrance. It was also found that the rate constants for the hydrogenation of conjugated cycloienes were relatively greater than those of the respective unconjugated compounds. It was suggested that the conjugated compounds might be reacting in a more or less single step process whereas the non-conjugated compounds might be reacting in a several discreet step process. Thus, the following order was observed: 1,3-conjugated systems > 1,4-non-conjugated systems > 1,3,5-cycloheptatriene system > cyclooctatetraene system.

Table. The Hydrogenation of Cycloalkenes over Five Per Cent Ruthenium-on-Carbon Catalyst

Cycloalkene	Activation Energy Calories per Mole	K_{30} , min. ⁻¹ g. ⁻¹
Cyclopentene	5100	0.0410
1-Methyl-1-cyclopentene	3140	0.0276
Cyclohexene	2500	0.0627
1-Methyl-1-cyclohexene	3920	0.0041
3-Methyl-1-cyclohexene	6650	0.0583
4-Methyl-1-cyclohexene	3190	0.0437
3,5-Dimethyl-1-cyclohexene	8400	0.0017
Cycloheptene	7000	0.0215
1-Methyl-1-cycloheptene	17800	0.0170
Cyclooctene	6000	0.0759
Cyclohexadiene-1,3	10500	0.0495
Cyclohexadiene-1,4	2300	0.0495
Cyclooctadiene-1,3	6190	0.0967
Cyclooctadiene-1,5	2960	0.0620
Cycloheptatriene-1,3,5	9560	0.0085
Cyclooctatetraene	7870	0.0070
<u>trans</u> , <u>trans</u> , <u>cis</u> -1,5,9- Cyclododecatriene	11900	0.0365
Cyclododecene	3100	0.0212

CHAPTER I

INTRODUCTION

The purpose of this research was to determine the apparent rate constants of the hydrogenation of some cycloalkenes in the presence of five per cent ruthenium-on-carbon catalyst in order to study structural effects of the acceptors on these rates. It is apparent that the hydrogenations carried out in such a manner would involve a heterogeneous system. The catalyst and kinetics laws would, consequently, play very important roles. For this reason, a discussion pertaining to the nature of catalysts, characteristics of heterogeneous catalysis, some previous applications of ruthenium catalysts, and empirical treatment of reaction rates would be desirable and will be presented.

Heterogeneous catalytic reactions are those in which gaseous or liquid reaction takes 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 frequently metallic in character. The discussion of interest might, then be confined to metallic masses. These can be classified into three categories (1): (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

(1) M. Prettre, (translated by David Antin), Catalysis and Catalysts, Dover Publications, Inc., New York, 1963, p. 5.

evaporated metal films; and (c) Microscopic forms of metals serving as catalysts containing one or more other components. There is no doubt that of the three, the last is of wide use in chemical industry. This group may be further divided into (1) supported metal catalysts, (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 of 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, of course, one significant purpose of the support. As far as catalyst surface area is concerned, one will, in general, find that the reactivity of a solid catalyst needs not necessarily be directly proportional to the surface area. As Wheeler (2) has pointed out, the rate of reaction may be directly proportional to the surface area, directly proportional to the square root of the surface area, or completely independent of the surface area, depending upon the pore distribution within the catalyst and the reaction kinetics of the particular reaction system. Taylor (3), furthermore, in the theory of active points contended that only certain points on the surface of a metallic catalyst were active for a given

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

(3) H. S. Taylor, Proc. Roy. Soc., A 108, 105 (1925).

reaction. These have sometimes been given a geometric interpretation in the sense that they have been considered as corners or edges of crystals.

In promoted metal catalysts, the promoter may or may not have catalytic activity of itself. A promoted metal, however, will exhibit at some composition (generally 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).

The difference between carriers and promoters as defined above is frequently somewhat vague and arbitrary in that both act to increase the surface area of the active component. But for some purposes, 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.

A heterogeneous catalytic reaction localized at a solid-fluid interface necessarily consists of a sequence of steps. The first is the adsorption of at least one of the reactants in the fluid phase. Then the second step occurs at the interface: the reaction itself that produces

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

the final products, one of which at least remains adsorbed. The third step consists of the desorption or desorptions of the reaction products (5).

Since adsorption is of major significance, it might be pointed out that there are two types of adsorption on solids which have been recognized for many years. In the first type, termed physical adsorption or van der Waals' adsorption, the adsorbed molecule is held to the surface of the solid by the relatively weak van der Waals' forces. This sort of adsorption is non-specific with respect to adsorbent and adsorbate in the sense that a molecule or atom in this state is not bound to any particular surface metal atom. The heat of physical adsorption is relatively small and is comparable to the heat of liquefaction of the gases; it is, therefore, on the order of a few hundred calories per mole (6). While the study of physical adsorption can give one valuable information related to the surface area, the pore size, and the size distribution of a solid catalyst, it is of minor significance in the catalytic action itself. Its use is primarily as an aid to the interpretation of the catalytic process (7).

The second type of adsorption, termed chemisorption or activated adsorption, is specific in nature and occurs by a chemical reaction between the molecule being adsorbed and the catalytic surface. This can ultimately lead to formation of intermediate complexes. The forces in such adsorptions are much stronger than those in physical adsorption. The heat of

(5) M. Prettre, op. cit., p. 20.

(6) P. H. Emmett, Editor, op. cit., Vol. II, p. 75.

(7) P. H. Emmett, E. E. Reid, and P. Sabatier, Catalysis Then and Now, Franklin Publishing Co., Englewood, N. J., 1965, p. 29.

chemisorption is often in the neighborhood of heat of chemical reaction, values of 10 to 100 Kcal. per mole being common. Among the characteristics which may be observed in chemisorption are (8): (1) a complete chemisorbed layer is a unimolecular layer; (2) an appreciable activation energy, resulting frequently in a slow process; and (3) a considerable variation, generally, in the adsorptive capacities of the various surface sites.

In the study of contact surfaces reacting with bases, Langmuir developed his adsorption isotherm which is theoretically applicable to chemisorption on a perfectly smooth surface when there are no interactions between adsorbed molecules. When a single species is chemisorbed at constant temperature, the rates of adsorption V_1 and of desorption V_{-1} in a system are given by:

$$V_1 = K_1 p (1-\theta) \quad (1)$$

and

$$V_{-1} = K_{-1} \theta \quad (2)$$

where p is the gas pressure in equilibrium with a surface, θ is the fraction of the surface which is covered by adsorbed gas, $(1-\theta)$ is the fraction of the bare surface, K_1 and K_{-1} are constants.

At equilibrium,

$$K_1 p (1-\theta) = K_{-1} \theta \quad (3)$$

(8) P. H. Emmett, Editor, op. cit., Vol. I, p. 76.

or

$$\frac{\theta}{1-\theta} = \frac{K_1}{K_{-1}} p \quad (4)$$

$$= K' p \quad (5)$$

Where K' equals K_1/K_{-1} ; K' , therefore, is an equilibrium constant for adsorption.

For special cases, if the surface is sparsely covered by adsorbed molecules the term $(1-\theta)$ is approximately equal to unity, then Eq. (5) becomes

$$\theta = K' p \quad (6)$$

In this case the amount of gas adsorbed is proportional to the equilibrium pressure.

If the surface is completely covered by adsorbed molecules and θ approaches unity and Eq. (5) may be written as

$$1-\theta = \frac{1}{K' p} \quad (7)$$

The fraction of surface uncovered is inversely proportional to the gas pressure (9).

The surface reaction that occurs at the second step may be faster than the adsorption or desorption process and as a result, the rate of reaction may become dependent upon the adsorption or desorption rate.

The removal of reaction products from a catalytic contact surface,

(9) P. H. Emmett, editor, op. cit., Vol. I, p. 90.

or desorption, may be the slowest and most difficult step in the heterogeneous catalytic reaction. Consequently, the rate of the desorption process may be one of the major factors in determining the rate of reaction of the process as a whole (10). Thus, should the desorption process be slower than adsorption or than reaction, further reaction cannot occur unless surface becomes available for the adsorption of reactants. It might be pointed out here that certain substances may completely deactivate a catalyst by becoming so strongly adsorbed on the catalyst as to cover its surface completely; such materials may be termed poisons.

Ruthenium is one of the more powerful hydrogenation catalysts and has been the center of a number of studies. This metal, originally in the form of oxides, is now more frequently used supported on carriers such as carbon or alumina. The nature of the carrier has specificity on various reactions - carbon being preferred for hydrogenation (11,12) and alumina being favored for hydrogenolysis (13).

Balandin and coworkers (14) studied catalysts for the hydrogenation of polysaccharides and found that a good catalyst for hydrogenation of cellulose, hemicellulose, or starch is 0.1 per cent ruthenium-on-carbon or

(10) H. W. Lohse, Catalytic Chemistry, Chemical Publishing Co. Inc., Brooklyn, New York, 1945, p. 89.

(11) M. Freifelder, R. M. Robinson, and G. R. Stone, J. Org. Chem., **27**, 284 (1962).

(12) P. N. Rylander and D. R. Steele, Engelhard Ind. Tech. Bull., **3**, 91 (1962).

(13) G. E. Ham and W. P. Coker, J. Org. Chem., **29**, 194 (1964).

(14) A. A. Balandin, N. A. Vasyunina, G. S. Barysheva, and S. V. Chepigo, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 392, 1957.

silica in two per cent sulfuric acid when used at 156-160°C and 70 atmospheres. Thus, sulfite cellulose gave 82 per cent sorbital anhydrides in two hours, and hemicelluloses gave 78 per cent polyhydric alcohols.

Hydrogenation of perfluoroalkanoic acids to 1,1-dihydroperfluoroalkyl alcohols over ruthenium catalyst was studied by Schreyer (15). 1,1-Dihydroperfluoroalkyl alcohols, such as 1,1-dihydroperfluorooctanol, were produced in a liquid phase process at a reaction temperature in the range 150 to 300°C and at a pressure in the range 3,000 to 10,000 psi using five per cent finely divided ruthenium-on-carbon.

Acrolein has been found less susceptible to hydrogenation with ruthenium catalyst. Thus, ten grams of acrolein was hydrogenated using one gram of five per cent ruthenium-on carbon at 67 psia. and 50°C. After 5.5 hours, only 23 per cent of the acrolein was converted to propionaldehyde (16).

Greshan and coworkers (17) have shown that ruthenium catalysts, either ruthenium itself or ruthenium-on-carbon, can be used for the direct hydrogenation of carboxylic acids to the corresponding alcohols in good yields at temperature of about 150°C and at pressures ranging from 600 to 800 atmospheres. The reaction has been applied to mono- and di-carboxylic acids and to hydroxy acids.

Direct and complete conversion of glycolic acid to ethylene glycol

(15) R. C. Schreyer, U. S. Patent, 2,862,977 (Dec. 2, 1958).

(16) W. B. Howsmon, Jr., U. S. Patent, 3,056,840 (Oct. 2, 1962).

(17) J. E. Carnahan, T. H. Ford, W. F. Greshan, W. E. Grigsby, and G. F. Hager, J. Am. Chem. Soc., 77, 3766 (1955).

may be accomplished by liquid phase hydrogenation over a ruthenium oxide or a supported ruthenium catalyst. For example, glycolic acid, 20 parts; water, 80 parts; and ruthenium-on-carbon, 10 parts; all were placed in a silver-lined shaker tube and kept one hour at 145-150°C and under 650-710 atms. of hydrogen. The conversion of glycolic acid to ethylene glycol was 80 per cent (18).

Phenol, resorcinol, anisole, and p-dimethoxybenzene have been hydrogenated in dilute aqueous alkalies (0.1 to 0.02 N) with a five per cent Ru-on-carbon as the catalyst at room temperature and at 3.5 Kg/cm². In alkaline solution, the rate of hydrogenation with the Ru catalysts is increased as compared to the rate using five per cent Pt-on-carbon catalysts under the same conditions. The reverse is true, however, when dilute aqueous acids (0.1 to 0.02 N) were used as the liquid media (19).

Selectivity of carrier-based ruthenium catalysts has been reported by Gilman and Cohn (20). They found that using carrier based ruthenium the carbonyl group can be hydrogenated in the presence of an olefinic bond. Five per cent ruthenium-on-activated-carbon was also found to be selective for the hydrogenation of olefins at room temperature and low pressures (21). For instance, in mixtures of octene-1 and octene-2, the octene-1 is selectively reduced; in mixtures of 4-methyl-1-pentene and 2-methyl-2-pentene, the former is selectively reduced.

(18) W. F. Greshan, U. S. Patent, 2,607,805 (Aug. 19, 1952).

(19) P. N. Rylander and J. F. Kreidl, Fr. Patent, 1,320,373.

(20) G. Gilman and G. Cohn, Advances in Catalysis, Academic Press Inc., New York, Vol. IX, 733-42 (1957).

(21) M. Berkowitz and P. N. Rylander, J. Org. Chem., 24, 708 (1959).

The supported mixtures of ruthenium with other metals, such as platinum and palladium, are frequently catalytically more active than the individual supported metals. Specifically, supported ruthenium-platinum catalysts in which the metal content is 1-90 per cent ruthenium are very active for the hydrogenation of phenols and methoxybenzenes (22).

The reduction of mixed platinum-ruthenium oxides also gives a highly active hydrogenation catalyst. Thus at 30°C when 20 ml. of 0.6 M nitrobenzene in methyl alcohol was shaken with 10 mg. of the mixed oxides containing about 25 per cent ruthenium, hydrogen was adsorbed four times as fast as with platinum oxide (23).

One significant disadvantage of ruthenium catalysts is that they may be easily poisoned or deactivated by basic or nonaqueous, acid solvents (24,25,26). Consequently, they are best used in neutral aqueous solutions.

Since the treatment of the experimental data obtained in this research was subjected to the general kinetic laws, it is desirable to develop equations which might be applicable to these experimental data so that apparent rate constants can be calculated.

(22) P. N. Rylander and J. H. Koch, Jr., U. S. Patent 3,177,258 (Apr. 6, 1965).

(23) G. C. Band and D. E. Webster, Proc. Chem. Soc., 398, 1964.

(24) J. E. Carnahan, T. A. Ford, W. F. Greshan, W. E. Grigsby, and G. F. Hager, J. Am. Chem. Soc., 77, 3766 (1955).

(25) E. Breitner, E. Roginski, and P. N. Rylander, J. Org. Chem., 24, 1855 (1959).

(26) L. L. Frestandig and W. A. Pryor, U. S. Patent 2,828,335 (Mar. 25, 1958).

For a reaction whose stoichiometry is



and for which a, b, c, d are the stoichiometric coefficients of A, B, C, and D, respectively, the rate of the reaction can be expressed by

$$-\frac{d[A]}{dt} = k[A]^x [B]^y \quad (9)$$

In this expression, t is time, [A] and [B] represents the molar concentration of A and of B, and k is termed the specific reaction rate or rate constant. The minus sign indicates that the concentration of reactant A is decreasing. The order of the reaction n, is represented by the sum of x and y. Thus

$$n = x + y$$

Also, each individual exponent is the order with respect to that component.

While the overall reaction may be expressed by an equation such as (8), it may well be that the reaction is occurring in discrete steps. The slowest of such steps will, of course, be rate controlling and the overall rate of the reaction may then be dependent upon the concentration of one substance and not upon another. The "order of reaction" is usually a small whole number, but in special cases it may have fractional values or may even be zero. Smith and coworkers, for example, have established that the rate of hydrogenation of the benzene nucleus in various benzene derivatives is first order with respect to hydrogen but is zero order with respect to the acceptor molecule (27).

(27) H. A. Smith, D. M. Alderman, and F. W. Nadig, J. Am. Chem. Soc., 67, 272 (1945).

For zero order relationship the differential equation

$$-\frac{d[A]}{dt} = k \quad (10)$$

expresses the rate law. Integration with respect to t gives

$$- [A] = k t + \text{constant}$$

A plot of $[A]$ at various times, t , would give a straight line, the slope of which is $-k$, the specific rate constant. The units of k would be moles liters⁻¹ sec.⁻¹ if time is given in seconds.

For first order rate relationship the differential equation is

$$-\frac{d[A]}{dt} = k [A] \quad (11)$$

It may be readily integrated and if the limits of integration are taken as $[A] = [A_0]$ at $t = 0$ and $[A] = [A_t]$ at $t = t$, one may obtain, after conversion to base 10 logs:

$$\log \frac{[A_0]}{[A_t]} = \frac{kt}{2.303} \quad (12)$$

A plot of $\log [A_0]/[A_t]$ versus t would give a straight line, the slope of which equals $k/2.303$. The rate constant can be, therefore, obtained by multiplying the slope of line by 2.303. The units of k would be reciprocal time units.

Should A in expression (11) be hydrogen, its molar concentration would be proportional to the hydrogen pressure. By carrying out the same treatment as described above, one can obtain for the expression (12)

$$\log \frac{P_0}{P} = \frac{kt}{2.303} \quad (13)$$

Where P_0 is initial hydrogen pressure and P is hydrogen pressure at time t . By plotting $\log (P_0/P)$ versus t , a straight line is again obtained whose slope when multiplied by 2.303, gives the apparent rate constant in reciprocal time units.

The apparent rate constant obtained from the equation (13) is not the true constant for a heterogeneous reaction. Whenever the volume of a gaseous system is changed, conventional rate equations must be modified by the introduction of the dimension of volume (28). Thus if the rate of the reaction is given by the expression

$$-\frac{dP}{dt} = \frac{k}{V} P,$$

treatment in a manner similar to that of above yields

$$\log \frac{P_0}{P} = \frac{kt}{2.303 V} \quad (14)$$

V is the volume of the hydrogen. In the system used in this work the volume was 4.4 liters.

It is well known that the rates of chemical reactions are temperature dependent. This relationship is expressed by the Arrhenius equation, one form of which is

$$\frac{d \ln k}{dt} = \frac{E_a}{RT} \quad (15)$$

(28) H. A. Smith and J. F. Fuzek, J. Am. Chem. Soc., 70, 3743 (1948).

where E_a is the apparent energy of activation. This may be expressed as:

$$\ln k = -\frac{E_a}{RT} + \text{constant} \quad (16)$$

or

$$\log k = -\frac{E_a}{2.303 RT} + \text{constant} \quad (17)$$

A plot of $\log k$ against $\frac{1}{T}$ would give a straight line, the slope of which is equal to $-E_a/2.303 R$. Thus, apparent energies of activation can be calculated.

In addition, integration of Eq. (15) between the limits of k_1 at temperature T_1 and k_2 at temperature of T_2 will yield, after conversion to logs base 10:

$$\log \frac{k_1}{k_2} = \frac{E_a}{2.303 R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad (18)$$

In this form the Arrhenius equation is useful in comparing rate constants obtained at different temperatures or in correcting rate constants to a particular temperature. Of course, it must be pointed out in applications of the Arrhenius equation the apparent energy of activation must be constant over the temperature range to which it is applied.

CHAPTER II

EXPERIMENTAL

A. Apparatus

Hydrogenation Equipment

A series 867 low-pressure hydrogenator was obtained from the Parr Instrument Company of Moline, Illinois. This apparatus consists of the shaker assembly, electric motor, a four-liter hydrogen reservoir with a thermometer well all mounted on a thick, heavy metal base, and suitable valves and pressure gauge. The reaction bottle was placed in the shaker holder and clamped tightly by two thrust bolts on two screw-threaded rigid rods fastened on the base of the holder. This assembly was connected by a rod to an eccentric wheel which, in turn, was connected to an electric motor. This permitted the reaction bottle and its contents to be shaken in a rocking motion through an arc of about 30 degrees and at a rate of approximately 180 cycles per minute. The four-liter hydrogen tank was equipped with valves at both ends: at one end a two-way valve equipped with a pressure gauge was connected to commercial hydrogen cylinder; at the other end a three-way valve was connected by pressure tubing to the reaction bottle and to an evacuating system.

The evacuating system consisted of an oil-sealed type vacuum pump and a series of four glass tubes, the first two of which contained sodium hydroxide pellets and the last two of which were filled with calcium chloride. These four tubes were placed between the vacuum pump and the hydrogenation system and assisted in the removal of solvent vapors. A needle

valve, placed between the vacuum pump and the last tube, was used to admit air into the reaction bottle.

The bottles used in this work were standard thick-walled Parr pressure reaction bottles having a capacity of approximately 450 ml. A protective cylindrical shield made from a perforated metal sheet and opened at both ends was used to surround the reaction bottle for safety precautions.

The pressure gauge used was an Ashcroft Laboratory Test Gauge graduated in 0.2 lb./in.² intervals. When hydrogenation studies were carried out at initial gauge pressures of 2 psi. a U-type manometer was used to determine pressure changes rather than the Ashcroft pressure gauge. The reasons for this were that the precision of gauge pressure at this range was doubtful, and if the hydrogen uptake was greater than 2 psig., the pressure readings would become impossible.

The usage of the manometer in connection with the hydrogenation system will be discussed later.

Temperature Control Equipment

This system was constructed from an electric stirrer, a circulating pump, a large water bath, and a water jacket for the reaction bottle.

The water jacket was made of metal and 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. Several pieces of metal plates were used to adjust the position of the reaction bottle within the jacket.

Water from the large water bath was circulated through the jacket by means of a conventional circulating pump. The desired temperatures

could be achieved within 0.5°C by adding hot water or ice water to the water bath.

The Distillation Equipment

Distillation of all reagents used in this work was accomplished using a Todd Precision Distillation assembly manufactured by the Todd Scientific Company, Springfield, Pennsylvania. In handling small amounts of reagents, a one-half inch diameter Vigreux type column was used. Large quantities of reagents were distilled using a one-inch diameter column packed with one-fourth and one-eighth inch single turn glass helices. Each of the columns was three feet long. The Todd apparatus had separate heating units attached to the upper and lower portion of the column jacket. Powerstats were provided to control the temperatures of these units.

In some cases, the distillation was carried out in an atmosphere of nitrogen. This was done simply by introducing nitrogen into the distillation flask. At times, when vacuum distillation was required, a Welch Duo-Seal vacuum pump protected by a cold trap was connected to the distillation apparatus.

B. Reagents

Moist Ethanol

Absolute ethanol ($99^{+}\%$) 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, five per cent ruthenium-on-carbon, was purchased from

Englehard Industries, Inc., Newark, New Jersey. Lot number 7483 was used.

Olefins

Cyclopentene, 1-methyl-1-cyclopentene, cycloheptatriene, cyclooctatetraene, trans-trans-cis-1,5,9-cyclododecatriene, and cyclododecene were obtained from the Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.

Cycloheptene, cyclooctene, 1-methyl-1-cyclopentene, 1-methyl-1-cycloheptene, 1-methyl-1-cyclohexene, 3-methyl-1-cyclohexene, 4-methyl-1-cyclohexene, cyclohexadiene-1,3, cyclohexadiene-1,4, cyclooctadiene-1,3, cyclooctadiene-1,5, and cyclododecene were obtained from the Columbia Organic Chemicals Company, Inc., Columbia, South Carolina.

Cyclohexene was obtained from the Distillation Products Industries, Rochester, New York.

3,5-Dimethyl-1-cyclohexene* was made from the dehydration of 3,5-dimethyl cyclohexanol over phosphorus pentoxide.

All of the above materials were distilled using a suitable column of the Todd apparatus. Table 1 shows the nature of the column used for distillation as well as the boiling points of each olefin. All distillates were stored under nitrogen pressure in 30-ml. brown bottles.

C. Procedure

Preparation for Hydrogenation

Since traces of foreign materials in the reaction system could cause poisoning of the catalyst, extreme precautions were exercised to insure cleanliness of the system.

* See Appendix A.

Table 1. Boiling Points of Cycloalkenes

Cycloalkene	Observed B.P. °C./mm. Hg	Type of Distilling Column Used	Remarks
Cyclopentene	44/737	Helices-Packed Column	
1-Methyl-1-cyclo- pentene	74.4/738	Vigreux Column	
Cyclohexene	71.45-81.70/738	Helices-Packed Column	Distilled under Ni- trogen
1-Methyl-1-cyclo- hexene	108.6/737	Vigreux Column	
3-Methyl-1-cyclo- hexene	99.9/737	Vigreux Column	
4-Methyl-1-cyclo- hexene	101.4/740	Helices-Packed Column	
3,5-Dimethyl-1-cy- clohexene (mix- ture of isomers)	118-121/739	Vigreux Column	
Cycloheptene	117-120/737.3	Helices-Packed Column	Distilled under Ni- trogen
1-Methyl-1-cyclo- heptene	135.2/738	Vigreux Column	
Cyclooctene	142/8-143/739	Helices-Packed Column	Distilled under Ni- trogen
Cyclohexadiene-1,3	78.8-79/739	Vigreux Column	
Cyclohexadiene-1,4	87-87.4/739	Vigreux Column	
Cyclooctadiene-1,3	141.6- 141.8/740	Helices-Packed Column	
Cyclooctadiene-1,5	147-147.2/739	Helices-Packed Column	
Cycloheptatriene- 1,3,5	113.4-113.6/740	Vigreux Column	
Cyclooctatetraene	138.6-138.9/739	Vigreux Column	
<u>trans-trans-cis-1,</u> <u>5,9-Cyclododeca-</u> <u>triene</u>	100/28	Vigreux Column	
Cyclododecene	135-139/25	Vigreux Column	

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

All glassware, such as reaction bottles, hypodermic syringes, and graduated cylinders, was cleaned with detergent solution, rinsed, and filled with cleaning solution. After standing for at least half an hour, each was rinsed with tap water, then rinsed several times with distilled water, and finally dried in an electric drying oven at 105°C. All glassware subjected to this sort of cleaning procedure was capped or wrapped with aluminum foil until used.

Catalyst Pretreatment

In order to obtain maximum activity of the catalyst and to prevent an induction period when the catalyst was used, 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. The catalyst 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.

The brass inlet tube of the hydrogenation apparatus was cleaned with a pipe cleaner soaked in absolute alcohol or methanol. The rubber stopper was also cleaned with a piece of soft paper towel.

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 bottle 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 30 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 excess hydrogen was removed. Air could then be admitted safely into the bottle and the bottle removed from the shaker assembly. The inlet tube and rubber stopper were cleaned again.

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 a 5-ml. hypodermic syringe. The reaction bottle and its contents were placed and clamped tightly on the shaker. After following the same treatment described above to expel the air, the pressure was adjusted to 50 ± 0.20 psig. and recorded. The shaker and a stop watch were then started simultaneously and the pressure was observed and recorded. At regular time intervals pressure readings were observed and recorded.

At the completion of the reaction, the residual hydrogen in the reaction bottle was expelled and the bottle removed from the shaker. The brass inlet tube and rubber stopper were cleaned. After filtering the reaction mixture, the spent catalyst was preserved and the filtrate was either discarded or retained.

Hydrogenation Procedure at Low Pressure

Procedures for the hydrogenation studies at 2 psig. were slightly different from the normal 18 or 50 psig. reaction since a U-type manometer was used instead of the Ashcroft pressure gauge. The steps to remove the

air from the reaction bottle were the same as usual. When the reaction system was adjusted to 2 psig., the tubing to the vacuum pump was removed and the manometer was connected to this position on the valve system and the appropriate valve opened. The pressure recordings were now taken by observing the height of the right-hand side mercury. By proper conversion, the actual gauge pressures could be obtained. When the reaction was completed, the valve to the manometer was closed, the manometer disconnected, and the original tubing to the vacuum pump was replaced. Completion of the experiment was made then in the usual way.

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 circulating pump described above.

Usually, the temperature studies in this work were effected over the range of 12-32°C. These temperatures could easily be achieved by adding hot water or ice to the water bath. In this way the temperature could be controlled within 0.5°C.

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 five minutes of water circulation was found necessary for this. Completion of the experiment was made in the usual way.

CHAPTER III

DISCUSSION OF EXPERIMENTAL RESULTS

The Kinetics of the Reaction of Cycloalkenes

As mentioned in Chapter, if a plot of $(C_0 - x)$ versus t , where C_0 was the initial concentration of substrate, and x was the decrease in concentration of substrate at time t , gave a straight line, the reaction would be zero order with respect to the concentration of substrate; if a plot of $\log P_0/P$ versus t , where P_0 was the initial pressure of hydrogen, and P was pressure at time t , gave a straight line, the reaction would be first order with respect to hydrogen pressure. The data in each hydrogenation was treated in these manners, and it was found that the reaction was zero order with respect to cycloalkene and first order with respect to hydrogen pressure. Figures 1 and 2 show typical plots of the data for the hydrogenation of cyclohexene treated in these ways.

The plot of $\log P_0/P$ versus time in all cycloalkenes showed that over the relatively small pressure drop of a single run the rate of hydrogenation was constant over sixty to eighty per cent of reaction completion, but beyond this showed a slight deviation from a linear relationship with increasing time. This decrease in rate with time might be explained by the effect of poisoning; the term poisoning as used herein refers to the lack of complete desorption of the product or products of the reaction. It is, therefore, realized that as the concentration of hydrogenated products builds up, the product might be found adsorbed on

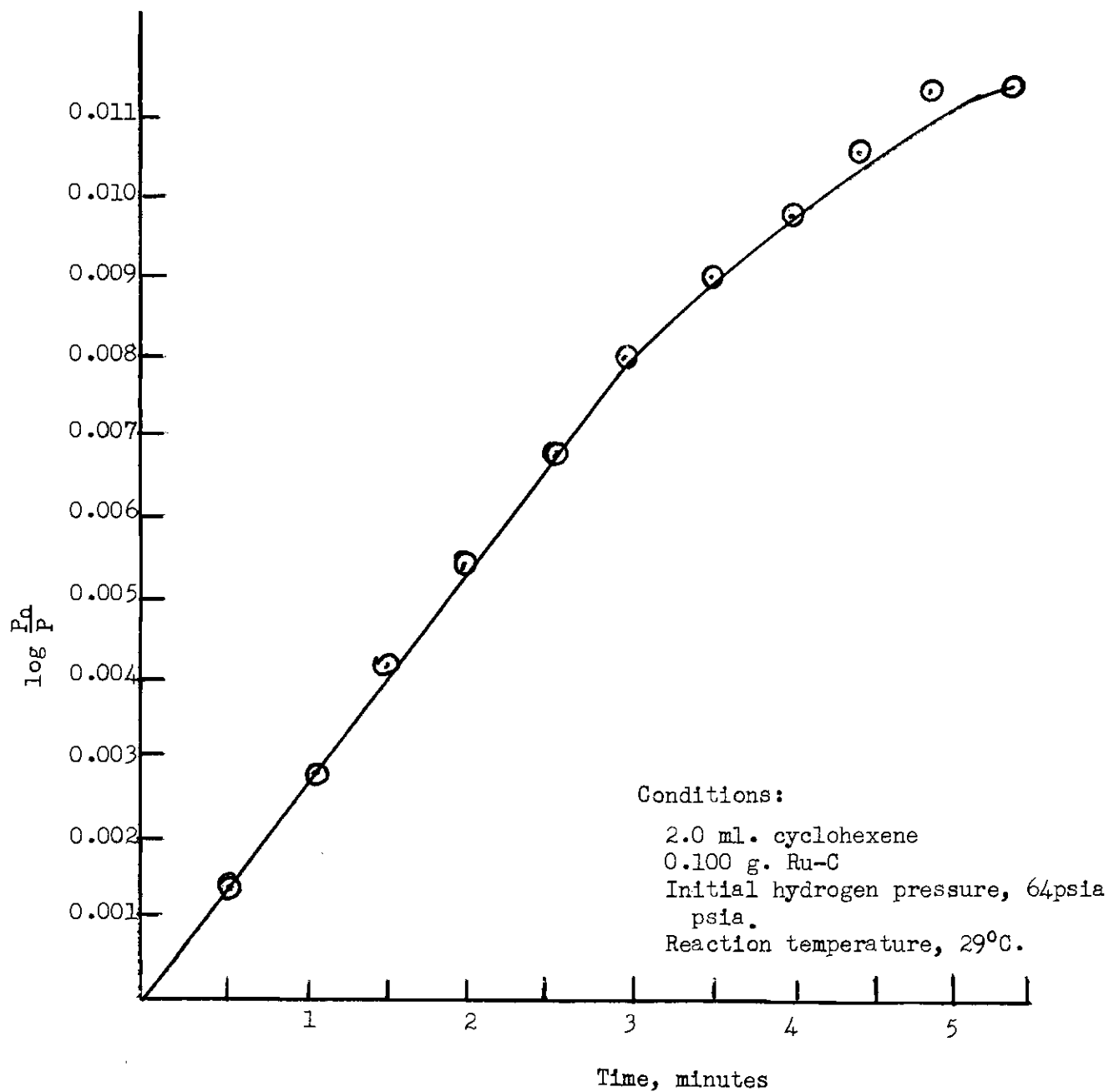


Figure 1. Hydrogenation of Cyclohexene. Plotted as First Order in Hydrogen Pressure.

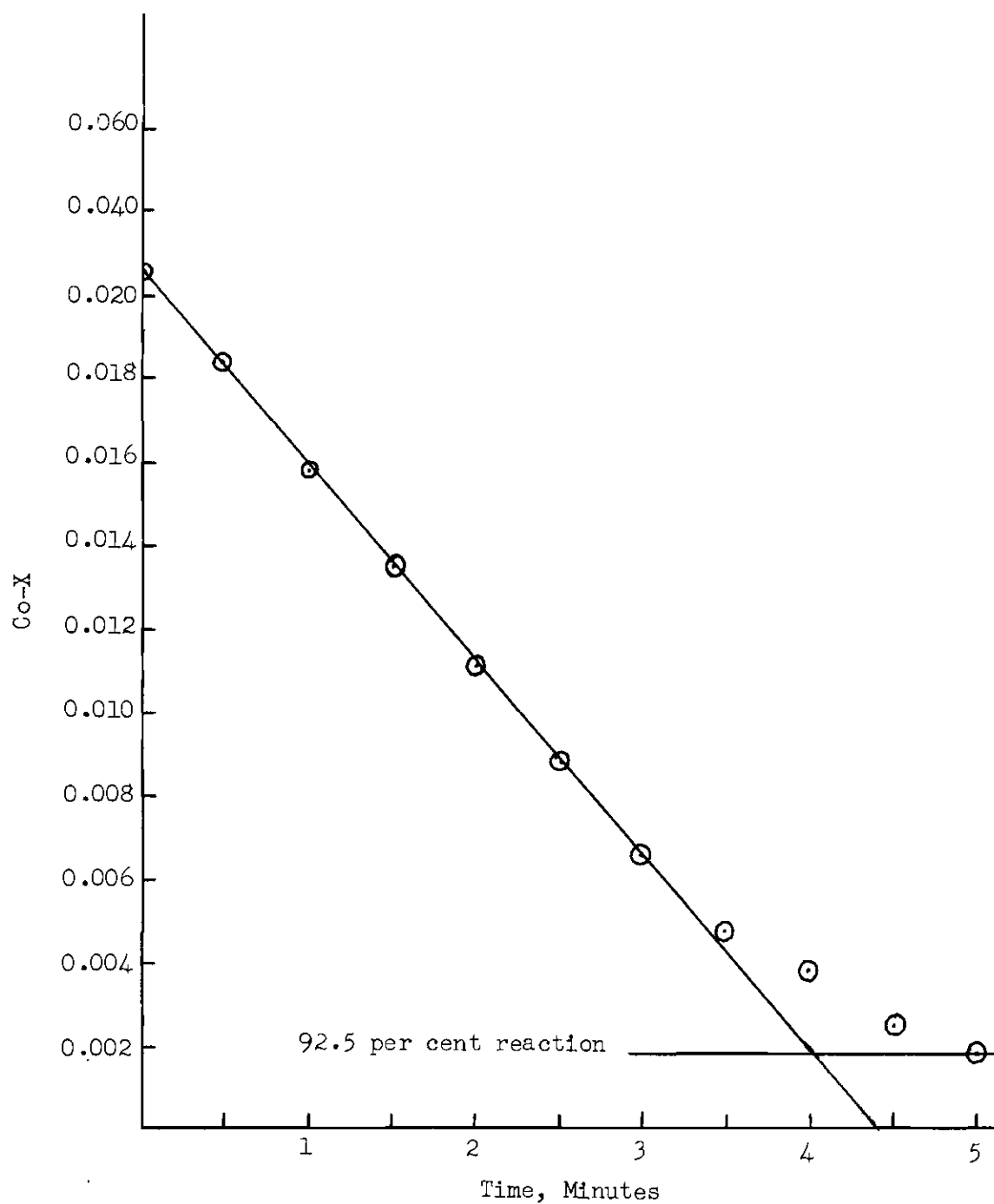


Figure 2. Hydrogenation of Cyclohexene Plotted as Zero Order in Cyclohexene Concentration.

the catalyst surface to a greater extent than in earlier stages of the reaction, thus inhibiting the reaction. It also should be mentioned that the deviation observed could also be due to a lack of real first-order kinetic relationship. As will be pointed out below, results obtained at very wide initial hydrogen pressures seem to support the latter possibility. However, in spite of the rate decreasing at final stage, the initial rate was deemed sufficient as a measure of an "overall" rate. Thus, the straight line observed for all cycloalkenes indicated that the rate of the hydrogenations could be obtained by considering the reaction to be first order with respect to hydrogen.

The pressure data were reprocessed by appropriate conversion to the concentration of the substrate, and plotted as $(C_0 - x)$ versus t , straight lines were again expected for the cycloalkenes. This indicated that the reaction was zero order with respect to cycloalkene concentration over the relatively small concentration changes of a single run. The plot, made as described, followed a linear relationship for approximately sixty to eighty per cent of the total reaction time.

Effect of the Amount of Catalyst on Rate Constant

The increase in rate with an increase in the amount of catalyst used in catalytic hydrogenation studies was reported by the work of Smith and coworkers (29,30,31). For this reason, several cycloalkenes were

(29) H. A. Smith, D. M. Alderman, and F. W. Nadig, J. Am. Chem. Soc., **67**, 272 (1945).

(30) H. A. Smith and E. F. H. Pennekamp, ibid., **67**, 276 (1945).

(31) H. A. Smith and H. T. Meriwether, ibid., **71**, 413 (1949).

chosen and studied to determine whether or not the rate of hydrogenation was directly proportional to the amount of catalyst used. These examples are given in Table 2.

While the rate constants, expressed in units of min.^{-1} , did increase with the amount of catalyst used, the relationship was not in direct proportion. This is clearly shown by expressing the rate constants per unit weight of catalyst. With the exception of cycloheptene, it may be noted that the rate per unit weight of catalyst decreased with increasing amounts of catalysts. Williams (32) described the relationship between the rate and the catalyst weight by a $k/g.$ plot. He noted that three possible types of relationships might arise. The first situation was evident when the slope of the curvature is equal to zero. Here the catalyst is being used under equilibrium conditions; in other words, the entire catalyst surface is unimolecularly covered with reactants. When an adsorbed molecule reacts, the product is desorbed and is replaced by reactant species. The entire system is at an equilibrium condition. The second condition is evident from the plot when the slope is negative. All of the catalyst surface is not being used, probably indicating the reactants cannot reach the catalyst surface as fast as they are adsorbed and react. This generally occurs at high relative catalyst weights or with rather rapid reactions. As a result, only a portion of the catalyst surface is used at any given time for the purpose of effecting the reaction. If the slope is positive, it is likely that the useful surface of

(32) A. Williams, Jr., Catalytic Hydrogenation Studies Using Five Per Cent Rhodium Supported Catalysts. Unpublished Ph.D. Dissertation, Georgia Institute of Technology, 1962, p. 46.

Table 2. Effect of Amount of Catalyst on the Reaction Rate Constant

Cycloalkene	Amount of Catalyst	k min. ⁻¹	k/g. ⁻¹ min. ⁻¹ g. ⁻¹	Temperature °C
1-Methyl-1-cyclopentene	0.100	0.00276	0.0276	30
1-Methyl-1-cyclopentene	0.200	0.00322	0.0161	30
Cyclohexene	0.050	0.00414	0.0828	29
Cyclohexene	0.100	0.00627	0.0627	29
Cyclohexene	0.150	0.00690	0.0460	29
Cyclohexene	0.200	0.00782	0.0391	29
1-Methyl-1-cyclohexene	0.100	0.00041	0.0041	30
1-Methyl-1-cyclohexene	0.200	0.00064	0.0032	30
1-Methyl-1-cyclohexene	0.400	0.00064	0.0016	30
4-Methyl-1-cyclohexene	0.100	0.00437	0.0437	30
4-Methyl-1-cyclohexene	0.150	0.00587	0.0391	30
4-Methyl-1-cyclohexene	0.200	0.00668	0.0334	30
Cycloheptene	0.050	0.00080	0.0016	30
Cycloheptene	0.100	0.00215	0.0215	30
Cycloheptene	0.150	0.00429	0.0286	30
Cycloheptene	0.200	0.00576	0.0288	30

the catalyst is affected, possibly by product adsorptions or poison adsorptions. Under such conditions where a certain amount of surface is "destroyed" for reaction purposes, effects are much more pronounced in slow reactions or small relative amounts of catalysts. Figures 3 and 4 show typical plots of $k/g.$ versus $g.$ For cycloheptene, the positive slope indicated that the amount of catalyst was not sufficient to allow equilibrium to be reached. Therefore, the increase in the amount of catalyst used over certain range would cause an increase in rate constant. One other explanation might be that for a reaction the same amount of poison could be expected regardless of the amount of catalyst used. Consequently, a larger percentage of the catalyst would be poisoned when a small amount of catalyst was used. For cyclohexene, the negative slope indicated that the catalyst surface was not being used efficiently. The same was true in other cycloalkenes studied here, and it would appear that, generally, about 0.2 g. of catalyst for two ml. of acceptor was necessary for the rate to appear directly proportional to the weight of catalyst used.

Effect of Initial Hydrogen Pressure on Rate Constant

The effect of initial hydrogen pressure on rate constant is given in Table 3. The data in Table 3 indicate that the rate constant varied slightly as the initial hydrogen pressure changed. It is realized that if the reaction was indeed to obey the first order kinetics with respect to hydrogen pressure, the rate constant should be expected to be independent of the initial hydrogen pressure. The results shown here seemed to indicate the necessity to reexamine the reaction order as determined

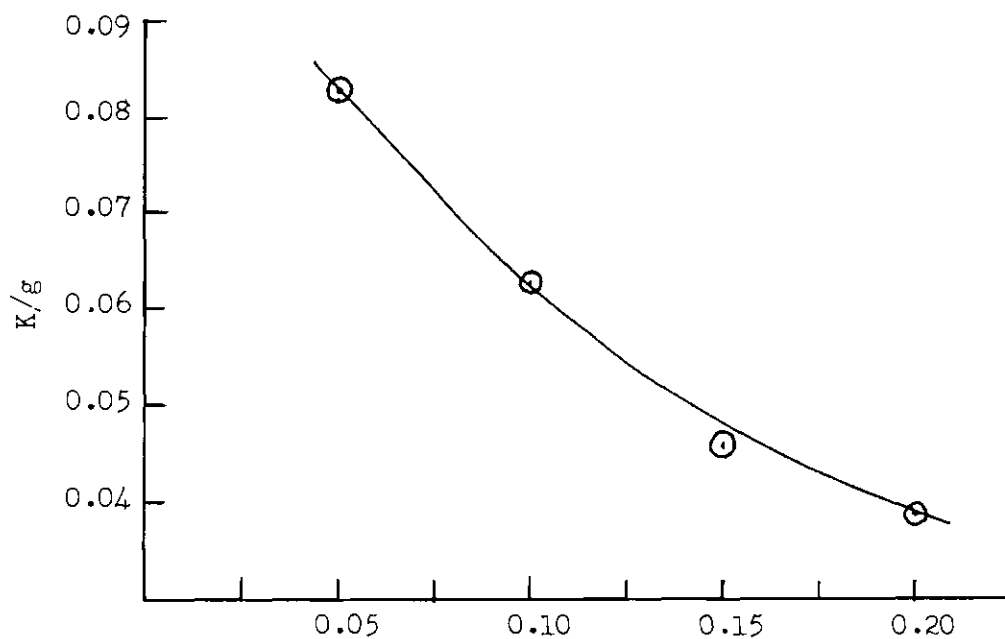


Figure 3. Hydrogenation of Cyclohexene Plotted as K/g versus g .

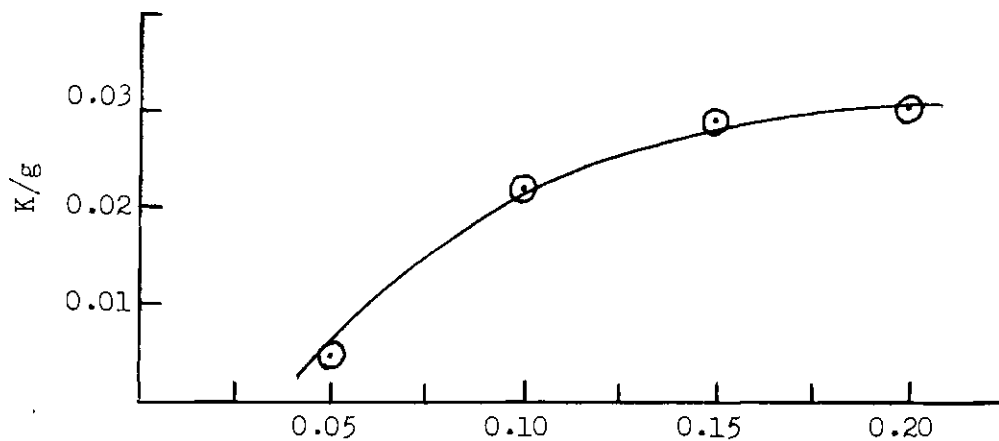


Figure 4. Hydrogenation of Cycloheptene Plotted as K/g versus g .

Table 3. Effect of Initial Hydrogen Pressure on the Reaction Rate Constant

Cycloalkene	Initial Hydrogen Pressure psia.	Reaction Rate Constant min. ⁻¹	Reaction Temperature °C.
Cyclohexene	64.00	0.00627	29
Cyclohexene	32.14	0.00564	29
Cyclohexene	16.28	0.00518	29
Cycloheptene	64.00	0.00215	30
Cycloheptene	32.55	0.00156	30
Cycloheptene	16.40	0.00104	30
Cyclooctene	64.35	0.00759	30
Cyclooctene	32.42	0.00646	30
Cyclooctene	16.30	0.00630	30
Cyclooctadiene-1,3	64.30	0.01030	32
Cyclooctadiene-1,3	32.53	0.00728	32
Cyclooctadiene-1,3	16.30	0.00472	32
Cyclooctadiene-1,5	64.30	0.0067	32
Cyclooctadiene-1,5	32.42	0.0059	32
Cyclooctadiene-1,5	16.30	0.0052	32

by the method mentioned in Chapter I. This may be achieved by considering the expression (33):

$$\frac{dp}{dt} = kp^n \quad (19)$$

where p represents pressure of hydrogen and n the order of the reaction with respect to hydrogen. If equation 19 is rearranged and then integrated, one obtains:

$$\frac{p^{-n+1}}{-n+1} + C = kt \quad (20)$$

C , the integration constant, can be evaluated since at the beginning of the reaction, i.e., when $t = 0$, equation 20 yields:

$$C = - \frac{p_0^{-n+1}}{-n+1} \quad (21)$$

where p_0 is the pressure when $t = 0$, or in other words the initial pressure. Substitution of this value of C into equation 20 gives, then, the useful expression:

$$k = \frac{p^{-n+1} - p_0^{-n+1}}{t(-n+1)} \quad (22)$$

In applying this expression to determination of the correct reaction order, hydrogenation of the same compound at the same temperature,

(33) J. A. Stanfield, The Kinetics of Catalytic Hydrogenation, Part A. Methyl-Substituted Benzoic Acids, Part B. Pyridine and Methyl-Substituted Pyridines, unpublished Ph.D. Dissertation, University of Tennessee, 1947, pp. 100-102.

acceptor concentration, and amount of catalyst but at different initial hydrogen pressures were selected. The final pressure (p in equation 22) used in each case was selected so that the same amount of acceptor was hydrogenated. The time interval, t , was different in each case and was the time necessary to reach the same degree of hydrogenation of acceptor. For each sample the value of k was calculated, using the above equation and assuming various values of n from 0.7 to 1.0. The differences in the k values for the two runs obtained at a particular reaction order were then plotted against the assumed reaction order. Where the line thus obtained crossed the x-axis represented, then, the reaction order at which there would be no difference in rate constant. The reaction order thus obtained had an average value of 0.98 with respect to hydrogen pressure. This value is not significantly different from the value of 1.00.

Effects of Initial Amount of Cycloalkene on the Rate Constant

The variation of the rate constant with changing initial concentration of cycloalkene was also studied. Table 4 gives data for cyclohexene, cycloheptene, and cyclooctene. In the first two of these, deviations from zero order reaction with respect to acceptor was noted. By use of an equation similar to 22 in which pressure units were replaced by concentration units of acceptor, the deviation from a zero order reaction was, on the average, only 0.065.

Effect of Temperature on the Rate Constant;

Activation Energies Studies

The effect of temperature on the rate of reaction is dependent on

Table 4. Effect of the Amount of Cycloalkene on the Reaction Rate Constant

Cycloalkene	Moles	Ru-C g.	$k_{30} \text{ min.}^{-1}$
Cyclohexene	0.0205	0.050	0.00414
Cyclohexene	0.0410	0.050	0.00621
Cyclohexene	0.0205	0.100	0.00627
Cyclohexene	0.0410	0.100	0.00897
Cyclohexene	0.0205	0.200	0.00783
Cyclohexene	0.0410	0.200	0.01196
Cycloheptene	0.0183	0.100	0.00170
Cycloheptene	0.0366	0.100	0.00153
Cycloheptene	0.0549	0.100	0.00113
Cyclooctene	0.0158	0.100	0.00759
Cyclooctene	0.0316	0.100	0.00816
Cyclooctene	0.0474	0.100	0.00760

the nature of the substrate being hydrogenated and on the type of catalyst being used. For almost all hydrogenations studied, the rates were approximately doubled for each twenty to thirty degree rise in temperature, and showed an Arrhenius type temperature dependence over 12 to 34°C. A typical case is the hydrogenation of cyclohexene. A plot of $\log k$ versus $1/T$ given in Figure 5 is nearly linear with negative slope. From the slope of the straight line multiplied by $-2.303 R$, the apparent activation energy has been calculated to be 2500 calories per mole. Table 5 gives a tabulation of the apparent activation energy for all cycloalkenes studied.

Effect of the Structure of Cycloalkene on Activation Energy

There is no uniform relationship observed between the magnitude of activation energy and the size of ring in hydrogenation studies of cyclopentene, cyclohexene, cycloheptene, cyclooctene, and cyclododecene. However, it was generally found that the substitution of a methyl group in the ring would result in an increase in activation energy compared to the unsubstituted cycloalkene. Cyclohexene, for instance, has an activation energy of 2500 calories per mole, while methyl cyclohexenes have activation energies from 3190 to 6650 calories per mole, an increase of 690-4150 calories per mole, depending on the position of methyl substituent group relative to double bond. Dimethyl cyclohexene, furthermore, has an activation energy of 8400, an increase of 5900 calories per mole over cyclohexene. It might be pointed out that the increase in activation energy per methyl, while possibly dependent upon position, is on the average about 2100 calories per mole based on the monomethyl derivatives,

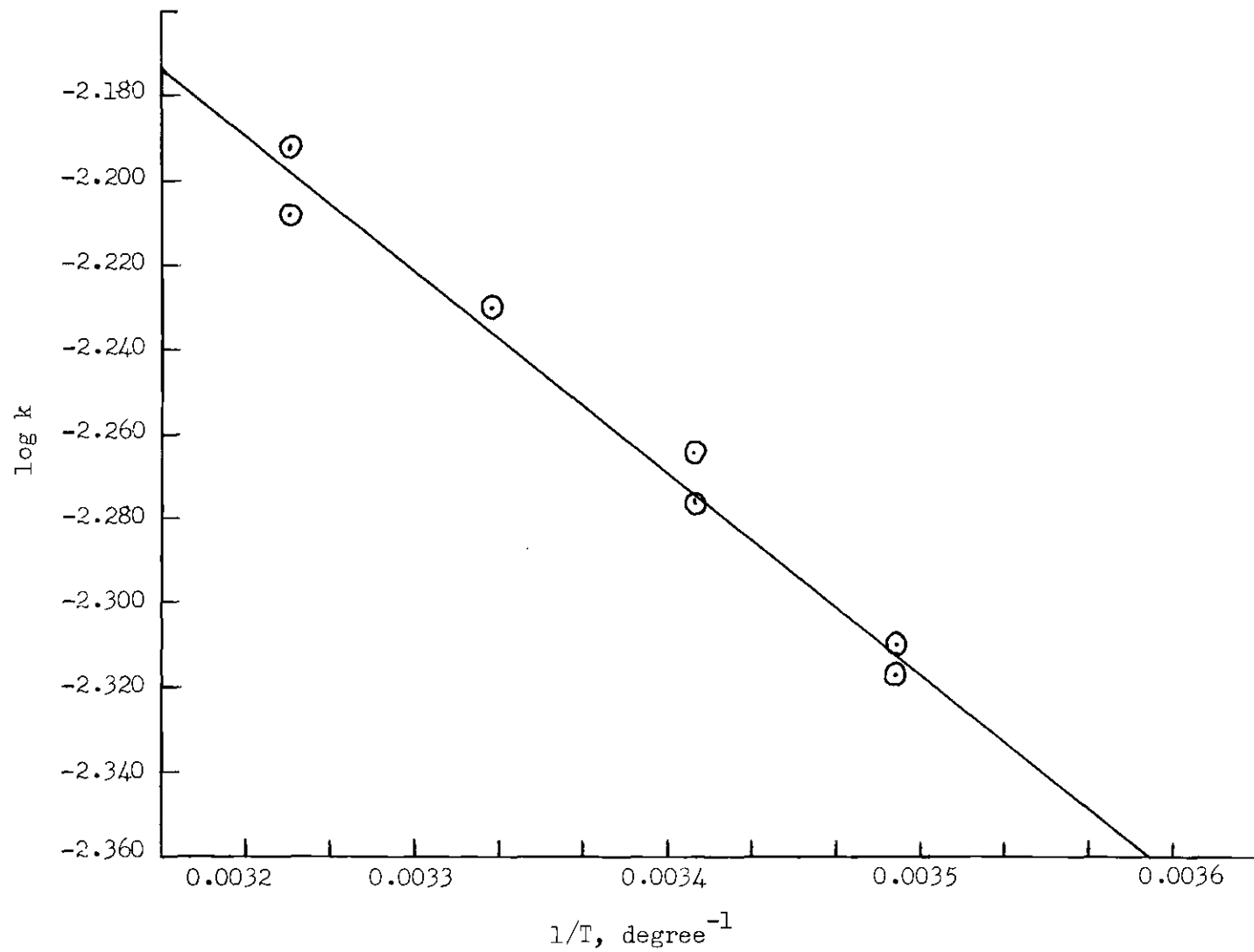


Figure 5. Activation Energy Plot for Cyclohexene.

Table 5. The Arrhenius Activation Energy for Hydrogenation of Cycloalkenes

Conditions: 0.100 g. Ru-C, 2 ml. Acceptor, 50 ml. Absolute Alcohol,
and 64 psia Initial hydrogen Pressure

Cycloalkene	Reaction Rate Constant at Temperature t°C. min. ⁻¹ K _t			Activation Energy, Calories per Mole
Cyclopentene	K ₁₂ = 0.00286	K ₁₇ = 0.00346	K ₂₇ = 0.00379	5100
1-Methyl-1-cyclopentene	K ₁₄ = 0.00207	K ₂₂ = 0.00242	K ₃₀ = 0.00276	3140
Cyclohexene	K ₁₃ = 0.0046	K ₂₀ = 0.0052	K ₃₄ = 0.0064	2500
1-Methyl-1-cyclohexene	K ₁₅ = 0.00029	K ₂₂ = 0.00034	K ₃₀ = 0.00041	3920
3-Methyl-1-cyclohexene	K ₁₅ = 0.00311	K ₂₂ = 0.00437	K ₂₉ = 0.00565	6650
4-Methyl-1-cyclohexene	K ₁₄ = 0.00322	K ₂₂ = 0.0038	K ₃₀ = 0.00437	3190
3,5-Dimethyl-1-cyclohexene	K ₁₄ = 0.000736	K _{23.5} = 0.00118	K ₃₂ = 0.00173	8400
Cycloheptene	K ₁₈ = 0.00154	K ₂₅ = 0.00198	K ₃₂ = 0.00272	7000
1-Methyl-1-cycloheptene	K ₁₄ = 0.000633	K ₂₁ = 0.000978	K ₂₈ = 0.00142	17800
Cyclooctene	K ₁₇ = 0.00483	K ₂₃ = 0.00630	K ₃₀ = 0.00759	6000
Cyclohexadiene-1,3	K ₁₄ = 0.00199	K ₂₂ = 0.00345	K ₃₀ = 0.00495	10500

Table 5. Continued

Cyclohexadiene-1,4	$K_{14} = 0.00288$	$K_{22} = 0.00322$	$K_{30} = 0.00356$	2300
Cyclooctadiene-1,3	$K_{12} = 0.0050$	$K_{22} = 0.0074$	$K_{32} = 0.0103$	6190
Cyclooctadiene-1,5	$K_{12} = 0.0046$	$K_{21} = 0.0055$	$K_{28} = 0.0062$	2960
Cycloheptatriene-1,3,5	$K_{14} = 0.000357$	$K_{22} = 0.000587$	$K_{30} = 0.000851$	9560
Cyclooctatetraene	$K_{14} = 0.000345$	$K_{22} = 0.000508$	$K_{30} = 0.00070$	7870
<u>Trans, trans, cis-1,5,9-</u>				
Cyclododecatriene	$K_{14} = 0.00161$	$K_{22} = 0.00241$	$K_{30} = 0.00365$	11900
Cyclododecene	$K_{14} = 0.00148$	$K_{22} = 0.00184$	$K_{30} = 0.00212$	3100

and about 2900 calories per mole based on the dimethyl derivatives. The same result was noted with 1-methyl-cycloheptene although the increase was much greater. One exception to these cases is 1-methyl-cyclopentene in which the activation energy of the methyl substituted compound is 1960 calories per mole less than the unsubstituted cyclopentene.

Effect of the Structure of the Cycloalkene on Rate Constant

Eighteen cycloalkenes were hydrogenated under the following conditions: 0.100 gram of ruthenium-on-carbon catalyst; 2.0 ml. of hydrogen-acceptor; 50 ml. of absolute alcohol; an initial pressure of about 64 psia; and a temperature near 30°C. Table 6 gives the hydrogenation rate constants, calculated in the manner previously described and referred to one gram of ruthenium-on-carbon catalyst for the eighteen compounds included in this study. All rates are corrected to 30°C. This table clearly shows that the rate constants obtained vary with the structures of different cycloalkenes.

The relative rates of hydrogenation of several unsubstituted cycloalkenes at the conditions stated above are listed in Table 7. From this table, the following order of the relative magnitudes of the rate constants is: cyclooctene > cyclohexene > cyclopentene > cycloheptene \approx cyclododecene. It does not appear that the ring size affects the rate of reaction in any orderly manner. Models indicate only a very slight difference in structural appearance of the adsorbed cycloalkene, particularly for C₅, C₆, C₇, and C₈ molecules. In fact, of these, any structural effects would seem to indicate that the cyclopentene should hydrogenate more rapidly than any of the others. This was not observed when these cycloalkenes were hydrogenated. The slow rate of hydrogenation of cyclododecene might be explained by steric hindrance to the approach of hydrogen molecules to the catalyst surface.

Table 6. The Reaction Rate Constants for Hydrogenation of Various Cycloalkenes

Conditions: 30°C and 64 psia. in the presence of five per cent ruthenium-on-carbon, 2.0 ml. of acceptor

Cycloalkene	Density g./ml.	Rate Constant K_{30} min. ⁻¹ g. ⁻¹
Cyclopentene	0.7740	0.0410
1-Methyl-1-cyclopentene	0.7883	0.0276
Cyclohexene	0.8402	0.0627
1-Methyl-1-cyclohexene	0.8435	0.0041
3-Methyl-1-cyclohexene	0.8585	0.0583
4-Methyl-1-cyclohexene	0.8136	0.0437
3,5-Dimethyl-1-cyclohexene	0.8163	0.0017
Cycloheptene	0.8807	0.0215
1-Methyl-1-cycloheptene	0.8277	0.0170
Cyclooctene	0.8460	0.0759
Cyclohexadiene-1,3	0.8605	0.0495
Cyclohexadiene-1,4	0.8623	0.0356
Cyclooctadiene-1,3	0.9085	0.0967
Cyclooctadiene-1,5	0.8715	0.0620
Cycloheptatriene-1,3,5	0.9137	0.0085
Cyclooctatetraene	0.9235	0.0070
<u>Trans, trans, cis</u> -1,5,9-cyclododecatriene	0.8652	0.0365
Cyclododecene	0.8940	0.0212

Table 7. Relative Rates of Hydrogenation of Some Unsubstituted Cycloalkenes

Cycloalkene	Reaction Rate Constant min. ⁻¹ g. ⁻¹	Relative Rate
Cycloheptene	0.0215	1.00
Cyclododecene	0.0212	0.99
Cyclopentene	0.0410	1.91
Cyclohexene	0.0627	2.92
Cyclooctene	0.0759	3.53

Due to the large number of ring atoms, cyclododecene is a very "flexible" ring and may easily "flip" or rotate over the adsorbed portion of the molecule to such certain degree that a blocking effect toward the approach of hydrogen can occur. This could effect a significant decrease in the rate constant. Hindrance by the adsorbed acceptor toward adsorption of hydrogen on the catalyst has been suggested by other workers (34) to explain slowness of the hydrogenation of the benzene nucleus in certain substituted benzenes.

The substitution of a methyl group on a carbon atom of the double bond might also be expected to increase the hindrance of the approach of hydrogen to the catalyst surface, thereby decreasing the rate constant. Such results were observed for all 1-methyl-1-cycloalkenes when compared

(34) H. A. Smith, D. M. Alderman, and F. W. Nadig, J. Am. Chem. Soc., **67**, 272 (1945).

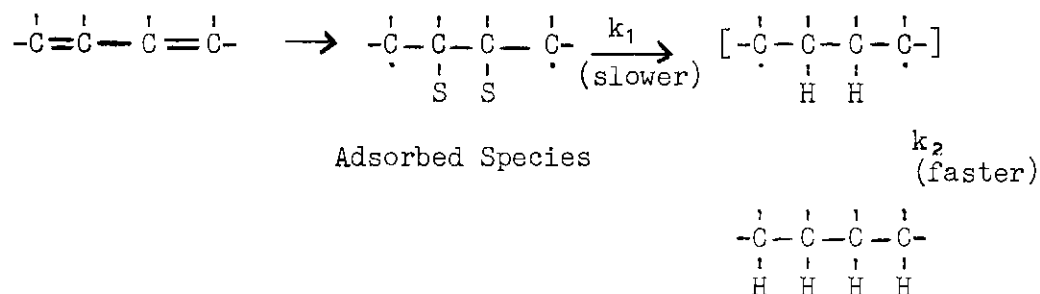
to the corresponding unsubstituted cycloalkenes.

The comparison of 3-methyl-1-cyclohexene, 4-methyl-1-cyclohexene, and 3,5-dimethyl-1-cyclohexene may also be made. The rate constant of 3-methyl-1-cyclohexene is greater than others. The reason might be that when the 3-methyl derivative approaches the catalyst surface it can only approach in such a way that the methyl group is in an equatorial position.* On the other hand, the approach of the 4-methyl compound to the catalyst can be in such a manner that the methyl group may become either equatorial or axial in the adsorbed molecule. For both the 3-methyl-equatorial and the 4-methyl-equatorial the same degree of hindrance to the approach of hydrogen to the catalyst results. The 4-methyl-axial molecules, however, would cause a greater hindrance to the approach of hydrogen. A decrease in rate for the 4-isomer would be expected. This is what was observed in fact. The 3,5-dimethyl-1-cyclohexene, which one may consider as having a 4-methyl substituent and a 3-methyl substituent, might be expected to show the combined effects of a 3- and a 4-methyl group as described above. Its rate of hydrogenation would, therefore, be much slower than the less highly substituted compounds.

The rate constants of conjugated dienes, such as cyclohexadiene-1,3 and cyclooctadiene-1,3, are relatively greater than the respective unconjugated compounds. While the conjugated olefins may be adsorbed at either

* It might be noted that adsorption of a cyclohexene would result in the sp^2 -type bonding of the olefin linkage likely assuming a typical sp^3 -type bonding; thus, the unadsorbed cyclohexene likely appears as something similar to a cyclohexane when it becomes adsorbed. The significant difference, however, would be the lack of capability of the adsorbed cyclohexane-like molecule to "flip" from chair to boat to chair structure. The adsorbed hydrocarbon would most likely be more or less fixed in a structure nearly like the boat structure of cyclohexane.

of the ethylenic bonds of the conventionally written structure. It should be realized that because of the conjugation, any or all of the four involved carbons could become bound to the surface. If adsorption occurs so that reaction takes place between one mole equivalent of hydrogen and carbons 2 and 3, a very active "intermediate" would result. This might be pictured as shown below.



Certainly, the reaction of the "diradical" would be the most rapid. Consequently, reaction k_1 would be the rate determining step. In the unconjugated compounds, two separate steps would be required to complete the whole reaction. In other words, the hydrogenation would proceed by adsorption at one olefin site, reaction, then desorption followed by adsorption at the other olefin site, reaction, and desorption. Consequently, the rate of reaction of unconjugated compounds might be expected to be less than that of the conjugated ones.

It should be pointed out that the term "conjugated" as used above should include the possibility of resonance stabilization of the system. Thus hydrogenation of cyclooctatetraene would involve a series of four possible adsorption-reaction-desorption processes. One might anticipate the order, therefore, to be 1,3-conjugated systems > 1,4-unconjugated systems > 1,3,5-cycloheptatriene system > cyclooctatetraene system. This is the

order which was observed. The 1,5,9-cyclododecatriene system is complicated in such a picture because of cis-trans variations possible. However, as an approximation, one might expect this material to hydrogenate nearly as rapidly as a 1,4-diene.

CHAPTER IV

CONCLUSIONS

The rates of hydrogenation of cycloalkenes, using five per cent of ruthenium supported on carbon catalyst and absolute alcohol as solvent, showed a first-order dependence with respect to hydrogen pressure for the small range of pressure drop of a single run, and zero order initially with respect to the concentration of cycloalkenes.

The rate constants of cycloalkenes were increased with the initial hydrogen pressure increased. Over a wide change in hydrogen pressure, the reaction order was calculated to be 0.98 with respect to hydrogen pressure rather than true first order observed for a single run.

The effect of initial concentration of cycloalkenes on rate constant was varied with the nature of individual cycloalkene used. Over large initial concentration differences, the rate was calculated to be 0.065 order (average value) with respect to cycloalkene.

The Arrhenius type of temperature dependence of the rate constant was observed over 12 to 34°C. in all cycloalkenes studied. The rates were approximately doubled for each twenty to thirty degrees increase in temperature. The value of the activation energy varies from 2500 calories per mole for cyclohexene to 17800 calories per mole for 1-methyl-1-cycloheptene. The substitution of one methyl group in cyclohexene resulted in an increase in activation energy of about 2100 calories per mole based on the monomethyl derivatives and of about 2900 calories per mole based on the dimethyl derivatives.

The order of the relative magnitudes of the rate constant for the unsubstituted cycloalkene was found to be: cyclooctene $>$ cyclohexene $>$ cyclopentene $>$ cycloheptene \approx cyclododecene. No uniform relationship was observed between the ring size and the rate constant in this category. All 1-methyl-1-cycloalkenes had a smaller rate constant than the corresponding unsubstituted cycloalkenes due possibly to steric hindrance to the approach of hydrogen to the adsorbed molecule. The slower rate of 4-methyl-1-cyclohexene than 3-methyl-1-cyclohexene was again explained by a greater steric hindrance to the approach of hydrogen.

The rate constants of the conjugated compounds were relatively greater than those of the respective unconjugated compounds. It might be explained that the conjugated compounds would proceed in a more or less single step process to complete the whole reaction, while the unconjugated compounds might proceed by several separate steps. Thus, the following order was observed: 1,3-conjugated systems $>$ 1,4-unconjugated systems $>$ 1,3,5-cycloheptatriene system $>$ cyclooctatetraene system.

CHAPTER V

RECOMMENDATIONS

The discussion described in Chapter 3 concerning the mechanisms of the reaction of conjugated and unconjugated compounds should be investigated further through studies of interrupted hydrogenation. It is therefore recommended that several cycloalkenes possessing more than one double bond be selected to be hydrogenated and the reaction stopped before complete reaction occurs. An estimation of the pressure drops for the adsorption of one mole of hydrogen from the actual volume used in this work was found to be 84 psia. Knowing this relationship would enable one to stop the reaction at any point short of completion, and the hydrogenation products thus obtained could then be subjected to vapor phase chromatography analysis. Thereby the reaction paths might be determined.

Further work seems also desirable on the rates of hydrogenation of the unsubstituted cycloalkene by studying the C-9 to C-11 compounds.

Substituent effects of additional mono substituted cyclopentene and cyclohexenes should also be made.

APPENDIX

PREPARATION OF 3,5-DIMETHYL-1-CYCLOHEXENE ISOMERS

The mixture of cis- and trans-3,5-dimethyl-1-cyclohexene (I) was made by the dehydration of the isomers of 3,5-dimethylcyclohexanol (II) over phosphorus pentoxide. Thus, 58.1 g. of (II) was placed in a 200-ml. beaker and preheated to 80-90°C. With constant stirring, 44.8 g. of P_2O_5 was slowly added. At the conclusion of the addition, the reaction mixture was immediately transferred to a 200-ml. round-bottomed flask and refluxed at a temperature of about 120°C. for one hour. The reaction products were then distilled through ordinary distilling equipment. The boiling range of the product was 115-125°C. The crude product was washed twice with 30 ml. of five per cent NaOH, then washed with water three times, and finally dried over $CaCl_2$ overnight. The dried product was distilled through the Todd apparatus equipment with the Vigreux column. The yield was 62.3%.

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* Abbreviations used here follow the form employed by Chemical Abstracts, 50, 1 J (1956).

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