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To the Graduate Council:

I am submitting herewith a dissertation written by Burch Byron Stewart entitled "Part I: The Catalytic Hydrogenation of Nitro Compounds Over Supported Rhodium in Acetic Acid; Part II: The Exchange of Deuterium Gas and Methanol in the Presence of Raney Nickel." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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Dean of the Graduate School

PART I: THE CATALYTIC HYDROGENATION OF NITRO COMPOUNDS OVER SUPPORTED RHODIUM IN ACETIC ACID

PART II: THE EXCHANGE OF DEUTERIUM GAS AND METHANOL IN THE PRESENCE OF RANEY NICKEL

A DISSERTATION

Submitted to
The Graduate Council
of
The University of Tennessee
in
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Doctor of Philosophy

---

by

Burch Byron Stewart

June, 1959

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PART I

THE CATALYTIC HYDROGENATION OF NITRO COMPOUNDS OVER SUPPORTED RHODIUM IN ACETIC ACID

CHAPTER I

INTRODUCTION

A. Historical

Interaction between gases in contact with a catalyst is a common phenomenon and was explained in 1833 by Faraday in terms of the attraction between the surface of a catalyst and the gases.[1] Other investigators believed that the gases dissolved in the catalyst forming a solid solution with accompanying dissociation to give particles which could react more rapidly. Berzelius used the concept of a "catalytic force" which was supposed to influence the reactions.[2] The catalytic substances were unchanged chemically at the end of the reactions that he studied.

Langmuir[3] in 1916 determined the extent of dissociation of hydrogen gas on tungsten wire by measuring the heat loss by convection from the heated wire and showed that the reaction must occur on the surface of the wire. From a consideration of the unsaturated forces holding the hydrogen atoms on the surface, he derived the important adsorption isotherm equation, which makes the assumption that adsorption is limited to a unimolecular layer. The valence forces holding the molecules on the surface constitute chemical bonds.

A quantum mechanical treatment, using for a model a metal in which electrons move freely through a potential field, shows that the potential energy of the electron in the surface of the metal is lowered due to an overlap (exchange phenomenon) giving an electron-pair; the second elec-

tron comes from the metal.[4] The donor-acceptor bond type has been discussed in a recent publication.[5] Pollard[6] believes that only one electron in the bond is probable so that a stable charge distribution can exist. The simplest possible example might be the H_2^+ bond.

Roberts[7] verified Langmuir's assumption by showing that sufficient hydrogen was adsorbed to cover a tungsten wire in a unimolecular layer, if a reasonable roughness factor was assumed. He used the same type of apparatus as Langmuir's. Langmuir[8] described two types of bimolecular catalytic reactions:

(1) The two gases compete for sites in the chemisorbed monolayer, and adjacent particles react.

(2) One chemisorbed substance reacts with another which is in a van der Waals layer or in the gas phase.

The first is called the Langmuir-Hinshelwood mechanism;[9] the second, the Rideal-Eley mechanism.[10,11] A knowledge of the surface coverage will tell which of these two mechanisms is more important for a given case.

Physical or van der Waals adsorption is weak and not too important in catalytic reactions. Most surface reactions occur by means of chemisorbed intermediates. Four features of chemisorption are given:[12a]

(1) A complete monolayer saturates the catalyst toward further chemisorption.

(2) An appreciable activation energy may exist and thus the process is slow.

(3) Adsorptive capacity over the catalyst surface varies widely.

(4) The heat of chemisorption is high (10 to 100 kcal. per mole).

B. Definitions

The rate of a reaction is usually expressed in terms of the moles or liters of reactant consumed per unit time. Letting n be the moles of reactant at time t, the rate is given by -dn/dt. Also the rate can be expressed in terms of the product. If n' is the number of moles of product at time t, the rate is +dn'/dt. When concentration is used, the expression for the rate of consumption of reactant is -dc/dt; for pressure, one has -dp/dt. The rates expressed in different units are related by the definition of molar concentration, $c = n/V$, and by the definition of pressure for an ideal gas, $p = \frac{n}{V} RT$.

The order of a reaction is the sum of the powers of the concentration terms expressed in the rate of the reaction. Thus the order for the reaction, $A + B \longrightarrow$ products, is the sum of the powers, a and b, in the rate expression:

$$-dc/dt = k\, c_A^{\,a}\, c_B^{\,b}$$

Also the reaction is of the "a"th order in A and "b"th order in B. For many reactions, such as surface reactions, the overall order may be complex and nonintegral. The molecularity of the reaction is the number of molecules involved in the reaction and tells nothing about the experimentally determined kinetic order.

The rate constant or specific reaction rate constant is the rate for unit concentrations or quantities of reactants. For a surface reaction the constant is dependent upon the surface area and the volume of the gas.[12b] For a series of determinations using a catalyst with an essentially constant activity, the surface area is constant per weight of catalyst and

the specific reaction rate constant remains the same. The rate constants must be corrected to the same volume as shown by Smith and Fuzek.[13]

The activation energy for homogeneous gas reactions has been derived from statistical thermodynamics and has in many cases agreed with the experimentally determined energy. The significance of this energy is that only molecules with at least this energy can react upon collision if steric and localization factors are favorable. The activation energy is the energy which the reactants in their average energy state need in order to give an activated complex, which in turn can then give products.

For heterogeneous reactions, the surface should be considered as one of the reactants since bonds to the adsorbed reactants are due to forces equivalent to chemical bonds. The solvent, which may affect the bonding, could also be considered as one of the reactants. The activated complex would be composed of the usual reactants, catalyst, and solvent. The catalyst lowers the energy of the activated complex and thus the reactants adsorbed need less energy to react than they would without the catalyst.

The activation energy, E, is obtained from experimental results by means of the Arrhenius equation:

$$k = A\, e^{-E/RT}$$

where k is the rate constant, R is the gas constant, A is a proportionality constant, and T is the absolute temperature. A plot of log k versus 1/T should give a straight line of slope m, where

$$m = -E/2.3\ R\ .$$

Actually an apparent activation energy is usually obtained for heterogeneous reactions due to the heat of adsorption of the reactants and desorption of the products. If the surface is completely covered with the reactant, the apparent activation energy and true activation energy are the same. However when two reactants are involved such as in hydrogenations, the kinetics are more complicated, and the apparent activation energy may include the heat of adsorption of the hydrogen and/or the acceptor plus the heat of desorption of the products.

C. Kinetics of Surface Reactions

1. The Rate-controlling Step

Heterogeneous reactions at a surface are accomplished by adsorption and activation of the reactants. Five steps can be visualized for the total reaction:[14]

(1) Diffusion of reactant molecules to the surface.

(2) Adsorption of reactant molecules.

(3) Reaction on the surface.

(4) Desorption of products.

(5) Diffusion of products from the surface.

For liquid-gas reactions over a catalyst, steps (1) and (5) can be the slow rate-determining steps. This is prevented by sufficiently rapid shaking of the reaction mixture so that diffusion will not be rate-controlling. Also it is necessary to use a sufficiently small amount of catalyst so that the rate of the reaction will be directly proportional

to the catalyst weight and thus independent of the diffusion effects.

This leaves (2), (3) or (4) for the rate-controlling step. However, distinguishing these is not necessary for elucidating the kinetic behavior.[15] If one assumes that the rate is determined by the rate of adsorption or by the surface reaction, the same expression for the rate constant is obtained. Steps (2) or (4) would be expected to be the slow step if the activation energy of adsorption or desorption is high, compared to the activation energy of the surface reaction.

2. First Order Mechanisms

The differential equation expressing the case in which reduction is first order in hydrogen pressure and zero order in acceptor is given by:

$$-\frac{dP}{dt} = kP$$

where P is the pressure of hydrogen at time t, and k is the first order rate constant. This should be modified, as shown by Smith and Fuzek[13] for heterogeneous reactions:

$$-\frac{dn}{dt} = kP$$

where n is the number of moles of hydrogen. Using the ideal gas law, and assuming constant T and V, one obtains:

$$-\frac{dn}{dt} = -\frac{V}{RT} \cdot \frac{dP}{dt} = kP.$$

Including the RT in a constant, k', one obtains:

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

Integrating between limits, one obtains:

$$\log P_o/P = k't/2.3\ V$$

where V is the volume of hydrogen gas. A plot of log P_o/P versus t should give a straight line of slope m, and thus

$$k' = 2.3\ m\ V\ .$$

The constant, k', has the dimensions of volume per unit time; the units used in this work are liters per minute. When equilibrium amounts of catalyst are used, k' is divided by the catalyst weight to obtain $k_{l.0}$, the rate constant per gram of catalyst.

For some systems, the kinetics have been found to be first order in the compound undergoing reduction and zero order in hydrogen pressure:

$$\frac{dn}{dt} = - k\ c$$

where c is the concentration of acceptor in moles per liter. Also one has:

$$\frac{dn}{dt} = a \frac{dP}{dt}\ .$$

The factor a is given by V_g/bRT where V_g is the volume of hydrogen gas. For nitro compounds, b = 3 since one mole of nitro compound requires three moles of hydrogen for complete reduction. The value of n_o/a has the significance of being the hydrogen pressure drop for a reduction of n_o moles of a mononitro compound to a corresponding amine. Since $c = n/V_l$, where n is the moles of acceptor and V_l is the volume of solvent and acceptor, one obtains

$$\frac{dP}{dt} = - \frac{k}{a} \frac{n}{V_l}\ .$$

Since n is given by $n_o - a\Delta P = n_o - aP_o + aP$, where n_o is the initial number of moles of acceptor and ΔP is the pressure drop on the gauge, one obtains:

$$\frac{dP}{dt} = -\frac{kn_o}{aV_1} + \frac{P_o k}{V_1} - \frac{Pk}{V_1} .$$

Letting $B = -k/V_1$ and $C = \frac{k}{V_1}(P_o - \frac{n_o}{a})$, one obtains:

$$\frac{dP}{dt} = BP + C .$$

Integration and substitution of values for B and C given above:

$$\log (P + \frac{n_o}{a} - P_o) = -(k/2.3\ V_1)\ t + \log n_o/a .$$

A plot of the first term versus t should give a straight line of slope m and thus

$$k = -2.3\ m\ V_1 .$$

In some cases simultaneous first order reactions may occur as follows:

$$H_2 + aA \begin{matrix} \nearrow bB \\ \searrow cC \end{matrix} .$$

Letting a equal the initial concentration of hydrogen in moles per liter, x equal the moles of hydrogen used to form B at time t and y equal the moles of hydrogen used to form C at time t, the rate of decrease of hydrogen due to formation of B and of C respectively is given by the following:

$$\frac{-d(a-x)}{dt} = k_1(a-x-y) \qquad \frac{-d(a-y)}{dt} = k_2(a-x-y) .$$

Therefore

$$-\frac{d(a-x)}{dt} - \frac{d(a-y)}{dt} = (k_1 + k_2)(a-x-y)$$

and

$$\frac{dx}{dt} + \frac{dy}{dt} = k(a-x-y).$$

Integrating between limits,

$$\log \frac{a}{a-x-y} = kt/2.3$$

is obtained where k is the sum of the rate constants for the simultaneous reactions. This case applies if two groups in a reactant have been simultaneously activated by the catalyst and simultaneously attacked by hydrogen.

With some compounds containing two or more reducible groups, only one is initially activated and the reaction proceeds until essentially all of the group is reduced. Then a sudden change in rate occurs as the second group becomes activated and begins to undergo reduction. Reaction intermediates are thus formed and in some cases these can be isolated. The example of nitrobenzene giving rise to aniline as an intermediate is an important example of this type. In the present work the complete reduction of beta-nitrostyrene via several intermediates is a very interesting example.

3. Intermediate Order Mechanisms

In some cases the kinetics are not first order in hydrogen nor first order in acceptor but some intermediate order for a given pressure or concentration range. With two very different types of molecules each may be attracted by select portions of the catalyst surface and it is possible that the order would be intermediate with respect to both reactants.

All first order hydrogenation reactions will not follow the first order expression throughout the reaction because, as the concentration of acceptor is reduced, the rate can become a function of the acceptor concentration. The reaction would thus be slowed and give deviation from

the first order law.

From a consideration of the Langmuir equation, it would be expected that a reaction could be first order in hydrogen pressure at low pressures, and zero order at high pressures. Likewise the acceptor might be expected to follow the Langmuir equation as was found experimentally in the present work for some compounds. For the acceptors nitromesitylene and nitroethane, it was found that the reactions approached first order in acceptor at low concentrations and zero order in acceptor at high concentrations.

In the case of consecutive heterogeneous reactions, the usual mathematical treatment is not valid. For two consecutive reactions, it is possible that the two species will give intermediate orders for the individual rate constants and a very complex mathematic treatment would be required. If the second reaction is faster than the first, no intermediate can be isolated. The nitro group absorbs three moles of hydrogen when reduced to the amine group but intermediates have not been identified chemically for the hydrogenation reactions of some nitro compounds.

For fractional order reactions, an expression used to ascertain the order is obtained by integrating the rate expression for an "n"th order reaction:

$$\frac{dc}{dt} = - k\, c^n$$

to obtain:

$$\frac{1}{1-n} (c_1^{1-n} - c_0^{1-n}) = -k\, (t_1 - t_0).$$

For time t_2 and concentration c_2, the expression is

$$\frac{1}{1-n} (c_2^{1-n} - c_0^{1-n}) = -k\, (t_2 - t_0).$$

Dividing the first by the second integrated expression, one obtains:

$$\frac{c_1^{1-n} - c_0^{1-n}}{c_2^{1-n} - c_0^{1-n}} = \frac{t_1 - t_0}{t_2 - t_0} .$$

This equation gives the value for "n" when two concentrations and times are known.

D. Catalytic Hydrogenation of Nitro Compounds

The kinetic behavior of hydrogenation for nitro compounds in several catalyst-solvent systems has been previously elucidated.[16,17,18] The hydrogenation of nitrobenzene using the Adams platinum catalyst-acetic acid system is first order in hydrogen and zero order in acceptor. For nitroethane in the same system, the kinetics are reversed. For compounds with a nitro group conjugated with a double bond, the kinetics are the same as for nitrobenzene. On the basis of Langmuir kinetics, this has been interpreted in terms of the relative strengths of adsorption on platinum:

nitrobenzene or nitroolefin > hydrogen > nitroethane.

For nitromesitylene the kinetics were complex with an order intermediate between zero and first for acceptor and zero and first for hydrogen.

The kinetics for reduction of aliphatic and aromatic nitro compounds in a Raney nickel-ethanol system are first order in hydrogen and zero in acceptor. Similarly for reduction in the Adams platinum catalyst-ethanol system, the behavior is first order in hydrogen and zero order in acceptor.

The effects of some nitro compounds upon the exchange of acetic acid with deuterium over Adams platinum catalyst were studied.[19,20] The effects of these compounds upon the exchange rate paralleled their respective hydrogenation kinetics. The compounds which gave zero order kinetics for the acceptor in hydrogenation reactions (indicating strong adsorption) were the ones which prevented the exchange reaction in the same catalyst-solvent system. Other such correlations have been made and the exchange studies are useful for elucidating the hydrogenation kinetics.

E. Purpose of the Research

Deuterium exchange reactions have been made earlier using supported rhodium catalyst and acetic acid solvent.[21a]

Compounds studied were nitromesitylene, nitroethane, aniline, methyl ethyl ketoxime, 2-nitro-1-butene, nitrobenzene and beta-nitrostyrene. It was found that the first two gave an increase in exchange for low concentrations. The last four gave a decrease in exchange for all concentrations. The purpose of the present work is to elucidate the kinetics of hydrogenation of some of these compounds in the same catalyst-solvent system. Such kinetics coupled with the deuterium exchange data should give some knowledge about the mechanisms involved. Also in some cases information about the intermediates involved might be obtained directly from the nature of the hydrogenation plots and by direct isolation.

CHAPTER II

EXPERIMENTAL

A. Supported Rhodium Catalyst

A detailed review of the function of a catalyst support is given in the literature.[22] Some of the functions are that it may reduce shrinkage, give physical strength, prevent sintering of the catalyst by heat dissipation, take up catalyst poisons, and give increased activity per unit weight of catalyst used. Two important types of supported rhodium catalyst are 5 per cent rhodium on carbon and 5 per cent rhodium on alumina. The latter was used in this work.

Five per cent rhodium on alumina is effective for the reduction of many substituted aromatic and heterocyclic compounds and has been shown to be somewhat more active than 5 per cent platinum on alumina.[23] The activity of rhodium on asbestos appears to be about the same as platinum on asbestos.[24] It was found that with platinum, rhodium, iridium, ruthenium, and palladium catalysts, only the first two continued to catalyze the hydrogenation of benzene at high temperatures.

The mechanism for rhodium catalyzed reductions has been reported to be different from that with palladium. The rate of hydrogenation of nitrobenzene over colloidal rhodium was sensitive to the pH whereas over colloidal palladium it was not.[25] In addition, it was found that the rate of reduction over rhodium of nitro groups attached to aro-

matic rings was dependent upon the substitutents of the ring.*

There is previous evidence that 5 per cent rhodium on alumina is much more active per weight of metal than is Adams platinum catalyst.[26] Also in the present work, it was found that this supported rhodium catalyst gave a rate constant for the hydrogenation of 0.02 moles of benzoic acid in 50 ml. of acetic acid which was eight times greater (metal weight basis) than the constant obtained with commercial platinum catalyst. Both of these catalysts were obtained from Baker and Company, Inc., Newark, New Jersey. A summary of the values for $k_{1.0}$ (liters per minute per gram) in terms of total catalyst weight for several bottles of the same lot of supported rhodium and for two samples of Adams platinum catalyst is given below. In general, these rate constants were reproducible to 2 per cent or less.

Catalyst	$k_{1.0}$
5% Rhodium on alumina (Bottle 1, Lot 2473)	0.0241[a]
5% Rhodium on alumina (Bottle 2, Lot 2473)	0.0238[b]
5% Rhodium on alumina (Bottle 3, Lot 2473)	0.0242[c]
5% Rhodium on alumina (Earlier work)	0.0285[d]
Adams platinum catalyst (Standard)	0.1120[e]
Adams platinum catalyst (Commercial)	0.0536[f]

*Dr. P. H. Emmett in a private conversation has indicated that repetition of these experiments in his laboratory has not supported the original findings of Hernandez and Nord.[25]

[a]Average of seven determinations.

[b]Average of four determinations.

[c]Average of two determinations.[27]

[d]Average of two determinations.[26]

[e]Average of many determinations and adopted as standard.[28]

[f]Average of four determinations.

Since essentially the same rate constants were obtained with three different bottles of this commercial catalyst over a period of several months, it was concluded that a correction to a standard catalyst was unnecessary for the series of hydrogenations made in the present work.

B. Other Materials

1. Acetic Acid

E. I. du Pont c. p. glacial acetic acid was fractionated through an eight-foot Vigreux column. Constant boiling cuts were collected at reflux ratios of about 10:1. A typical cut boiled at 116.3° (constant) at 746.0 mm. Hg.

2. Benzoic Acid

Eastman white label benzoic acid was used without further purification.

3. Hydrogen

Commercial electrolytic hydrogen obtained from the National Cylinder Gas Company was used without further purification. This hydrogen has been shown to be satisfactory for catalytic hydrogenations.[33]

4. Nitrobenzene

Matheson, Coleman and Bell white label nitrobenzene was first steam-distilled and dried twice over anhydrous magnesium sulfate. It was then distilled *in vacuo* through a thirteen-foot helix-packed column equipped

with a total condensation, variable take-off head. The material was collected at a reflux ratio of 15:1. The pressure was regulated with a manostat using a modified magnetic relay as the flutter control. A typical cut boiled at 95.5° (constant) at 19 mm. Hg.

5. Nitroethane

Matheson, Coleman and Bell white label nitroethane was fractionated through a thirteen-foot helix-packed column, at a reflux ratio of 10:1. A typical cut boiled at 113.0-113.1° at 743.7 mm. Hg.

6. Nitromesitylene

Nitromesitylene was prepared by nitration of mesitylene as given in Organic Syntheses.[29] The crude product was treated with activated charcoal, and recrystallized three times from ethanol-water solutions to give a pale yellow crystalline material, m.p. 43.2-43.7° (reported 43-44°).[29]

7. beta-Nitrostyrene

beta-Nitrostyrene was prepared by the base-catalyzed condensation of benzaldehyde with nitromethane.[30] The crude compound was treated with activated charcoal and recrystallized three times from absolute ethanol, yielding a bright yellow material, with long needle-like crystals, m.p. 57.2-57.7° (reported 57-58°).[30]

8. 2-Nitro-1-butene

2-Nitro-1-butene was formed by warming 2-nitro-1-butyl acetate to split out acetic acid.[18] 2-Nitro-1-butyl acetate was synthesized by

esterification of 2-nitro-1-butanol with acetic acid. The 2-nitro-1-butanol, donated by Commercial Solvents Corporation, was distilled *in vacuo* from a 50-ml. flask, using a two-foot Vigreux column, to yield a clear, pale yellow liquid, b.p. 103.5-106.5°/8 mm. In a 1000-ml., round-bottom flask equipped with a water-cooled reflux condenser were placed 50 ml. of purified 2-nitro-1-butanol, 70 ml. of c.p. acetic anhydride, and 70 ml. of c.p. acetic acid. Upon addition of one drop of sulfuric acid the reaction began. The mixture was heated at reflux for one hour and while warm, water was added slowly to decompose the unreacted acetic anhydride. The mixture was cooled and 200 ml. of distilled water was added causing the ester layer to separate. The water layer was extracted with ether and the combined ester and ether solutions were placed in a 1000-ml., round-bottom flask equipped with a heating mantle, stirrer, and reflux condenser. Two hundred milliliters of 15 per cent sodium bicarbonate solution was slowly added to the flask through the condenser. The mixture was heated at reflux for about twenty minutes, after which time evolution of carbon dioxide had almost ceased. The organic layer was separated and the aqueous portion was extracted with ether. The combined ether extracts were steam distilled under the hood. The olefin, collected under sodium bicarbonate solution, was dissolved in ether and the solution was dried over anhydrous magnesium sulfate in a refrigerator overnight. After the magnesium sulfate was removed by filtration, the ether was allowed to evaporate yielding the crude nitroolefin. The olefin was purified by fractional distillation *in vacuo* in a two-foot Vigreux column to yield a bright yellow, oily liquid, b.p. 34°/9 mm., n_D^{20} 1.4381 (reported

60.8/46 mm., n_D^{20} 1.4382).[21b] 2-Nitro-1-butene is highly lachrymatory, and polymerizes readily. The product was stored in screw-cap bottles in the refrigerator, and was used soon after preparation. The compound was sent for analysis since a literature search did not reveal that the compound had been previously analyzed.

Anal.* Calcd. for $C_4H_7NO_2$: C, 47.49; H, 6.98; N, 13.85.
Found: C, 47.23; H, 6.97; N, 13.10.

9. Aniline

A sample of aniline previously fractionated by E. L. McDaniel[21b] was refractionated using a three-foot Vigreux column to yield a clear colorless liquid, b.p. 106.2-106.4°/59 mm., n_D^{20} 1.5860 (reported 101.9°/50 mm.,[31] n_D^{20} 1.586[32]).

C. Low-pressure Hydrogenations

1. Apparatus and Procedure

A low-pressure Parr apparatus containing certain modifications allowing more precision was used. The hydrogen pressure gauge was replaced with an Ashcroft testing gauge, which was graduated from 0 to 60 p.s.i. in subdivisions of one-fourth p.s.i. This permits a rough estimation to the nearest five-hundredths of a pound. The standard hydrogen tanks provided were replaced with smaller tanks so that small samples could be hydrogenated with a relatively large drop in pressure. The

*Analysis was made by Weiler and Strauss Microanalytical Laboratories, Oxford, England.

volumes, including reaction bottles and connections, of the two systems used were found to be 1.16 and 1.86 liters.

All rubber hose and stoppers on the apparatus were boiled in 20 per cent caustic solution to remove any catalyst poisons. Acetic acid attacks the rubber stopper and hose so that replacements are needed from time to time. The bottles were cleaned with warm chromic acid solution and rinsed ten times with tap water and ten times with distilled water. Steam cleaning was found to be unnecessary.

When the reaction rate was a function of concentration, the liquid acceptor and solvent were introduced into the reaction bottle by means of pipettes. Solid materials were weighed to the nearest 0.01 g. The solvent was added first and allowed to reach the temperature of the bath water; then the acceptor was added followed by the catalyst. This was followed by evacuation of the bottle and filling with hydrogen. It was found that the usual three evacuations and fillings of the bottle were not always adequate to prevent poisoning during a run. As a precautionary measure, the bottles were evacuated and filled with hydrogen at least five times. This procedure resulted in runs free from poisoning. Subsequently, the bath temperature, hydrogen reservoir temperature, atmospheric pressure and initial pressure were recorded. The shaking was begun, and pressure readings were recorded at one to five minute intervals. As the rate decreased, longer time intervals were taken. At the end of the reaction, the bottle was evacuated and removed from the apparatus. In order to prevent impurities from entering the apparatus while standing idle, a pipe cleaner was inserted into the hydrogen fitting

and the rubber stopper wrapped with absorbent tissue.

The initial hydrogen pressures for the hydrogenations were usually 60.0 p.s.i.g. except for the lower pressures used to study the effect of pressure. The changes in pressure during the course of the reaction were of the order of five to twenty pounds. The reaction bottle of the apparatus was enclosed in a metal jacket through which water from a constant temperature bath was circulated. The bath was usually maintained within 0.05° of the desired temperature. Early work indicated that 0.2° deviation gave a measurable change in the reaction rate constant. Runs were made at 20, 30 and 40° to determine the activation energies.

For most runs, shaking of the reaction mixture and timing began within five minutes after the vessel was filled with hydrogen. The amount of hydrogen uptake with no shaking was negligible. Several runs were delayed twenty minutes or more to check for leaks and the pressure change was usually less than 0.1 p.s.i. This was not due to leaks as indicated by a constant pressure at the conclusion of the reaction.

The catalyst weights used were generally from 0.02 to 0.30 g. The acceptor usually ranged from 0.5 to 2.0 g. for solids and 0.5 to 3.0 ml. for liquids. The majority of the runs were made with 1 ml. or 1 g. of acceptor and 50 ml. of glacial acetic acid.

2. Calibration

The general procedure for carrying out the hydrogenations was essentially the same as that described previously.[33] To calculate the rate constants for the hydrogenations, it was necessary to calibrate each apparatus by hydrogenating several weighed samples of benzoic acid, which

is known to absorb three moles of hydrogen per mole of acid. The pressure drop is related simply by the ideal gas law to the number of moles of benzoic acid, the volume of the apparatus, and the absolute temperature. A factor of "3" is needed since one mole of a nitro compound requires three moles of hydrogen.

Values of n_o/a, where $a = V_g/3RT$ as previously defined, were calculated for each compound for several temperatures so that it was possible to tell when three moles of hydrogen had been used for the hydrogenations. Where appropriate, other values of n_o/a were calculated for different numbers of moles of hydrogen so that other events could be ascertained.

At first it was thought necessary to allow for variation in catalyst activity for various samples of rhodium catalyst. However, as explained in a previous section, it was deemed unnecessary since three different samples of the same lot gave the same rate constant for the hydrogenation of benzoic acid in acetic acid.

For a given shaking rate the amount of catalyst can be varied over a limited range for which equilibrium exists and the rate of the reaction is then proportional to the catalyst weight. The shaking speeds used were 216 and 282 c.p.m. It has been found that the rate constants for several hydrogenations were virtually constant for shaking rates from 200 to 280 c.p.m.[26b]

3. Calculations

In order to obtain the rate constant for a reaction which is first order in hydrogen pressure, plots of log P versus time are made. From

the slope m, the rate constant is obtained:

$$k' = 2.3\ m\ V$$

where V is the volume of hydrogen in the system. When equilibrium weights of catalyst are used, this constant is divided by the catalyst weight to obtain $k_{1.0}$. All compounds used in this work gave good plots when first order dependence on hydrogen was assumed. Also the plots of ΔP/time versus pressure indicate that first order dependence on hydrogen is very nearly correct.

Other plots were made for some compounds assuming zero order behavior in hydrogen pressure and first order in acceptor, using the expression:

$$\log (P + n_o/a - P_o) = (k/2.3\ V_1) \cdot t + \log n_o/a$$

where the symbols have been previously defined in Chapter I. However, it was found that these plots showed a great deviation from linearity after 50 per cent reaction in the direction of increased rate. Since the first order plots were much better, first order dependence in hydrogen is more nearly correct.

The activation energies for the hydrogenation of the nitro compounds were calculated from the plots of log $k_{1.0}$ versus 1/T. The activation energy, E, is given by the following:

$$E = -\ 2.3\ m\ R$$

D. Identification of Intermediates and Products

Since the catalytic hydrogenations of the nitro compounds studied in this work have been previously reported in the literature, most of the amines formed when three moles of hydrogen was adsorbed were not isolated. When distinct breaks occurred in the plots, attempts were made to identify the intermediates, in most cases.

The nitrolic acid test for primary and secondary nitro compounds was useful to establish the presence or absence of the starting compound. The presence of oximes was indicated by addition of ferric chloride to give a reddish-orange solution. The presence of amines was shown by the odor of ammonia or an amine when alkali was added. Also direct isolation and identification of intermediates and products was made in some cases. Liquids were identified by their refractive index or boiling point and solids by their melting point.

CHAPTER III

RESULTS AND DISCUSSION

A. Nitrobenzene

The order of the reaction of the reduction of nitrobenzene (and the other nitro compounds) using the rhodium-acetic acid system was unknown at the outset of the work. To have equilibrium amounts of catalyst for the kinetic runs, preliminary runs were made using various amounts of catalyst. As can be seen from Figure 1, the catalyst weight for nitrobenzene should not exceed about 0.09 g. Figure 2 includes various concentrations of acceptor and it is seen that the reaction is zero order in acceptor for this concentration range.

First order dependence on hydrogen pressure is shown in Figure 2 for the pressure range 25 to 75 pounds (p.s.i.a.). The same kinetic results have been obtained for nitrobenzene in acetic acid using platinum catalyst.[16a] A typical plot of log P versus time for nitrobenzene at 30° is given in Figure 3. A plot showing the stepwise reduction is given in Figure 4. The nitro group is first reduced, followed by the ring. The intermediate aniline and end-product cyclohexylamine are obtainable in good yields. The stoichiometric point for complete reduction of the nitro group is shown in the figure.

An activation energy of 9330 calories per mole was obtained for reduction of the nitro group. This is rather high compared with 3700 calories per mole obtained using Adams platinum catalyst in acetic acid.[16b]

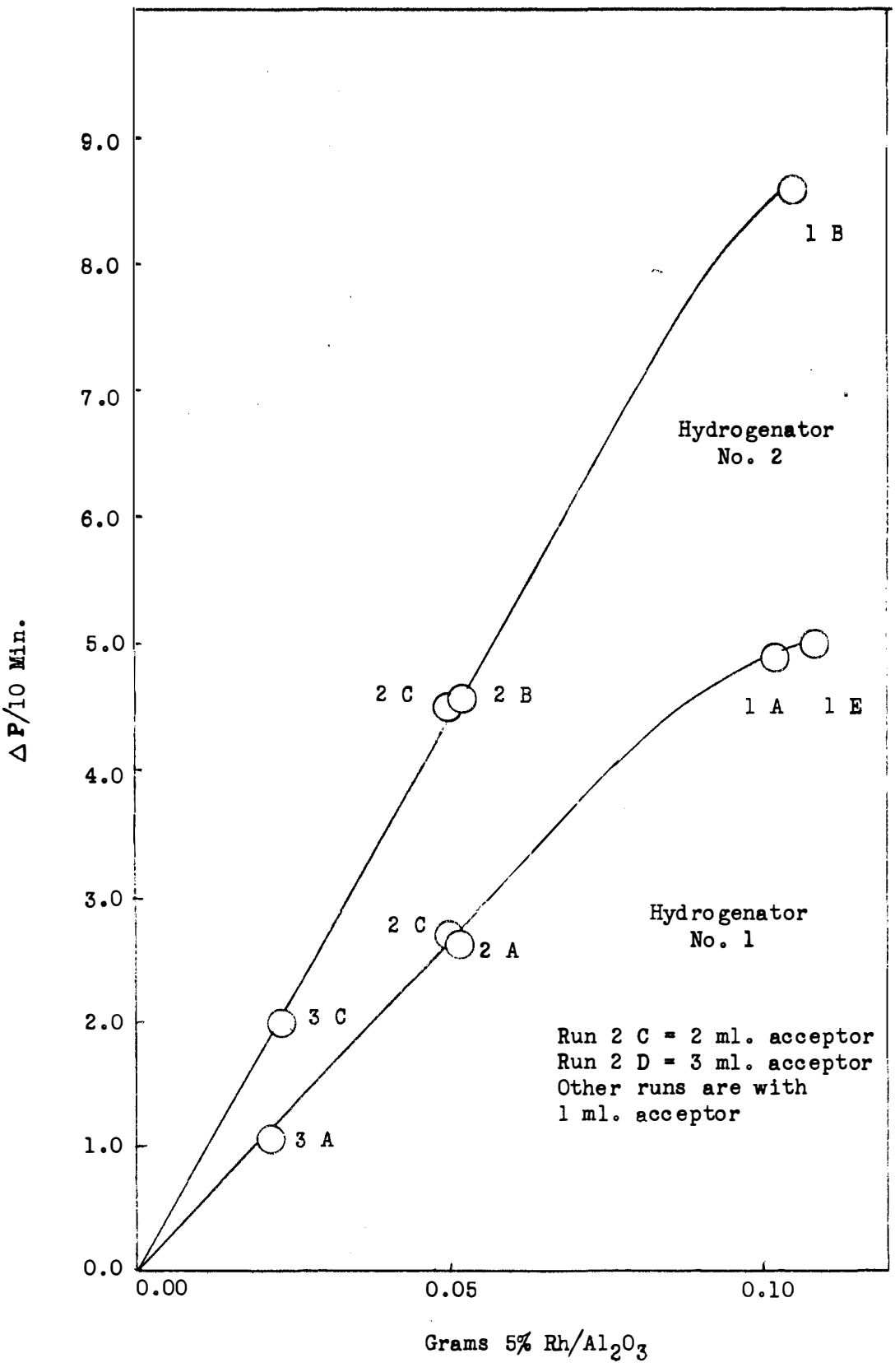


Figure 1. Plot of $\Delta P/10$ min. versus catalyst weight for hydrogenation of nitrobenzene in 50 ml. acetic acid at 30°.

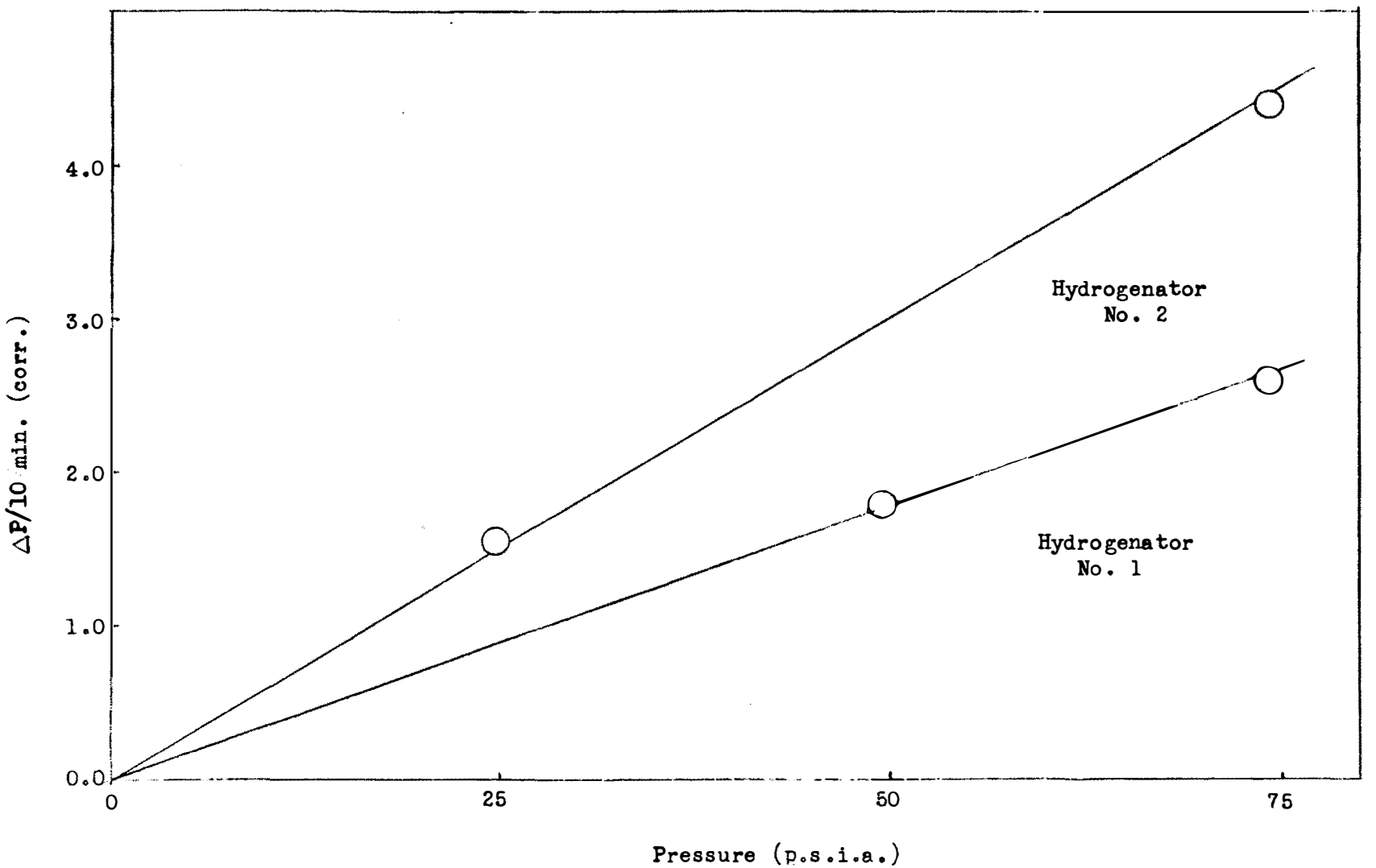


Figure 2. Plot of $\Delta P/10$ min. (corr.) versus p.s.i.a. for hydrogenation of nitrobenzene.

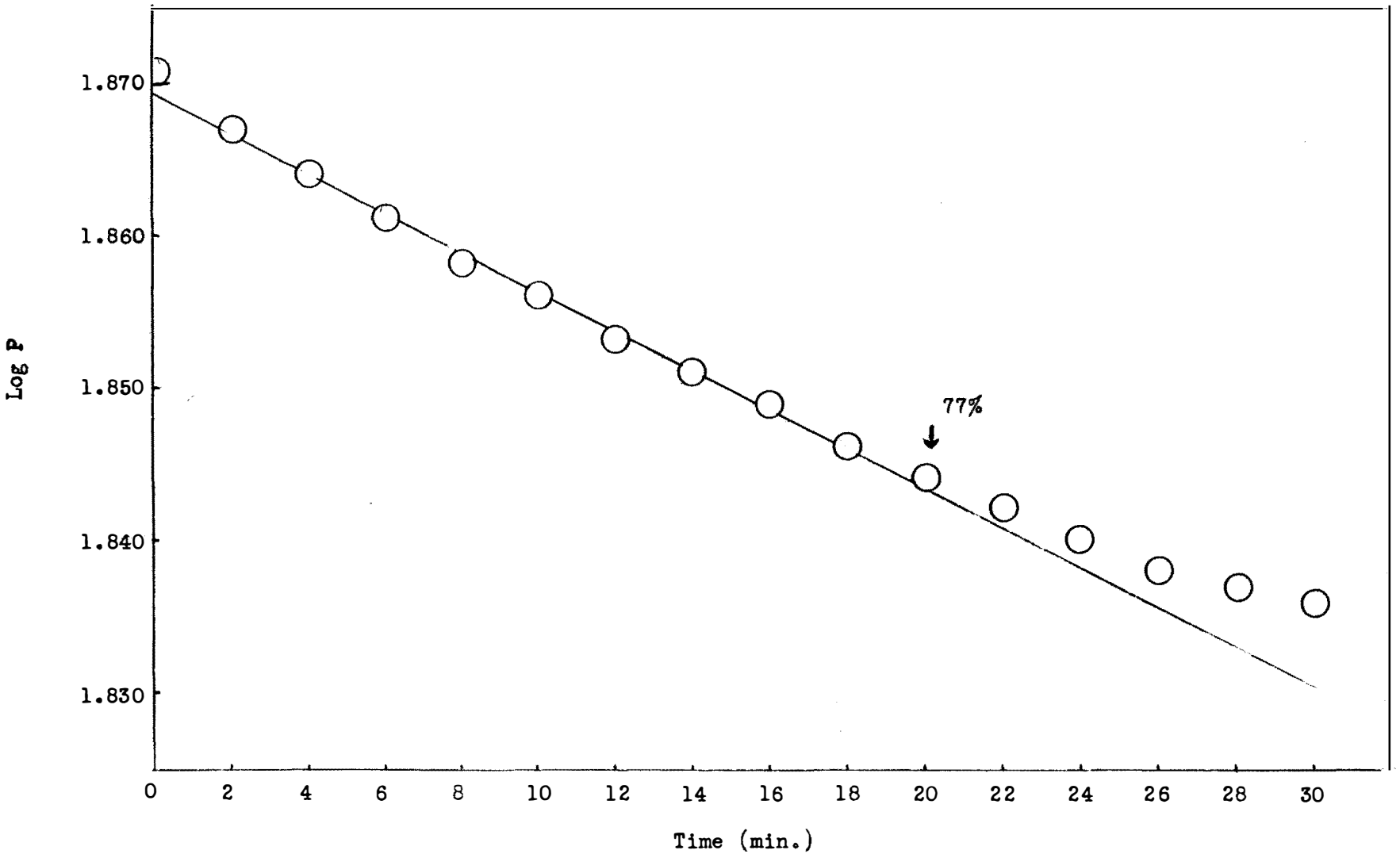


Figure 3. Plot of log P versus time for hydrogenation of nitrobenzene.

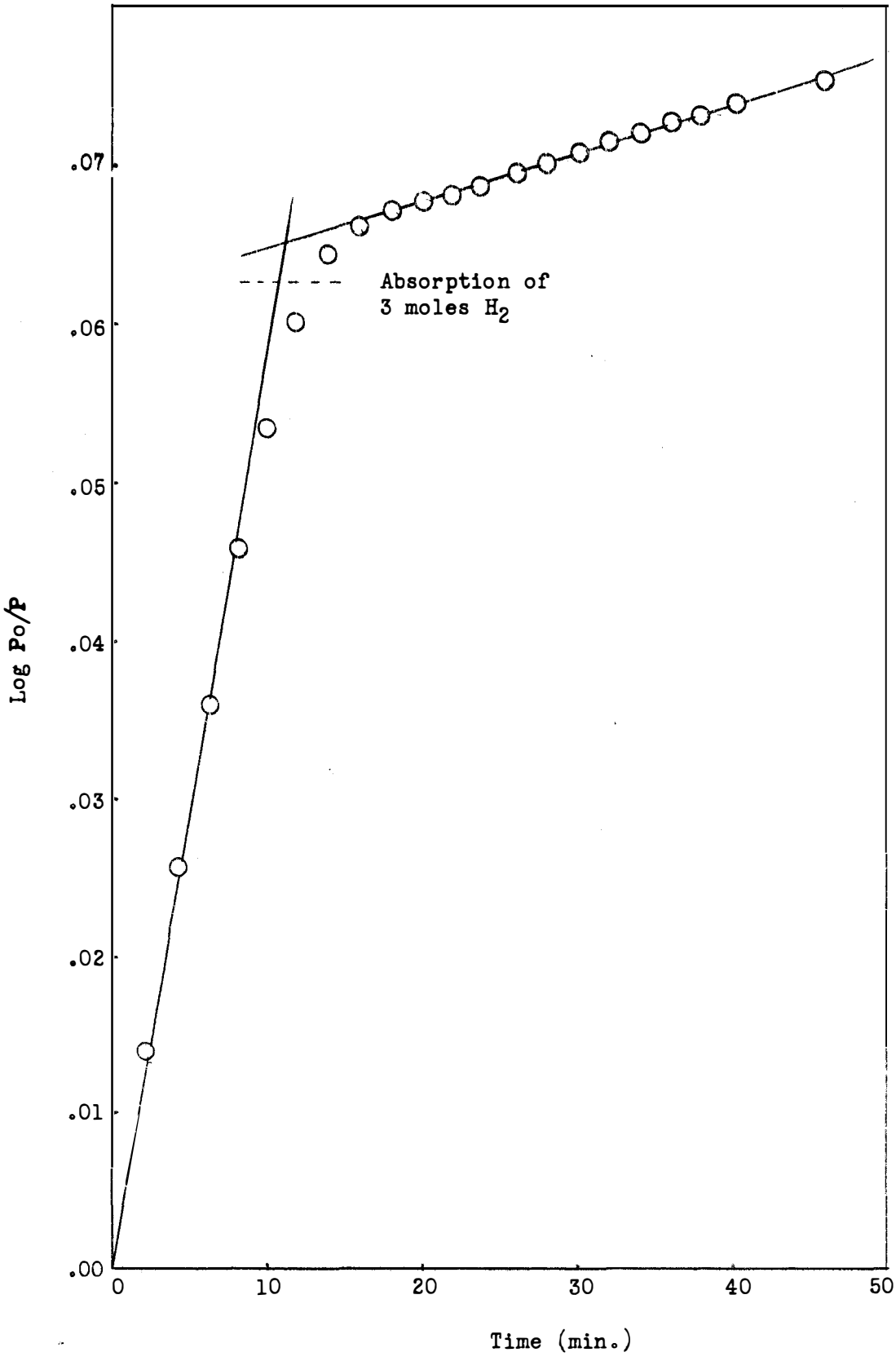


Figure 4. Plot of log Po/P versus time for hydrogenation of nitrobenzene.

With platinum the activation energy was low for nitrobenzene compared with other aromatic nitro compounds. The plot of $k_{1.0}$ *versus* 1/T is shown in Figure 5.

The rate constants for the hydrogenation of the nitro group are given in Table I. The average value for eleven runs is 0.115 liters $g.^{-1}$ $min.^{-1}$, which is rather high. This trend is paralleled by the platinum-acetic acid system kinetics with nitrobenzene; most of the other compounds studied previously gave lower rate constants.

It was noted that in runs using very low weights of catalyst, the kinetic plots showed more deviation from linearity. The formation of intermediates has not been definitely ruled out for the reduction of the nitro group in nitrobenzene, and the possibility that the deviations were due to some intermediates was considered. The most likely intermediates have been synthesized and hydrogenated, and the rate constants obtained indicated that the intermediates must not be involved.[34]

A hydrogenation of 10 ml. of nitrobenzene in 40 ml. of acetic acid using 0.10 g. of supported rhodium catalyst was carried out to attempt the isolation of any intermediates formed after two moles of hydrogen had been used. The solution after hydrogenation was filtered using a fritted funnel to remove the catalyst and pumped with a vacuum pump to remove acetic acid. When the acid had been removed, a bright yellow material identified as nitrobenzene came off. The remaining liquid was treated with sodium bicarbonate and ether extractions made. The ether extracts were dried with anhydrous magnesium sulfate and allowed to evaporate to give a dark red liquid. No solid substances were obtained.

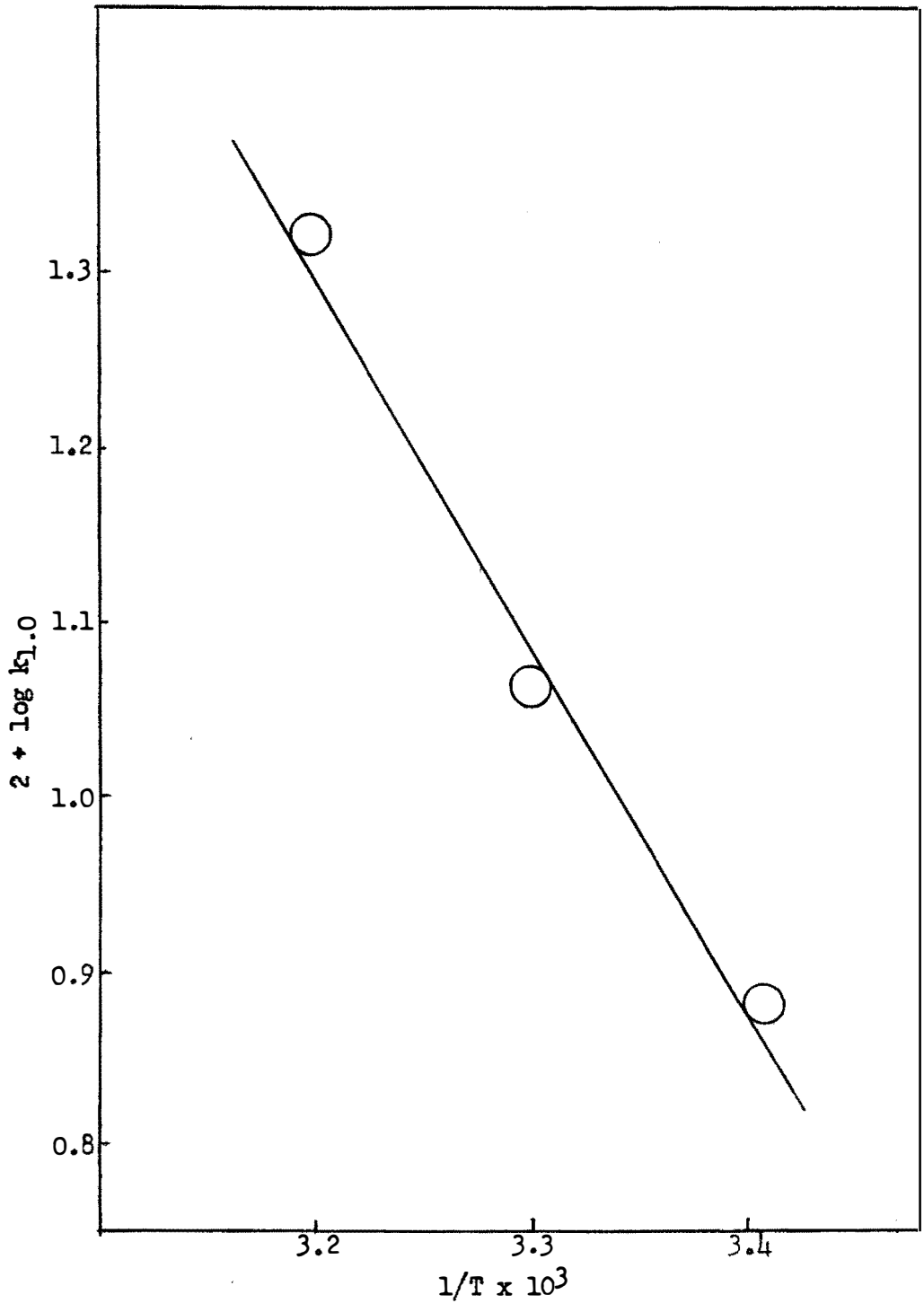


Figure 5. Activation energy plot for the hydrogenation of nitrobenzene.

TABLE I

HYDROGENATION OF NITROBENZENE OVER SUPPORTED RHODIUM

Weight of Catalyst	Initial Conc. (ml./ml.)	Initial Pressure (p.s.i.g.)	$k_{1.0}$ at 30° (l./g. min.)
0.1023	1/50	74.4	0.112
0.1023	1/50	74.4	0.132
0.1087	1/50	74.4	0.114
0.0510	1/50	74.3	0.115
0.0518	1/50	74.3	0.121
0.0500	2/50	74.4	0.117
0.0499	3/50	74.4	0.107
0.0496	1/50	49.4	0.126
0.0534	1/50	24.4	0.137
0.0215	1/50	74.4	0.103
0.0213	1/50	74.4	0.122
0.0223	1/50	74.4	0.095
0.0200	1/50	74.4	0.127

The red liquid was redissolved in ether and dry hydrogen chloride gas was passed through in order to precipitate the acid salt of any aniline or phenyl hydroxylamine present. A tan precipitate was obtained which after two washes with dry ether melted at 186°. After repeating the precipitation process using hydrogen chloride gas, a lighter tan compound was obtained which melted at 196° (reported for aniline hydrochloride, 198°).[35] No phenyl hydroxylamine was obtained. Only unreacted nitrobenzene and aniline were isolated. The red color of the liquid was probably due to the complex of nitrobenzene and aniline. Evidently the complex was destroyed in the presence of hydrogen chloride gas.

In previous work the presence of starting nitro compound using platinum in acetic acid has been shown by the nitrolic acid test.[16c] However the possibility of an addition complex intermediate has not been ruled out. Complexes formed between nitro compounds and amines are very common and some are very stable. Two physical properties of the nitrobenzene-aniline system that indicate the 1:1 compound are the freezing point and refractive index.[36]

The red color produced by nitrobenzene with aniline was probably due to the complex but it was not destroyed by the addition of acetic acid. Thus it seemed reasonable that the hydrogenation proceeded by way of the complex or by destruction of the complex after some aniline was produced by the reduction of the nitrobenzene. In some preliminary attempts to isolate the complex by vacuum distillation, it was found that the two components can be easily separated. However the distillate fractions were orange-red which might have been due to some complex. Ten milliliters of

fractionated aniline and 20 ml. of fractionated nitrobenzene were combined to give the complex plus excess nitrobenzene. This mixture was fractionated and a 10 ml. fraction boiling at 60.6-61.0°/5 mm. was collected. The color was almost the same as the original complex. However log P versus 1/T data were found to be identical with that for aniline. The next fraction boiled at 56.6°/1.2 mm. which checks for nitrobenzene. Continued fractionation yielded only nitrobenzene. Thus almost all of the complex must be destroyed at these temperatures.

A 1:1 molar mixture of aniline and nitrobenzene was hydrogenated using acetic acid and a small amount of supported rhodium catalyst. The plot shown in Figure 6 is essentially identical with the usual low catalyst weight runs with nitrobenzene. The initial slope was the same within experimental error as for the previous runs. Also the ratio of the first slope to the second was 1.70 which compares favorably with the average ratio (1.83) for six previous runs using about 0.02 g. of catalyst. The runs are listed in Table II.

The possibility that the departure from linearity was due to catalyst poisoning was investigated by interrupting a hydrogenation of 1 ml. of nitrobenzene in 50 ml. of acetic acid when 2.5 moles of hydrogen had been consumed. The catalyst was removed with a fritted funnel and fresh catalyst of exactly the same amount (0.0200 g.) was added to the mixture. The slope of the next portion of the hydrogenation plot thus obtained was identical with the slope of the previous portion as shown in Figure 7. Thus it is concluded that poisoning of the supported rhodium on alumina was very slight.

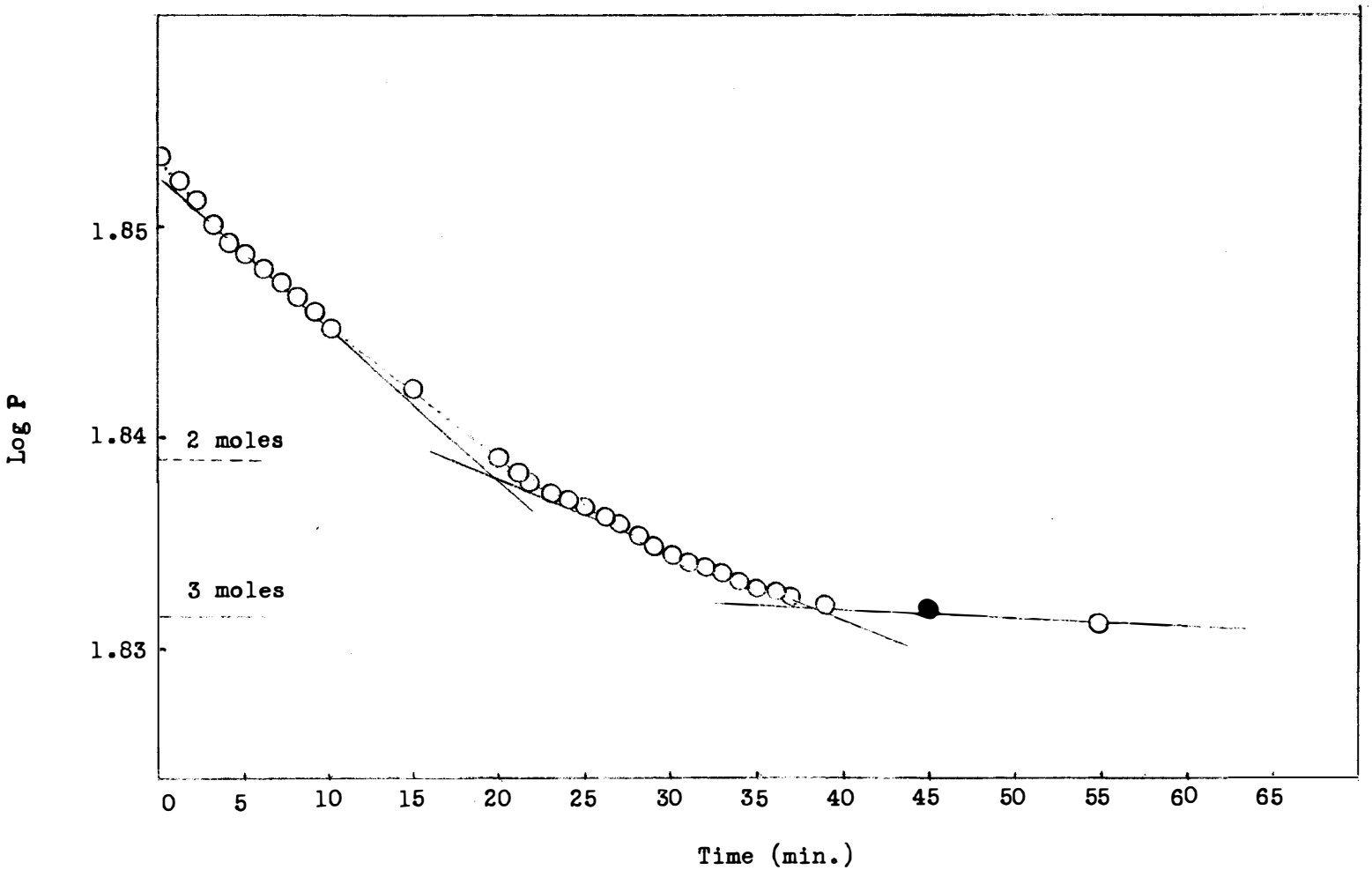


Figure 6. Plot of log P versus time for hydrogenation of nitrobenzene showing break points.

TABLE II

RATE CONSTANT RATIOS FOR NITROBENZENE HYDROGENATIONS AT 30° AND INITIAL PRESSURE OF 74.4 P.S.I.A.

Weight of Catalyst	Initial Conc. (Ml./Ml. of Solvent)	$\frac{k_{1.0'}}{k_{1.0}}$ [a]
0.0215	1/50	1.80
0.0213	1/50	1.77
0.0224	1/50	1.87
0.02	1/50	1.88
0.02	1/50	1.96
0.0200	1/50	1.72
	Average	1.83[b]

[a]Ratio of constant for first slope to constant for second slope.

[b]Standard deviation equals ± 0.08.

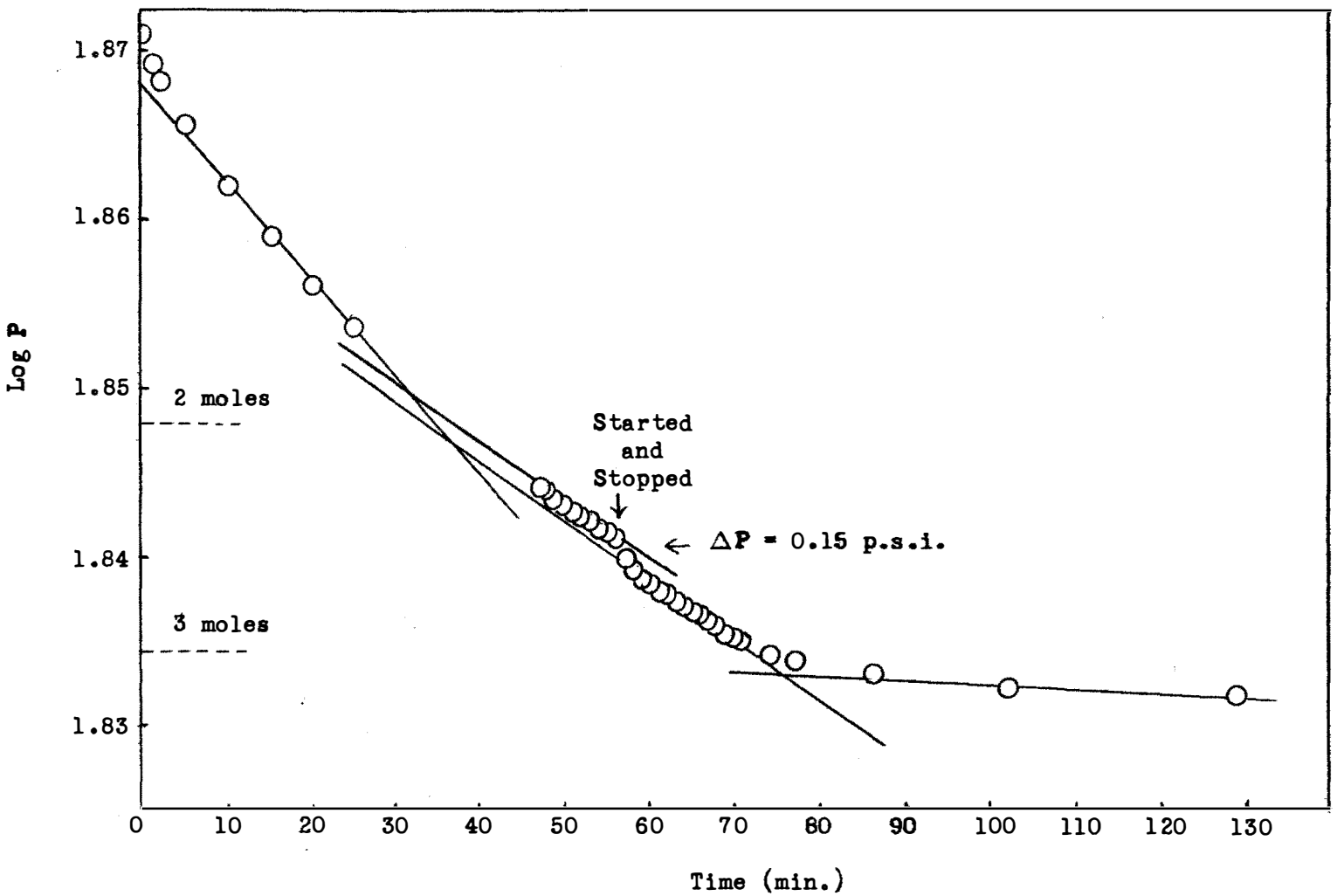


Figure 7. Plot of log P versus time showing lack of poisoning, for hydrogenation of nitrobenzene over supported rhodium.

The deviation from the initial linear portion of the kinetic plots might be due to a kinetic dependence of acceptor concentration under the conditions of the runs; namely, after formation *in situ* of aniline and/or addition complex. The fact that the preformed complex did not affect the kinetic plot is not conclusive evidence that the addition complex is not involved in the transition state. It is possible that the order of events involving the addition complex is important.

B. *beta*-Nitrostyrene

As shown in Figure 8 the weight of catalyst should not exceed about 0.07 g. Figure 8 includes various concentrations of acceptor and it is seen that the reaction is zero order in acceptor for this concentration range.

First order dependence on hydrogen pressure is shown in Figure 9 for the pressure range 24 to 74 pounds (p.s.i.a.). A typical plot of log P *versus* time for *beta*-nitrostyrene at 30° is given in Figure 10.

It was noted in the kinetic runs that the hydrogen uptake suddenly decreased when approximately two moles of hydrogen had been consumed. The average value at the break point for seven hydrogenations was two moles as shown in Table III. Thus it was concluded that an intermediate such as the oxime or hydroxylamine was involved.

A plot showing the stepwise reduction is given in Figure 11. The intermediate formed after two moles of hydrogen had been consumed was obtainable in good yield. The final reduction product, formed by the uptake of seven moles of hydrogen, was also obtainable in good yield.

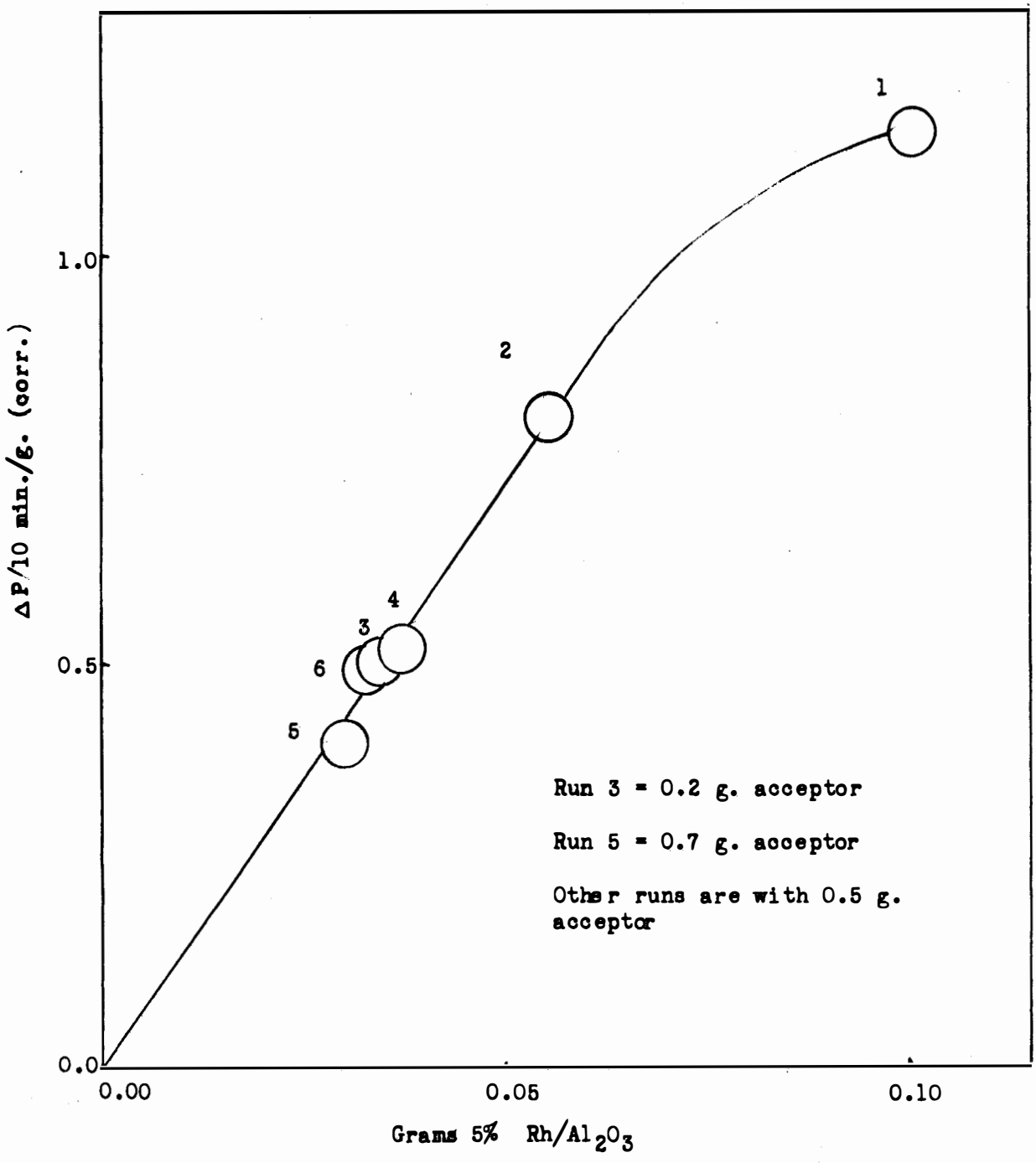


Figure 8. Plot of ΔP/10 min. (corr.) versus catalyst weight for hydrogenation of beta-nitrostyrene in 25 ml. acetic acid at 30°.

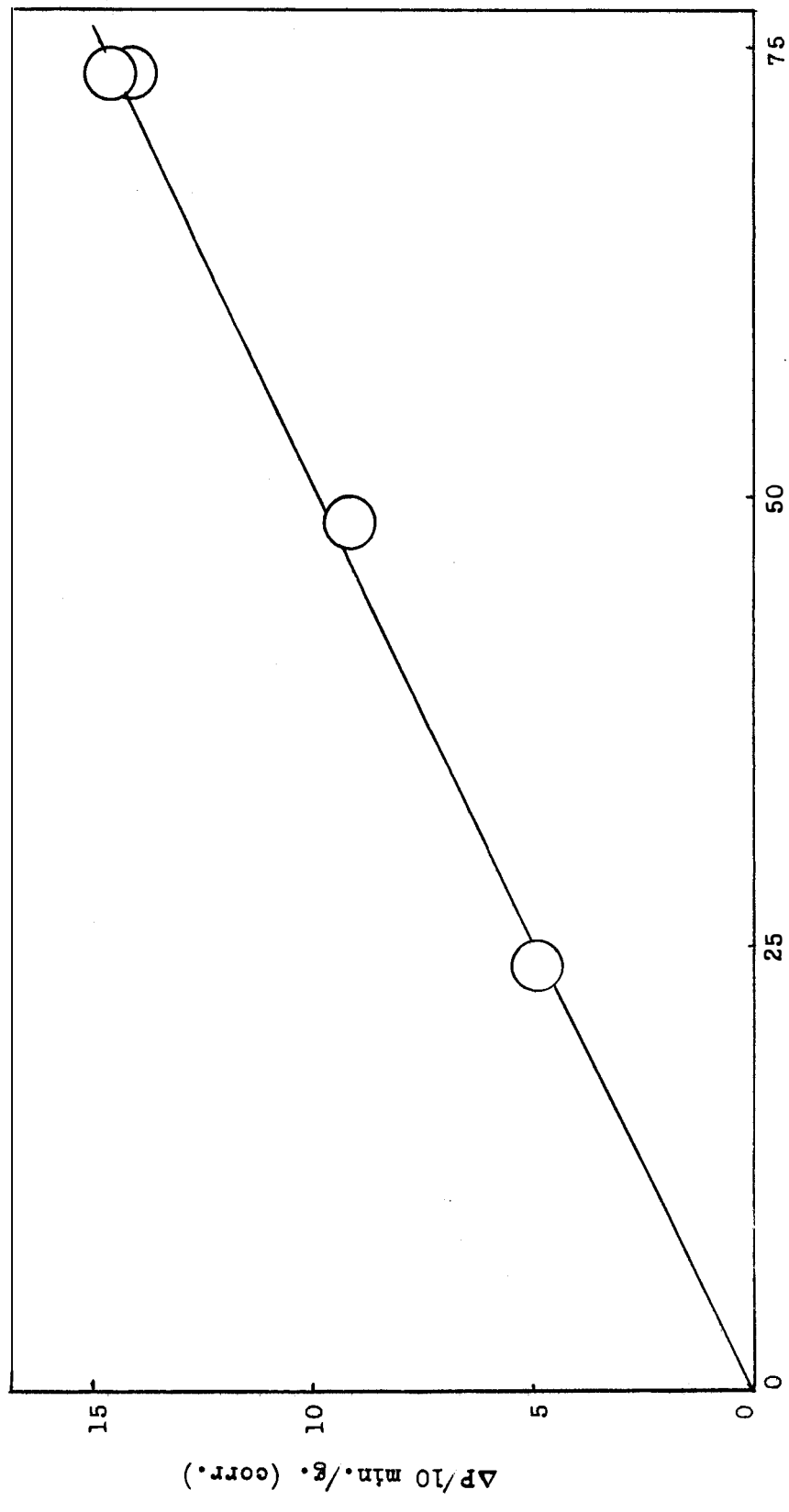


Figure 9. Plot of $\Delta P/10$ min./g. (corr.) versus p.s.i.a.

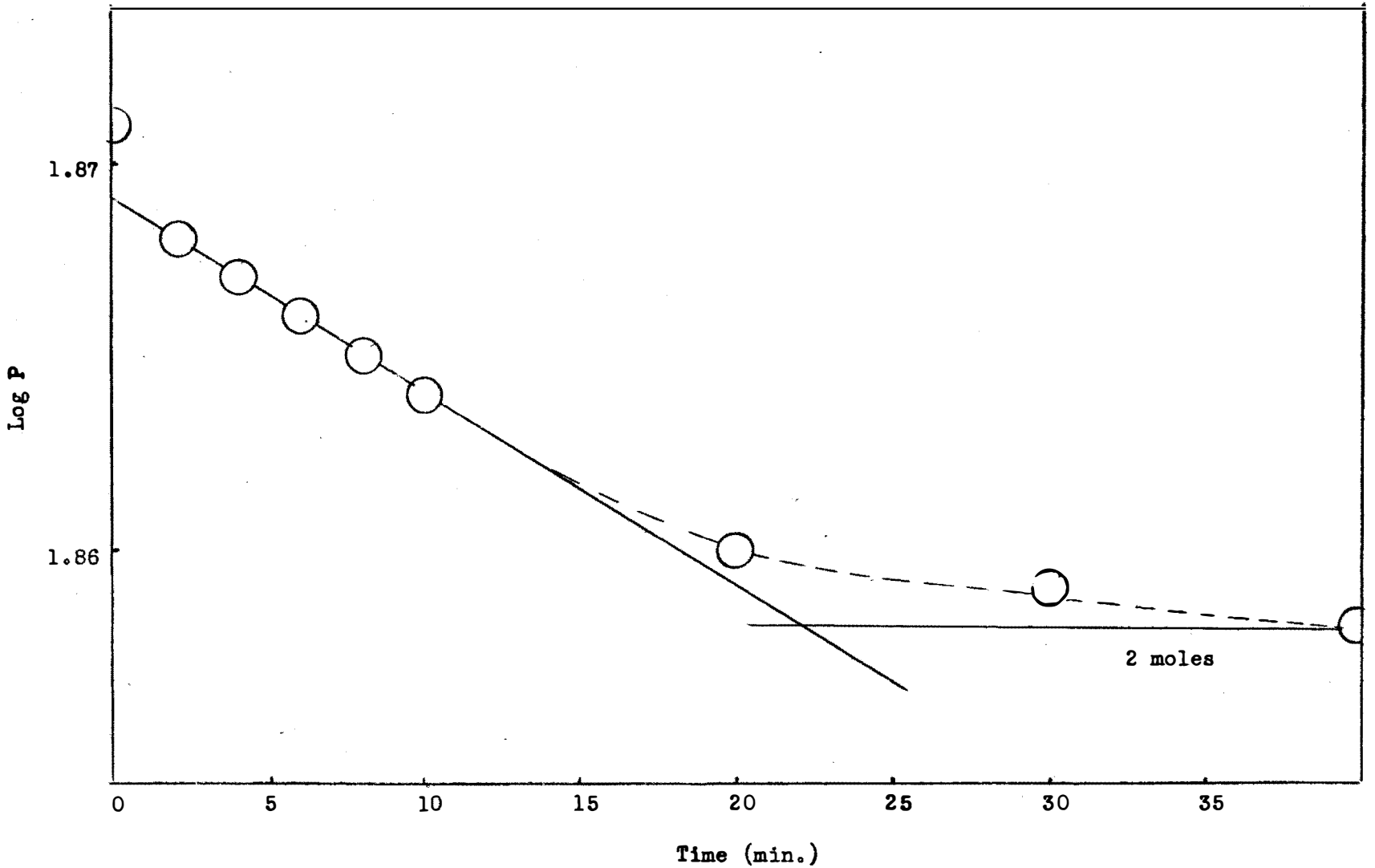


Figure 10. Plot of log P versus time for hydrogenation of beta-nitrostyrene showing break point at 2 moles of hydrogen.

TABLE III

MOLES OF HYDROGEN ADDED PER MOLE OF BETA-NITROSTYRENE AT FIRST BREAK POINT

ΔP at Break Point	Moles Hydrogen Per Mole beta-Nitrostyrene
1.35	2.0
2.15	2.0
0.60	2.3
1.95	1.8
1.25	1.9
Average	2.0[a]

[a]Standard deviation equals ± 0.17.

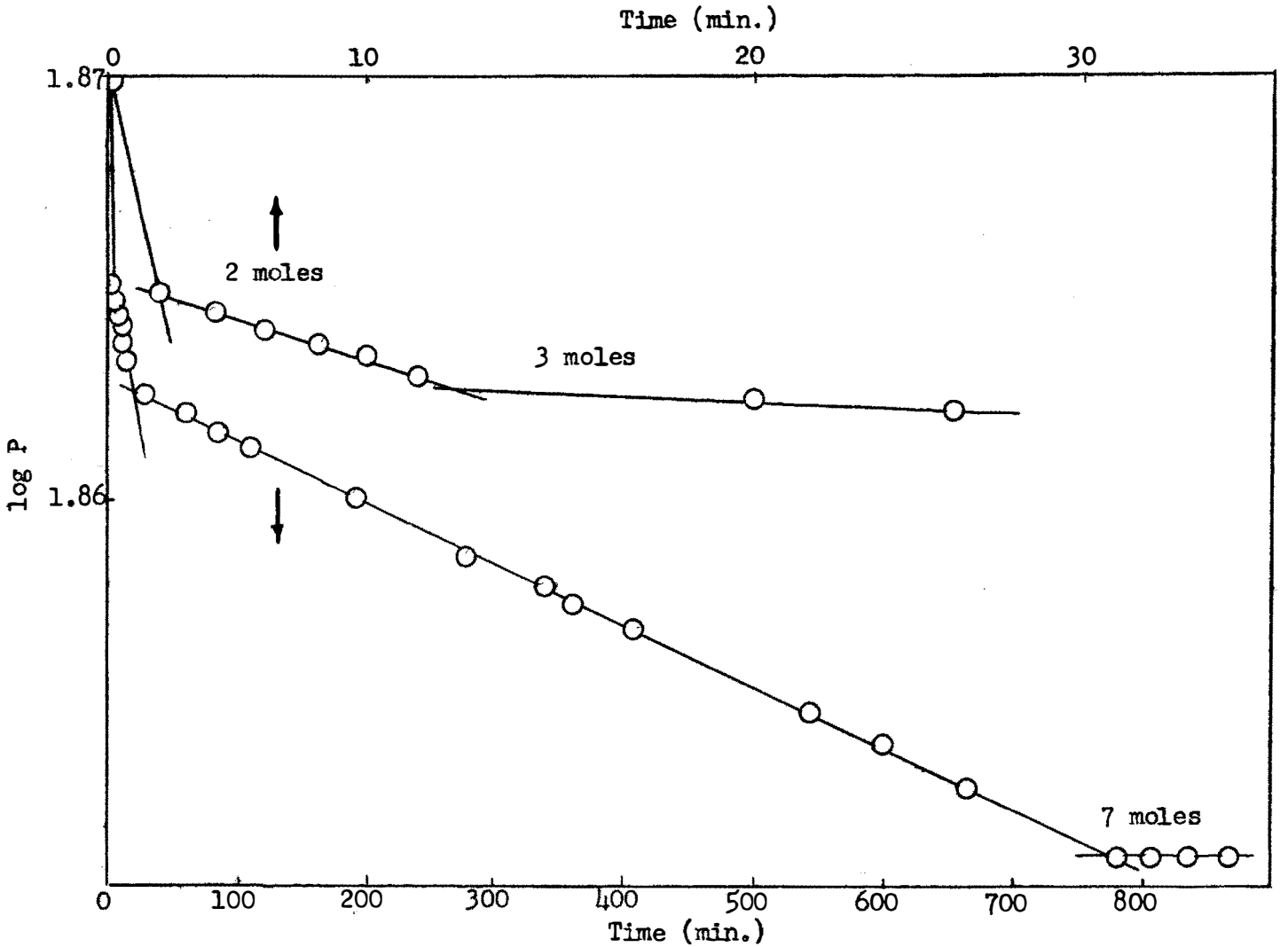


Figure 11. Plot of log P versus time for hydrogenation of beta-nitrostyrene showing break points at 2, 3 and 7 moles of hydrogen.

Three runs each using 0.5 g. of beta-nitrostyrene and 25 ml. of acetic acid were interrupted after two moles of hydrogen had been consumed and the solutions were combined. Chilling and filtration gave a small amount (less than 2 per cent) of the bimolecular reduction product (1,4-dinitro-2,3-diphenylbutane) reported earlier.[16d] The filtrate had an amine odor upon treatment with base and turned moist Alkacid test paper green. A dark brown resin was formed as has been previously observed. The melting point of the bimolecular reduction product was 242-243° (reported 242.5-243°).[16d]

One run using 1.00 g. of compound and 25 ml. of acetic acid was interrupted at two moles of hydrogen. The acetic acid was pumped off while warming. Only the bimolecular product and an amber oil could be obtained. The acid solution after the reduction was very intensely colored suggesting a carbonium ion. It was found that one very small crystal of beta-nitrostyrene dissolved in 5 ml. of 100 per cent sulfuric acid gave an intense yellow color. The sulfuric acid solution was poured into cold water to give a tan precipitate which had a melting point of about 140°. This does not suggest any compound known to be related to beta-nitrostyrene.

One run using 2.00 g. of beta-nitrostyrene and 25 ml. of acetic acid was interrupted at 1.86 moles of hydrogen. The solution was chilled and filtered to give 0.10 g. of the bimolecular reduction compound. The filtrate was poured into cold water to give a greenish-brown solution. Ether extracts were combined, dried over anhydrous potassium carbonate, and evaporated to give 1.40 g. of a yellow-brown crystalline mass which, after

several recrystallizations from aqueous ethanol, melted at 94-95°. The melting point of the oxime has been reported as 87.5°[16d] and 97°.[38] The compound gave a red color with ferric chloride. Thus the product was very probably the oxime. The original compound was present to a slight extent as shown by the characteristic odor.

Evaporation of the ethanol mother liquors gave a light yellow oil which crystallized to give white plates plus some yellow oil. The combined plates and oil weighed 0.3 g.; separation was not attempted. A summary of the results for this isolation is given below:

Compound	Amount Obtained	Theoretical
beta-Nitrostyrene	Not weighed	0.13 g.
Oxime derivative	Slightly less than 1.7 g.	1.60 g.
Bimolecular compound	0.10 g.	- - -

The theoretical amounts above are corrected for the bimolecular reduction compound actually obtained. No amine was obtained or indicated in this isolation procedure. The important thing is that the oxime compound can be obtained in very good yield, indicating that most of the nitro compound does give the intermediate in a stepwise reduction.

A comparison of several isolation runs indicates that more bimolecular compound is favored at higher concentrations of beta-nitrostyrene. This would be expected since the probability of this bimolecular reaction is increased.

One run using 0.20 g. of the nitro compound in 25 ml. of acetic acid was taken to completion to yield 0.12 g. of amber oil having a boiling point of 185° as determined by the Siwoloboff micro boiling point method

(reported for beta-cyclohexylethylamine, 188-189°).[37] This represents a 71 per cent yield. No other products were obtained. The bimolecular product was not obtained upon filtration. However the 29 per cent loss actually represents less than 0.04 milliliters. The isolation was made by pumping off the acetic acid, treating the residue with concentrated sodium hydroxide, extracting the solution with ether, drying the extracts with potassium carbonate, and evaporating the ether. No products were indicated upon evaporation of the aqueous portions.

The following steps are suggested for the main reaction to give the completely reduced compound:

$$C_6H_5CH{=}CH{-}NO_2 \xrightarrow{2H_2} C_6H_5CH_2{-}CH{=}NOH$$

$$C_6H_5CH_2CH{=}NOH \xrightarrow{1H_2} C_6H_5CH_2CH_2NHOH$$

$$C_6H_5CH_2CH_2NHOH \xrightarrow{4H_2} C_6H_{11}CH_2CH_2NH_2$$

The reduction of the oxime is very slow, and the reduction of the ring is even slower. As shown in Figure 11, the uptake of four moles of hydrogen, after the initial fast uptake of two moles and slow uptake of one mole, occurs at about the same rate. No hydroxylamine, however, was indicated in this work. Further study may show that it is formed.

A summary of some rate constants is given in Table IV. The average value of the rate constant for an initial pressure of about 74 p.s.i.a. using a concentration of 0.5 g./25 ml. is 0.0824 l. min.$^{-1}$ g.$^{-1}$. A plot of log $k_{1.0}$ versus $1/T$ is shown in Figure 12. The apparent activation energy is 9,150 cal./mole.

TABLE IV

HYDROGENATION OF BETA-NITROSTYRENE OVER SUPPORTED RHODIUM

Weight of Catalyst	Initial Conc. (g./ml. of Solvent)	Initial Pressure (p.s.i.a.)	$k_{1.0}$ at 30° (l./min./g.)
0.0507	0.50/25	74.3	0.0832
0.0573	0.53/25	74.0	0.0817
0.0378	0.48/25	74.0	0.0823
0.0394	0.45/25	49.7	0.0932
0.0520	0.47/25	24.6	0.106

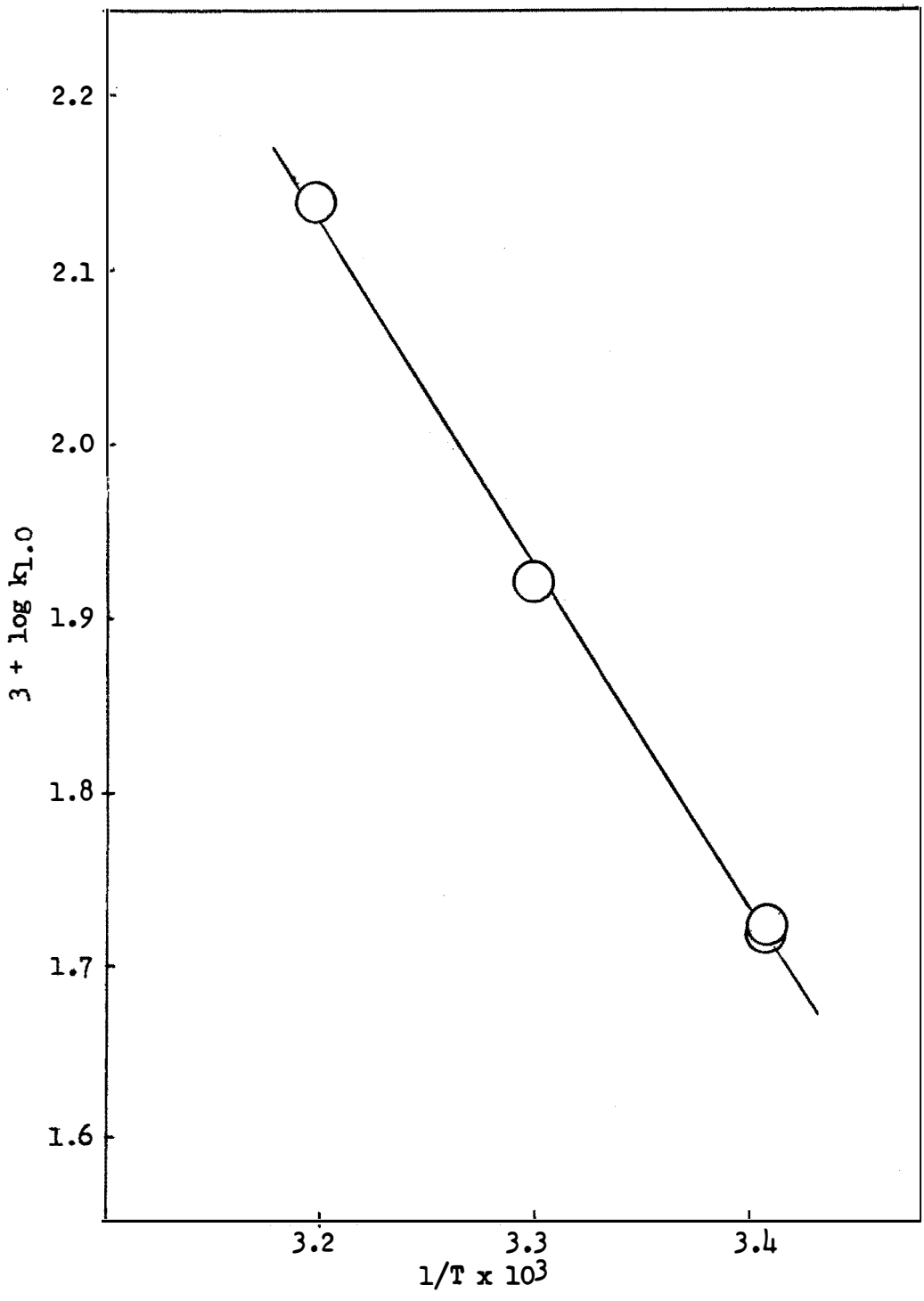


Figure 12. Activation energy plot for the hydrogenation of beta-nitrostyrene.

C. Nitroethane

In early runs the data for nitroethane were plotted as zero order in hydrogen pressure and first order in acceptor concentration. The rate constants thus obtained, when plotted versus catalyst weight, gave a deviation from linearity. When the reaction was treated as first order in hydrogen and zero order in acceptor, good kinetic plots were obtained for the initial portion of the curve.

Figures 13 and 17 show the effect of catalyst weight up to 0.3 g. Equilibrium conditions are present below this weight. The effect of initial pressure is shown in Figure 14. The hydrogenation of nitroethane in acetic acid using supported rhodium is first order in hydrogen pressure. As shown in Figure 15 the reaction approaches first order in nitroethane concentration at low concentrations and zero order at higher concentrations.

A typical plot of log P versus time is shown in Figure 16. The deviation at about 40 per cent reduction of the nitro group may be due to the first order dependence of nitroethane at low concentrations. Also it is possible that an intermediate is involved. A tabulation of runs at 74.3 p.s.i.a. initial pressure and 30° is shown in Table V. The rate constants for first order hydrogen dependence in terms of unit quantities of catalyst ($k_{1.0}$) are rather good and show that there is a dependence on the acceptor concentration. This dependence is also shown very well in Figure 17 where the rate constant, k (cc. $min.^{-1}$) is plotted against catalyst weight.

The activation energy for the hydrogenation of nitroethane using the rhodium-acetic acid system is 10,300 cal./mole. The plot is shown

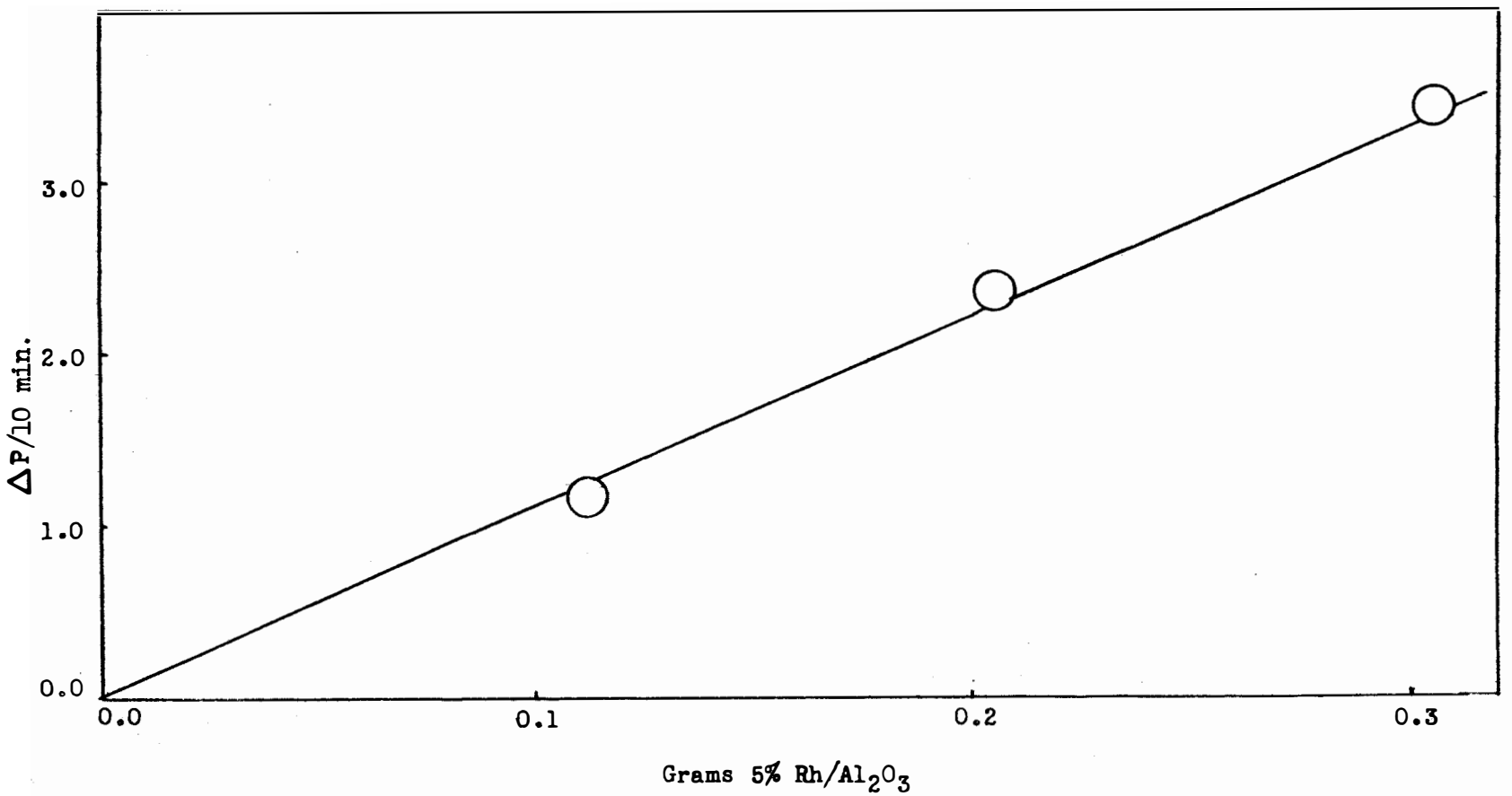


Figure 13. Plot of △P/10 min. versus catalyst weight for hydrogenation of nitroethane.

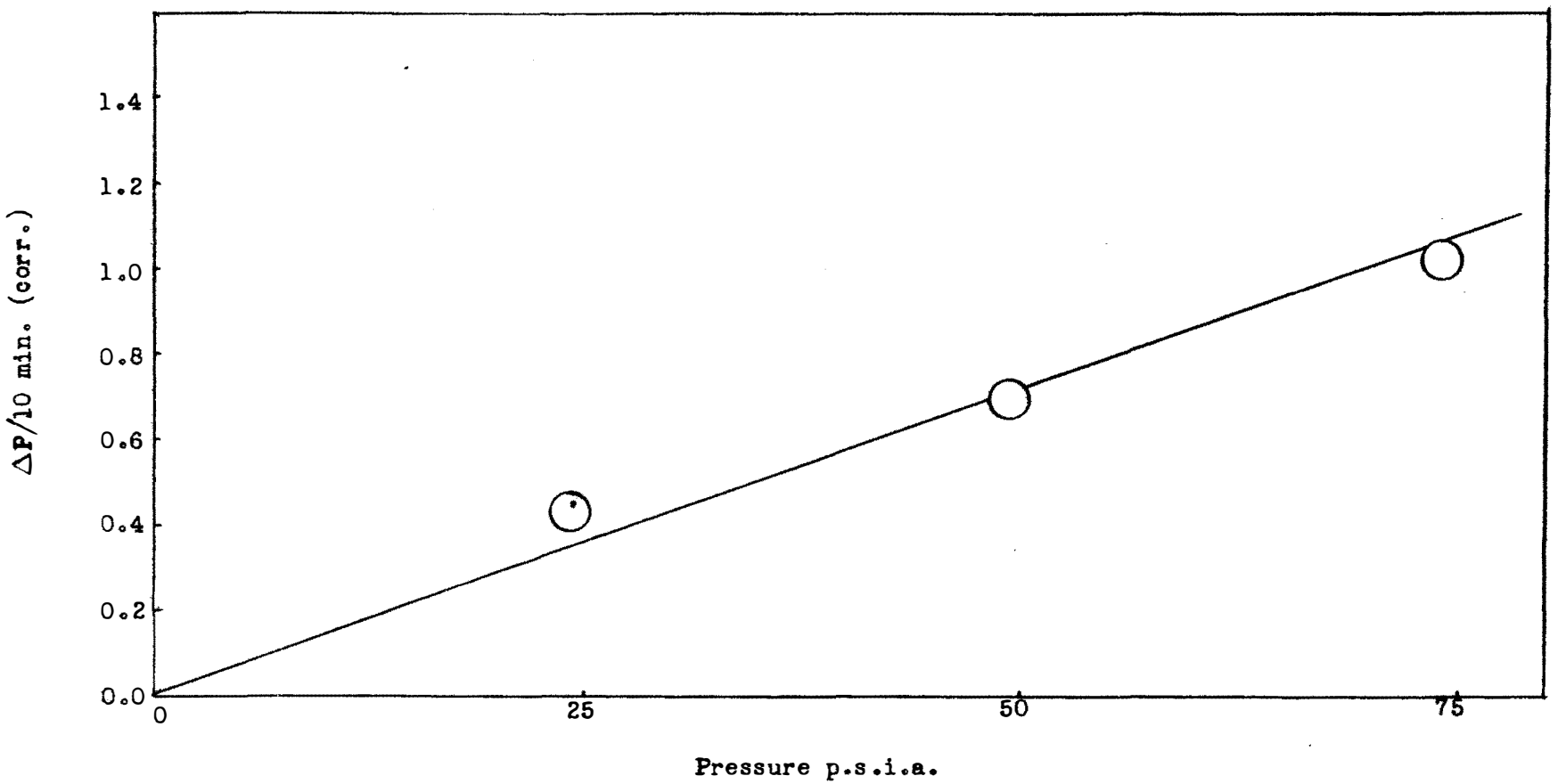


Figure 14. Plot of ΔP/10 min. (corr.) p.s.i.a. for hydrogenation of nitroethane.

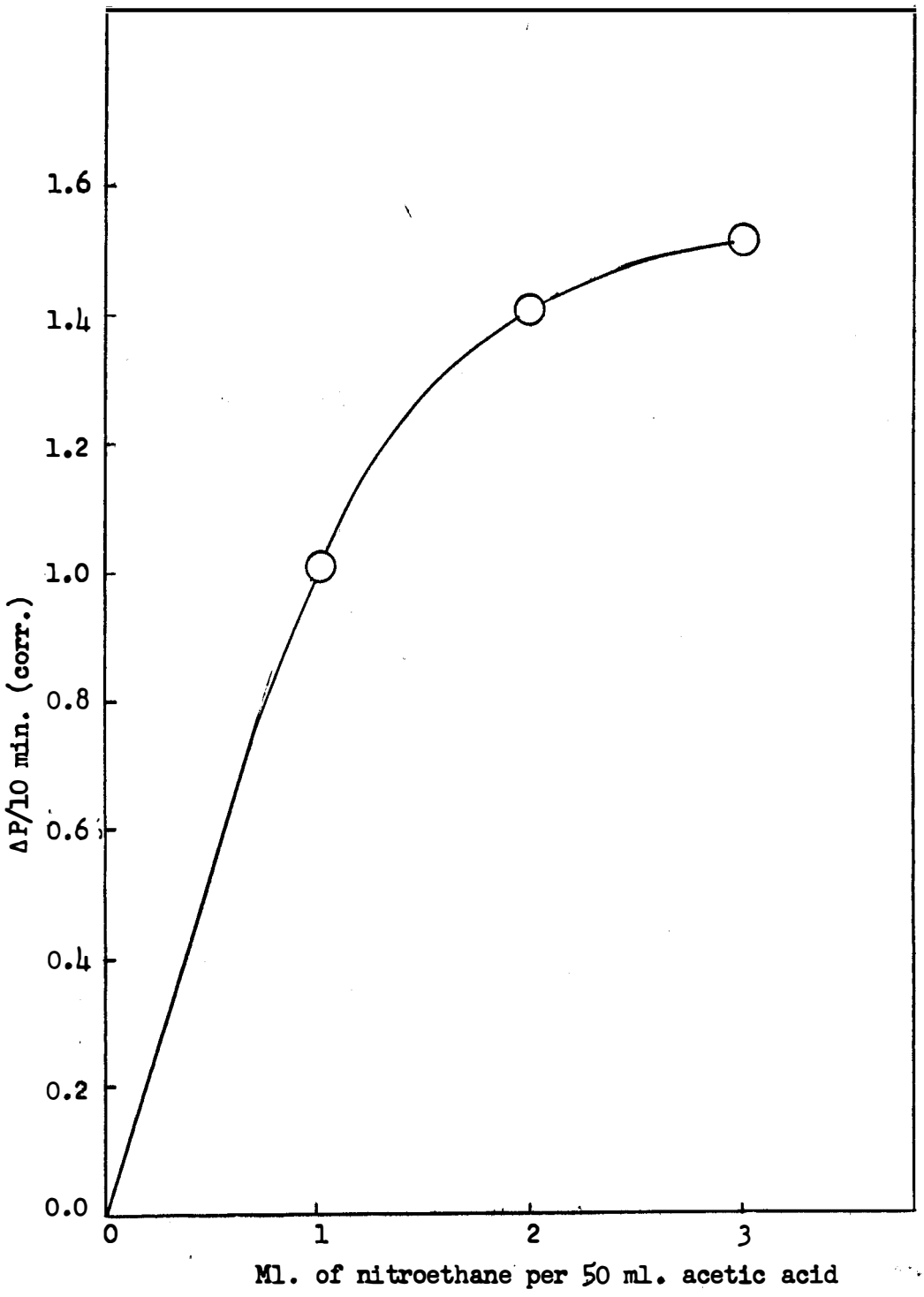


Figure 15. Plot of ΔP/10 min. (corr.) versus concentration of nitroethane.

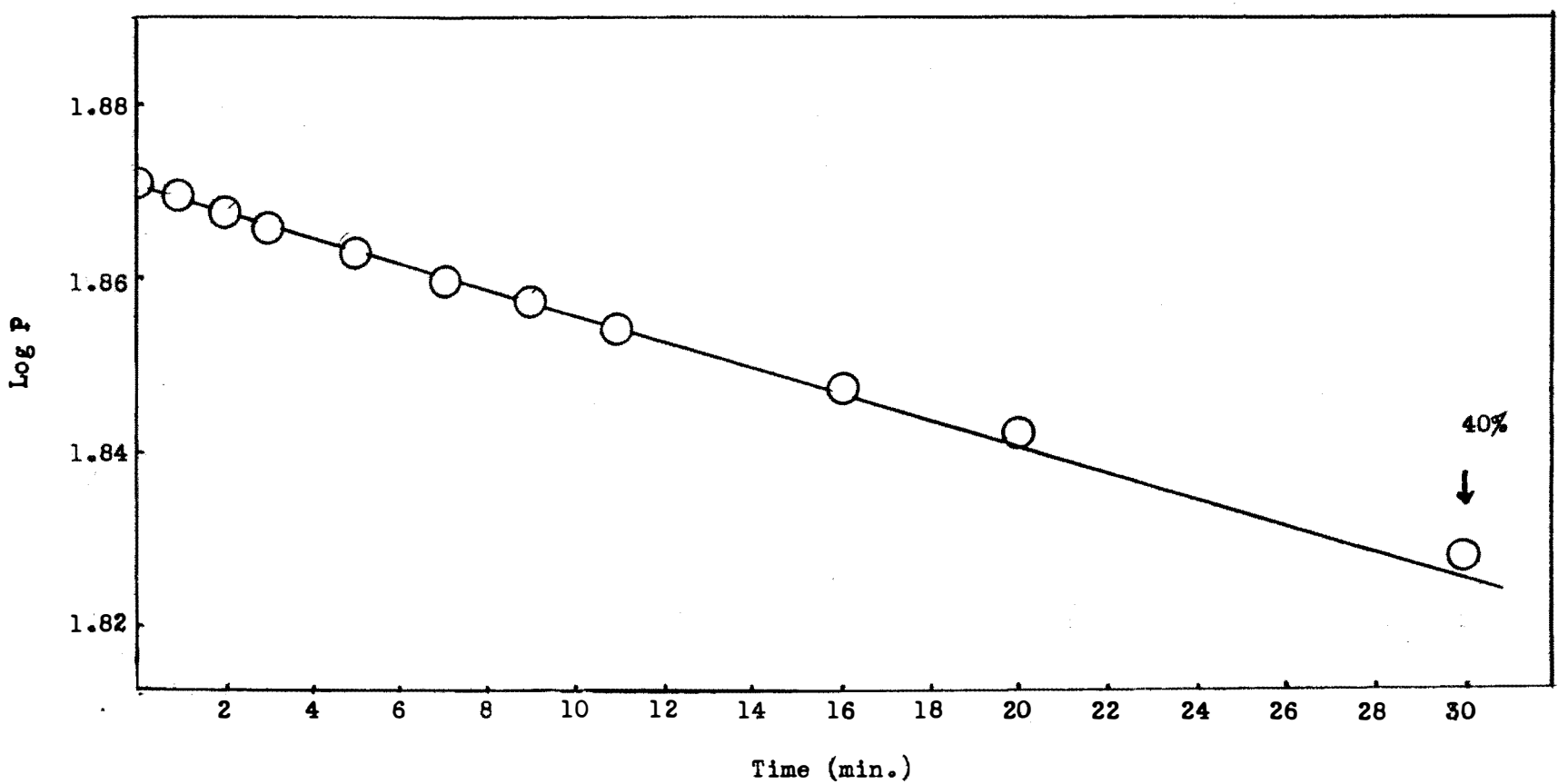


Figure 16. Plot of log P versus time for hydrogenation of nitroethane.

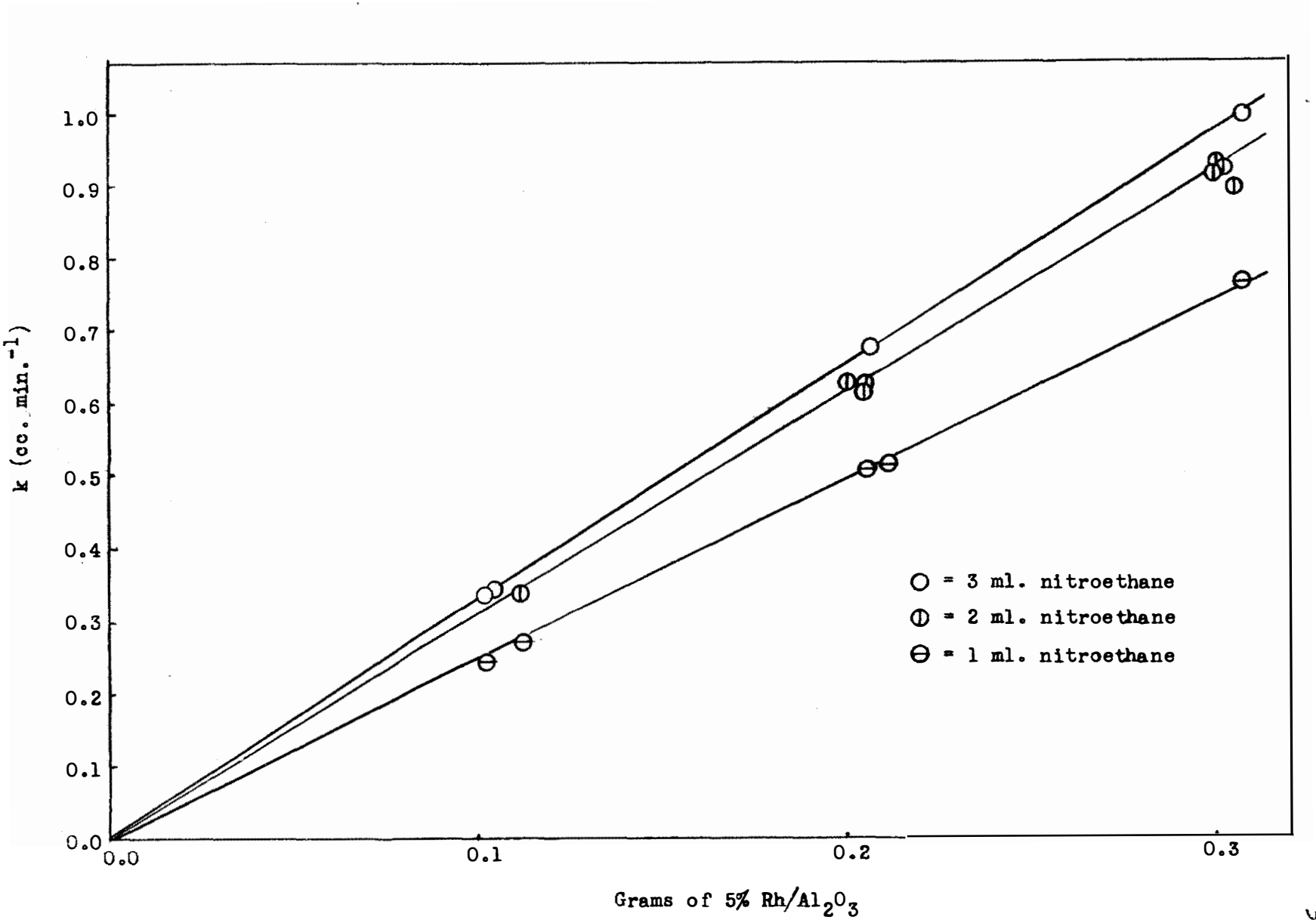


Figure 17. Plot of rate constant, k, versus catalyst weight for hydrogenation of nitroethane.

TABLE V

HYDROGENATION OF NITROETHANE OVER SUPPORTED RHODIUM CATALYST AT INITIAL PRESSURE OF 74.3 P.S.I.A.

Weight of Catalyst (g.)	Initial Conc. (ml./ml. Solvent)	k (cc./min.)	$k_{1.0}$ (l/min. g.)
0.1124	1/50	0.266	0.0237
0.1031	1/50	0.242	0.0235
0.2059	1/50	0.506	0.0246
0.2117	1/50	0.514	0.0243
0.3062	1/50	0.772	0.0252
0.1128	2/50	0.346	0.0306
0.2045	2/50	0.615	0.0301
0.1999	2/50	0.636	0.0318
0.2063	2/50	0.625	0.0303
0.2998	2/50	0.918	0.0306
0.3054	2/50	0.895	0.0293
0.3013	2/50	0.924	0.0309
0.3007	2/50	0.938	0.0311
0.1014	3/50	0.334	0.0329
0.1022	3/50	0.342	0.0334
0.2067	3/50	0.673	0.0325
0.3073	3/50	0.995	0.0324

in Figure 18. For the platinum-acetic acid system the apparent activation energy for nitroethane reduction is extremely high compared with other nitro compounds, whereas in the present work the value is intermediate with respect to those for the other nitro compounds studied. Also the kinetics are just reversed in the case of the reaction of nitroethane in the platinum-acetic acid system.

In Figure 19 is shown a kinetic plot for data carried beyond absorption of two moles of hydrogen per mole of acceptor. The deviation from the initial straight portion could be due to either a change in dependence for nitroethane (from zero to first order) or it could be due to a reaction intermediate. The nitrolic acid test for a primary nitro compound was negative for another run taken to 88 per cent reduction of the nitro group. Also no oil was indicated when the solution was poured into cold water. Treatment with ferric chloride gave an orange-red color indicating the presence of an oxime. Isolation and identification experiments were not made.

D. Nitromesitylene

The equilibrium amount of catalyst for the reduction of nitromesitylene can be as high as 0.1 g. as shown in Figure 20. The reaction is approximately first order in hydrogen pressure as shown in Table VI. Similar to the nitroethane reaction, this reaction becomes first order in acceptor at low concentrations and zero order at higher concentrations, as shown in Figure 21. A typical kinetic plot is shown in Figure 22. The deviation from linearity could be due to an intermediate after one or

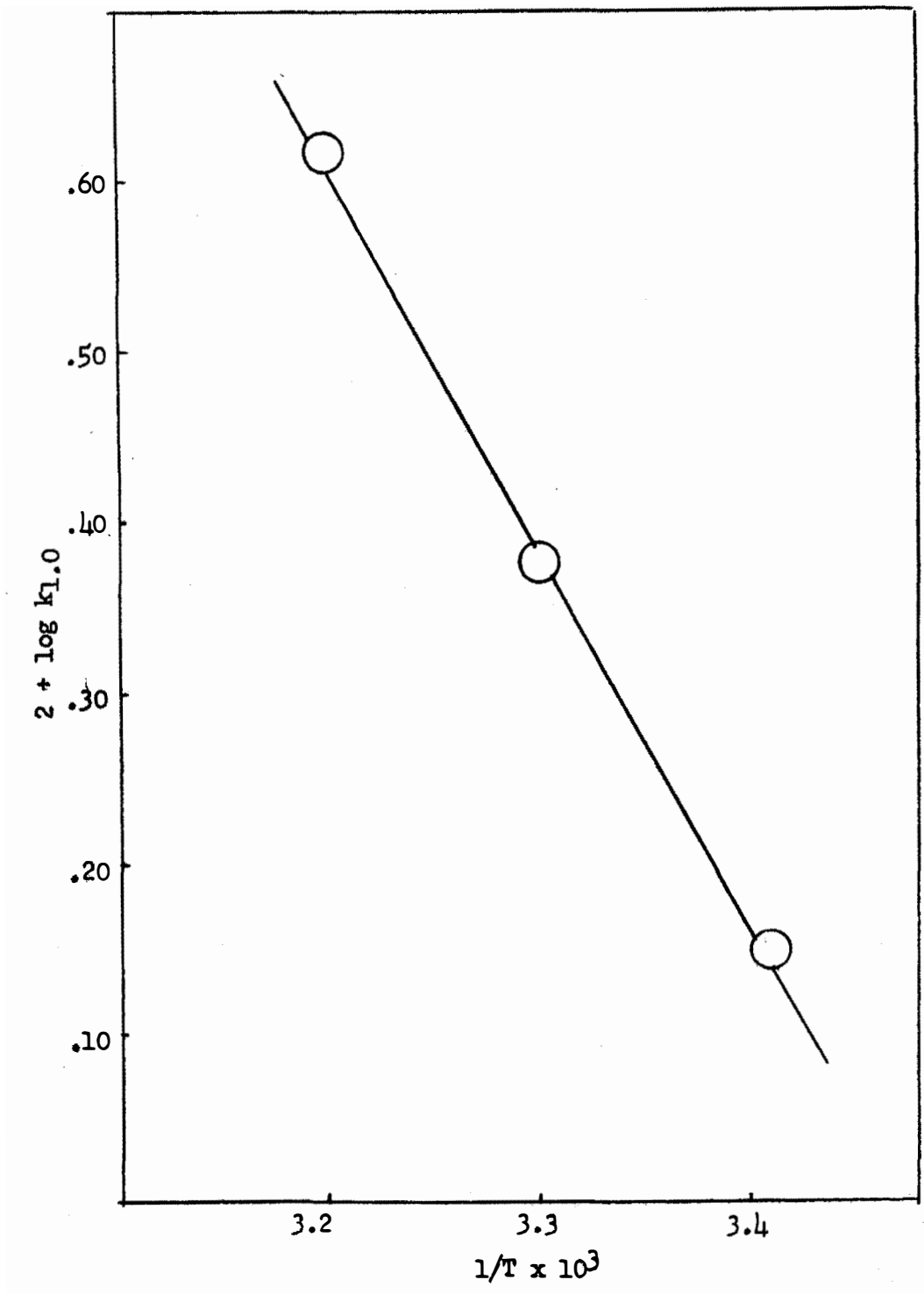


Figure 18. Activation energy plot for the hydrogenation of nitrobenzene.

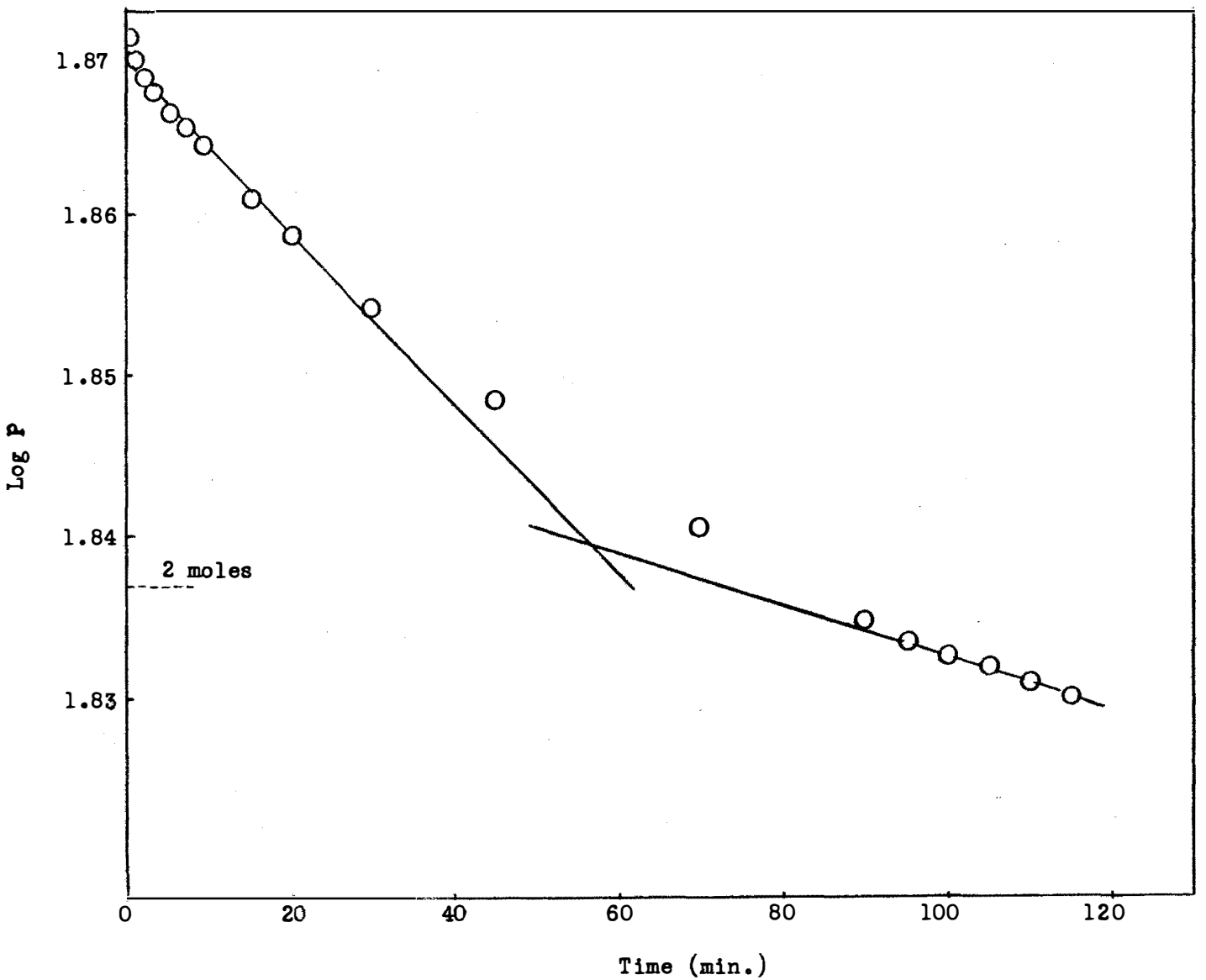


Figure 19. Plot of log P versus time for hydrogenation of nitroethane showing break point at 2 moles of hydrogen.

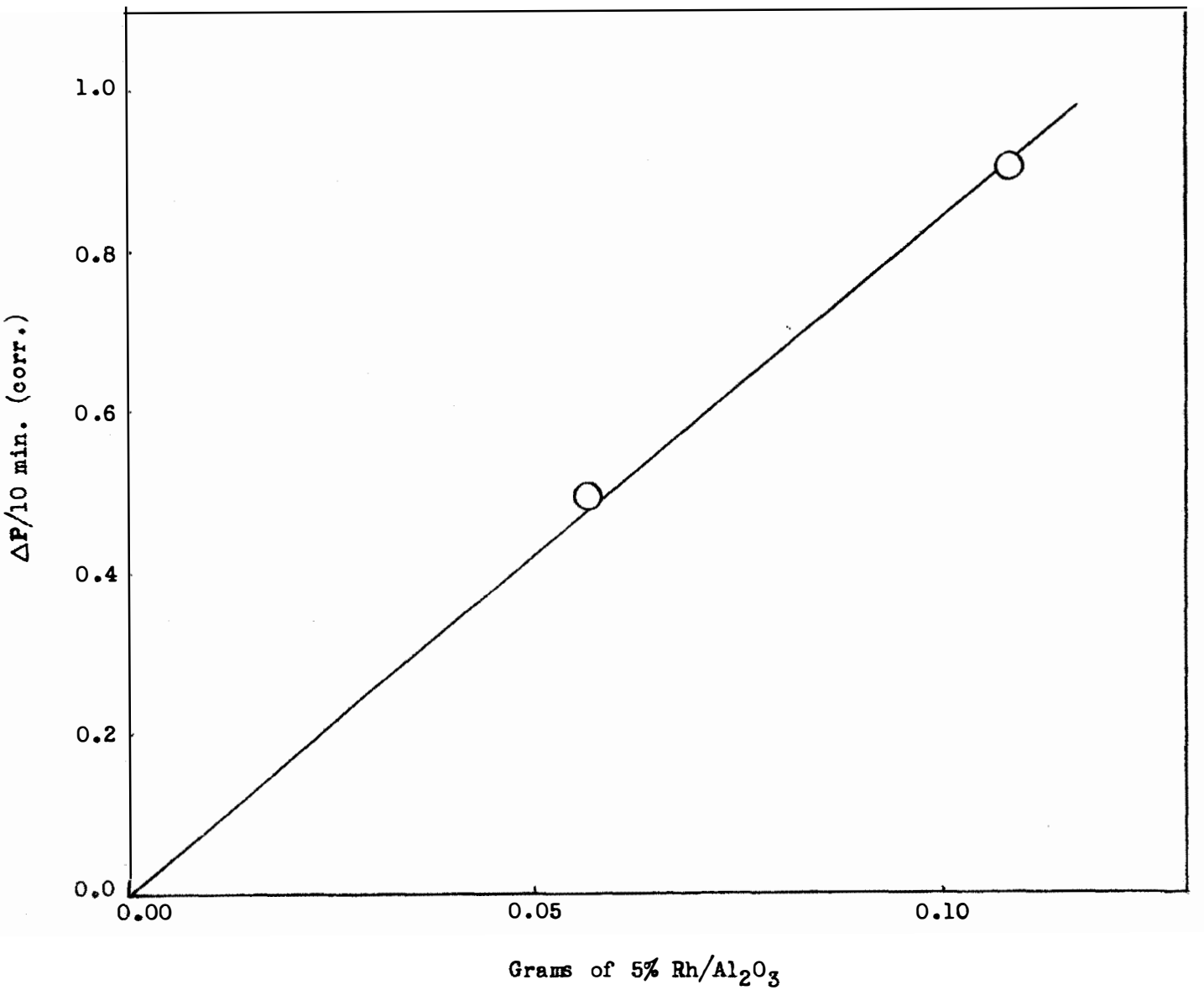


Figure 20. Plot of ΔP/10 min. (corr.) versus catalyst weight for hydrogenation of nitromesitylene.

TABLE VI

EFFECT OF INITIAL PRESSURE UPON THE RATE OF HYDROGENATION OF NITROMESITYLENE AT 30° OVER SUPPORTED RHODIUM

Weight of Catalyst (g.)	Initial Pressure (p.s.i.a.)	ΔP/10 min./g. (corr.)
0.1005	24.6	3.98
0.1005	49.4	5.23
0.1086	74.3	8.31

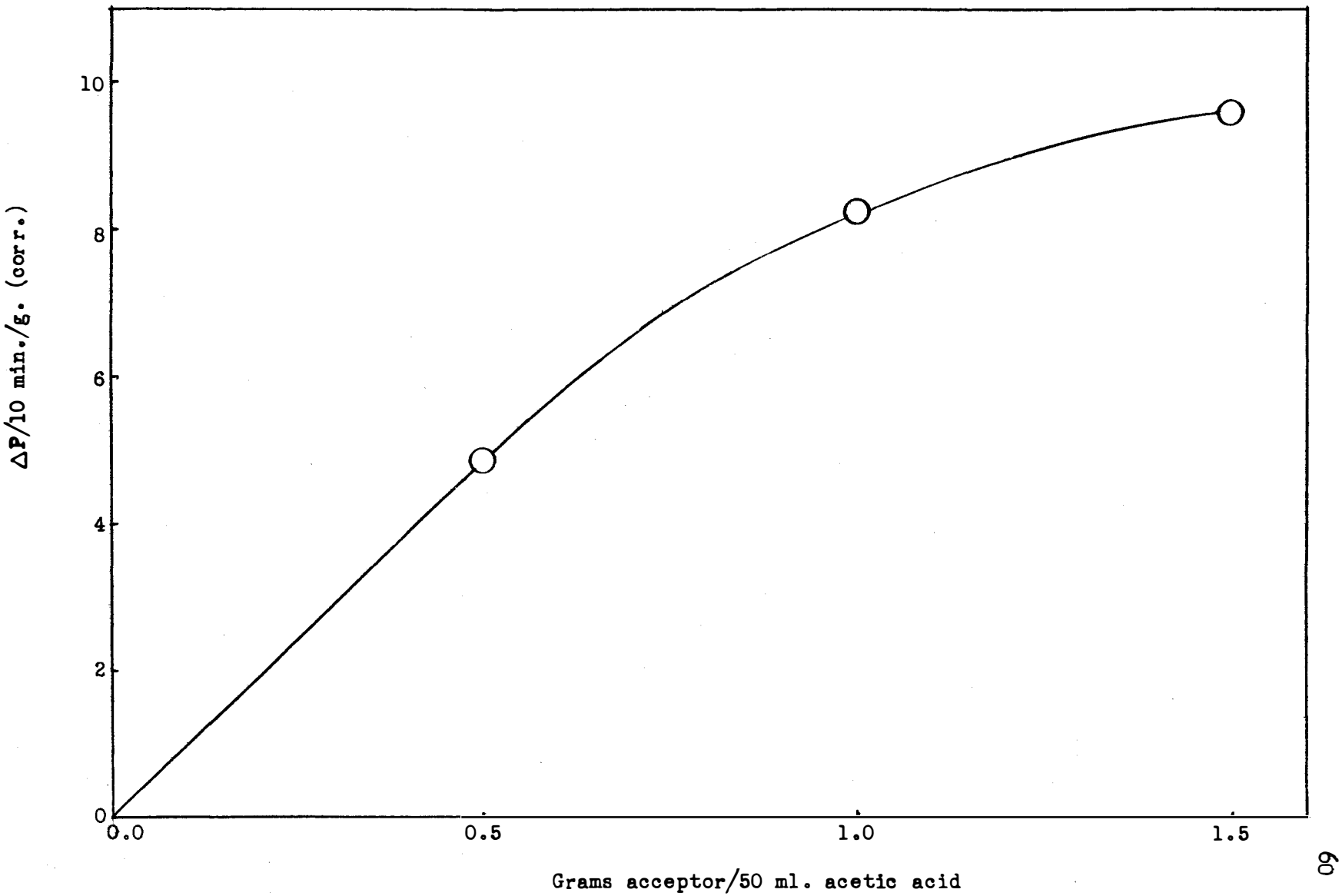


Figure 21. Plot of ΔP/10 min./g. (corr.) versus acceptor concentration for hydrogenation of nitromesitylene.

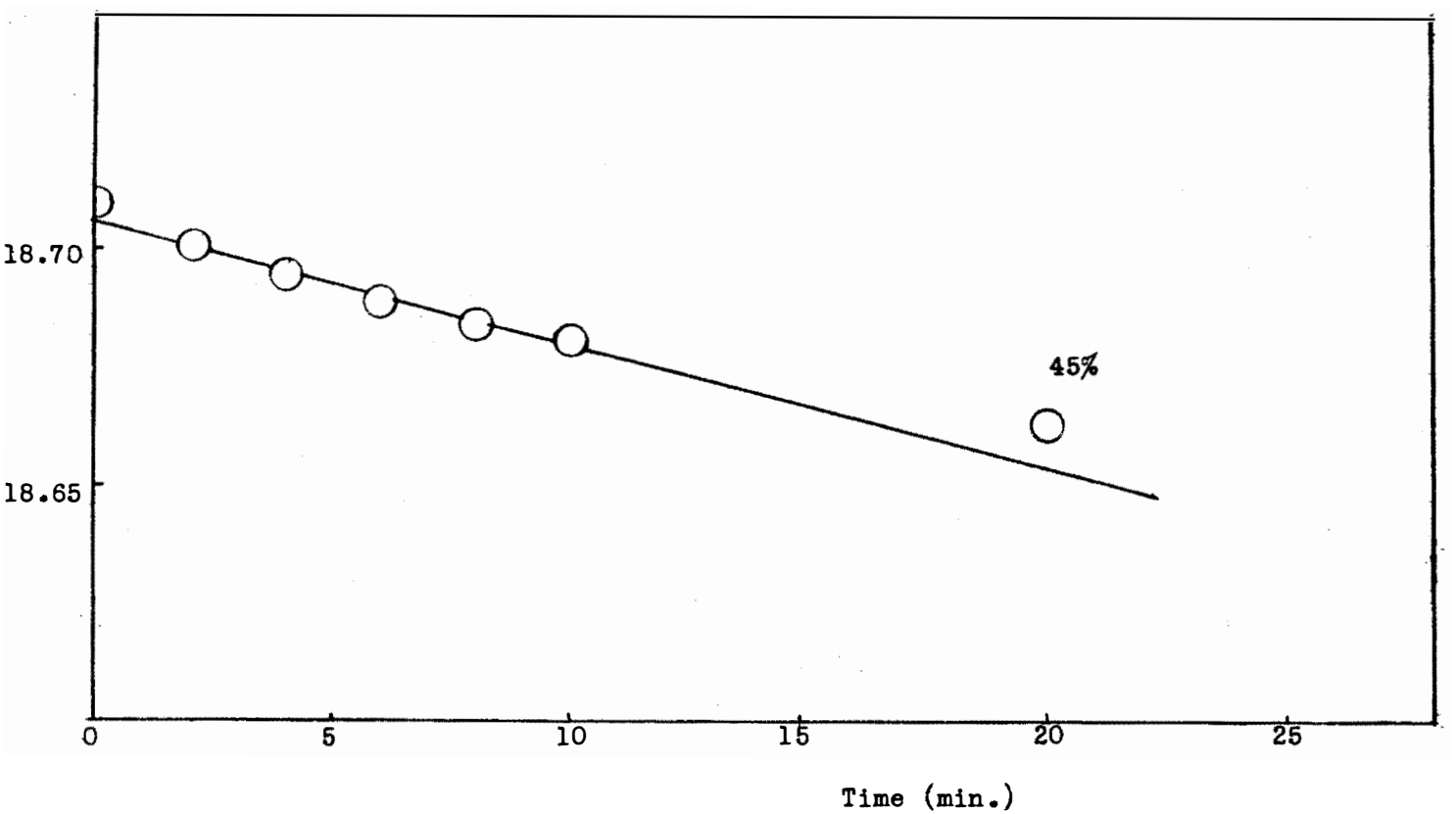


Figure 22. Plot of log P versus time for hydrogenation of nitromesitylene.

two moles of hydrogen have been utilized. Also the first order dependence on acceptor at low concentrations could give this deviation. A summary of runs at 30° is given in Table VII.

The activation energy for the hydrogenation is 10,700 cal./mole as calculated from the plot shown in Figure 23. This value is intermediate between those for the other nitro compounds studied and is nearly the same as that obtained for nitroethane.

One run was taken to completion to ascertain if any definite breaks in the kinetic plot were apparent. As shown in Figure 24 there appear to be slight breaks at one, two, and three moles of hydrogen. With such plots, other nitro compounds have shown definite breaks corresponding to intermediate formation. However, when the breaks are not very pronounced it is impossible to draw conclusions about the presence of intermediates. Actual isolation and identification of the materials present before absorption of three moles of hydrogen were not made. Calculated rate constants were based on the initial portion of the reduction.

E. 2-Nitro-1-butene

Equilibrium catalyst weights below 0.06 g. are indicated in Figure 25. Also in the same plot, the effect of acceptor concentration is shown. The reaction is essentially zero order in acceptor for the concentration range studied. The reaction is approximately first order in hydrogen pressure as shown in Table VIII.

A typical plot is shown in Figure 26, which indicates deviation from linearity at about 49 per cent reduction. The amount of deviation is

TABLE VII

HYDROGENATION OF NITROMESITYLENE OVER SUPPORTED RHODIUM

Weight of Catalyst (g.)	Initial Conc. (g./ml. Solvent)	Initial Pressure (p.s.i.a.)	$k_{1.0}$ (l/min. g.)
0.1086	1/50	74.3	0.0179
0.0566	1/50	74.3	0.0181
0.1040	1/25	74.4	0.0183
0.1038	.5/50	74.3	0.0105
0.1043	1.5/50	74.3	0.0201
0.1005	1/50	49.4	0.0190
0.1058	1/50	24.5	0.0234

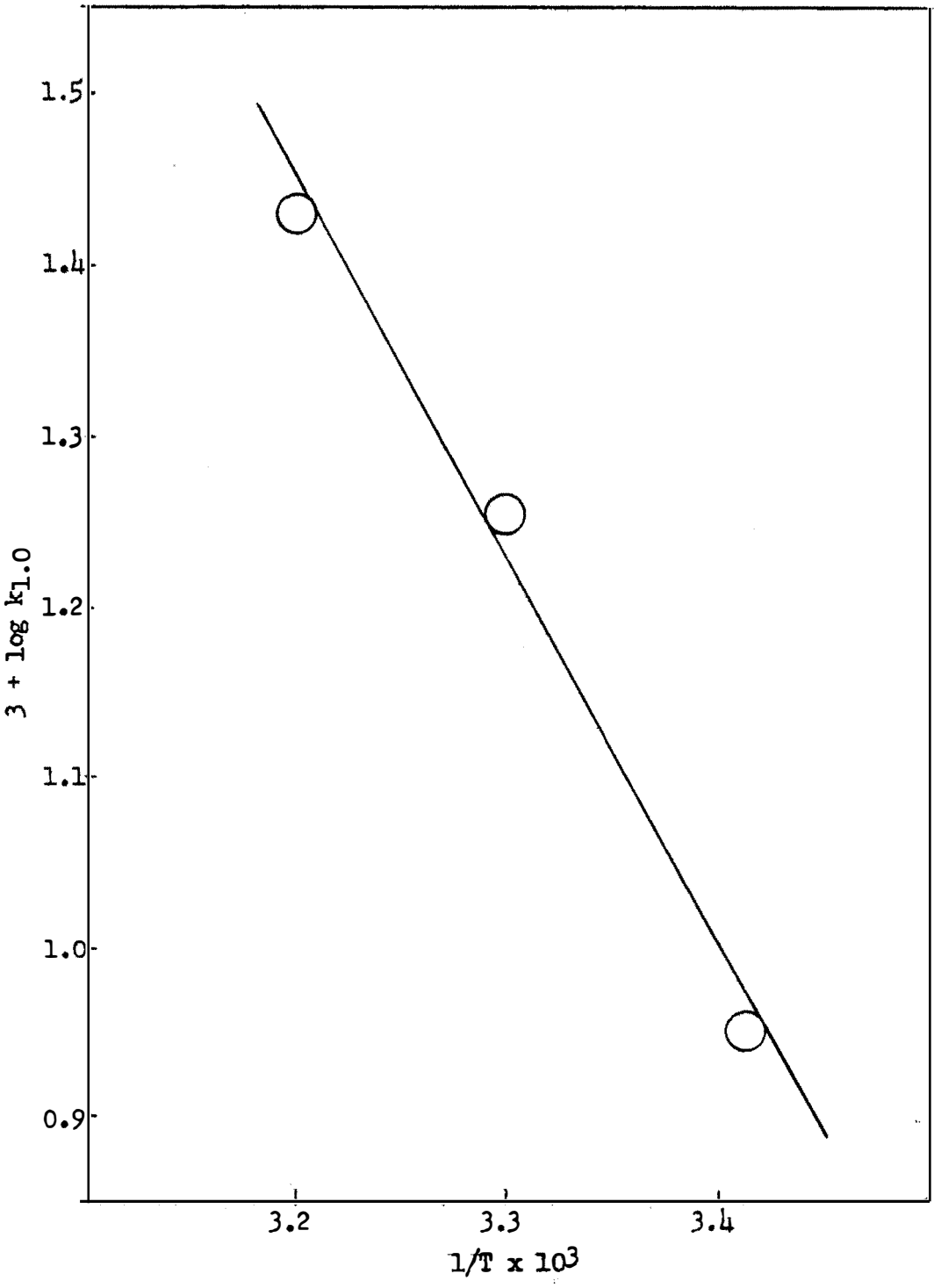


Figure 23. Activation energy plot for the hydrogenation of nitromesitylene.

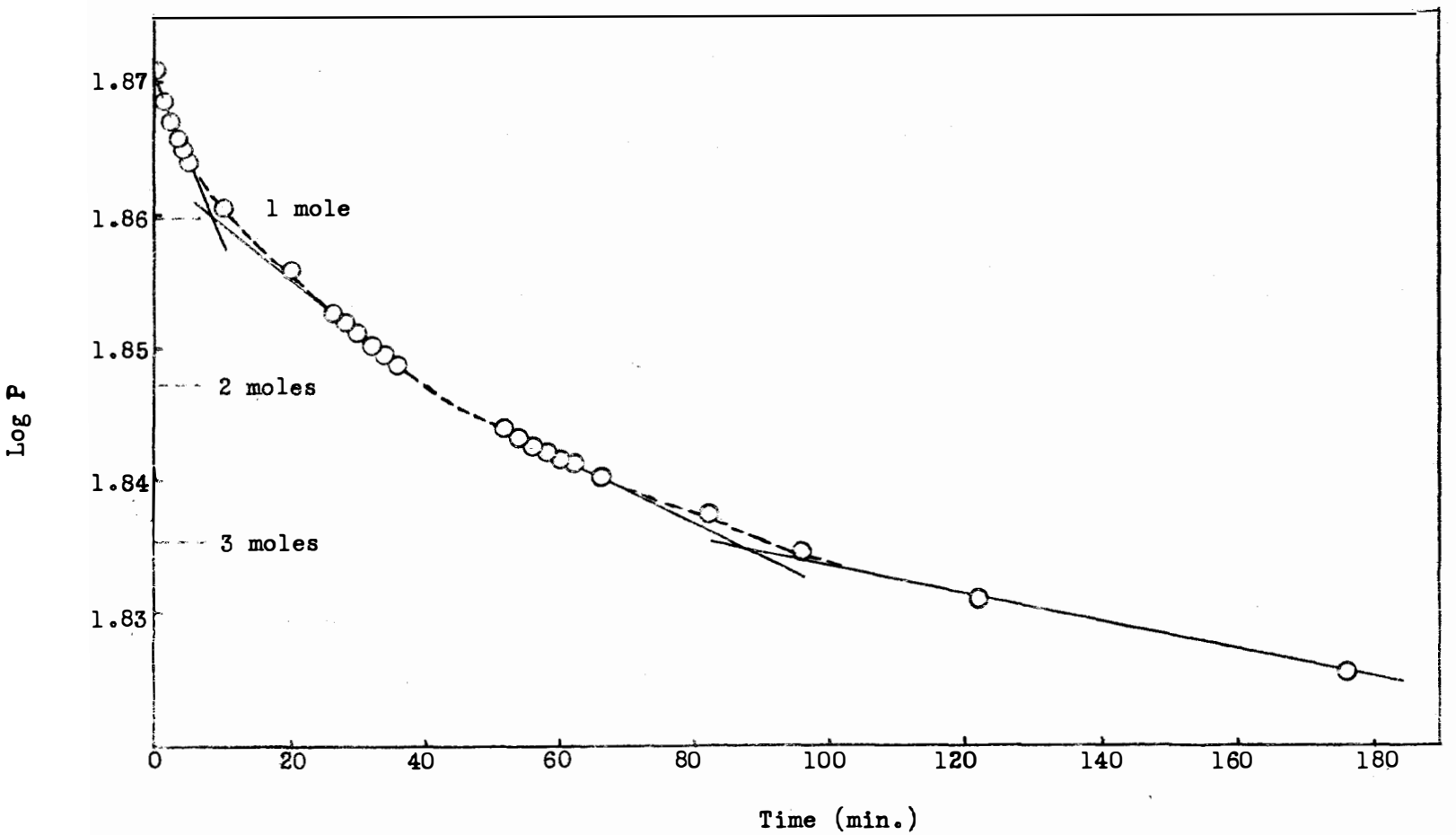


Figure 24. Plot of log P versus time for hydrogenation of nitromesitylene showing break points at 1, 2 and 3 moles of hydrogen.

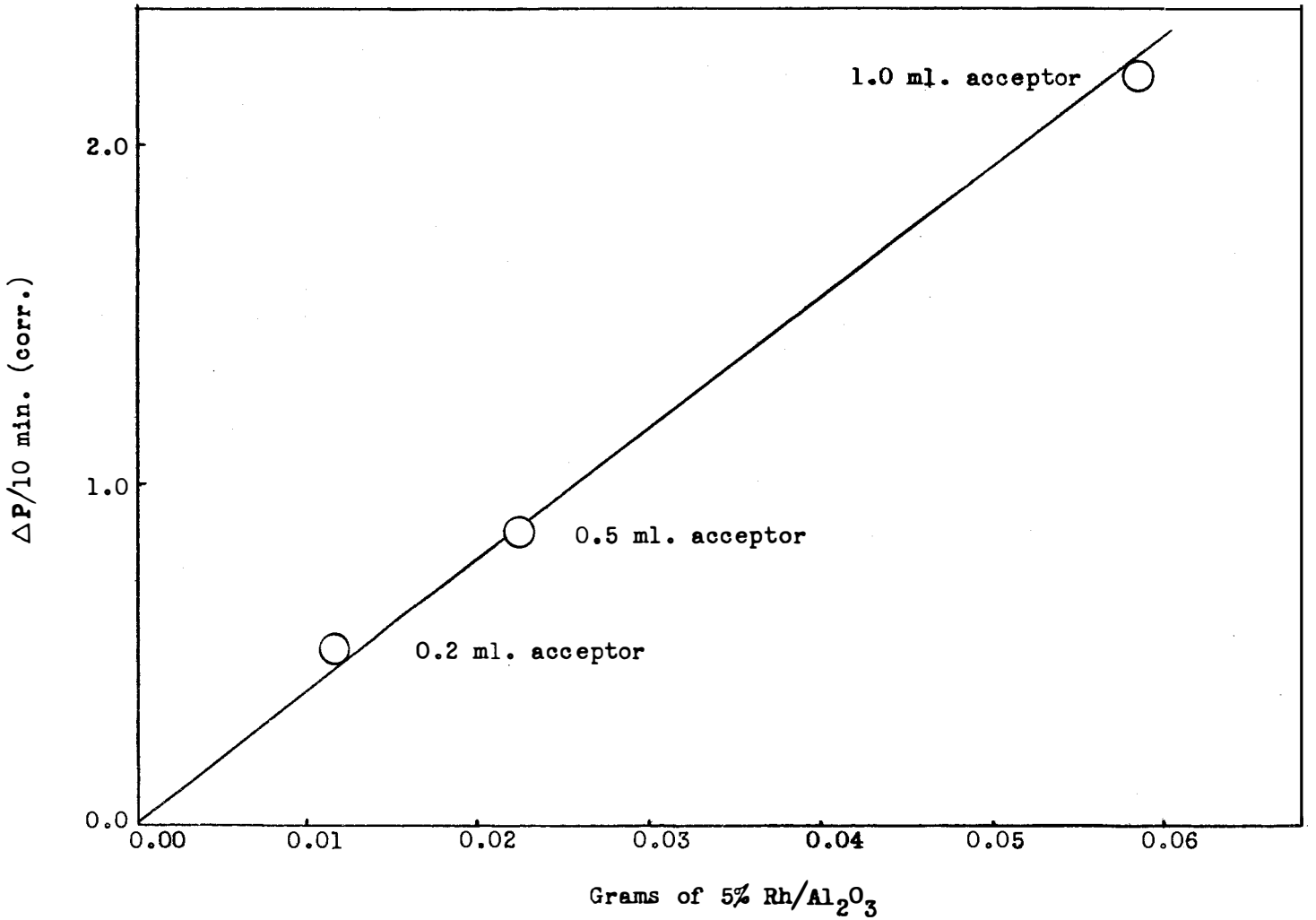


Figure 25. Plot of ΔP/10 min. (corr.) versus catalyst weight for hydrogenation of 2-nitro-1-butene.

TABLE VIII

EFFECT OF INITIAL PRESSURE UPON THE RATE OF HYDROGENATION OF 2-NITRO-1-BUTENE AT 30° OVER SUPPORTED RHODIUM

Weight of Catalyst (g.)	Initial Pressure (p.s.i.a.)	ΔP/2 min./g.
0.0497	24.50	12.0
0.0497	49.55	18.1
0.0495	74.55	24.3

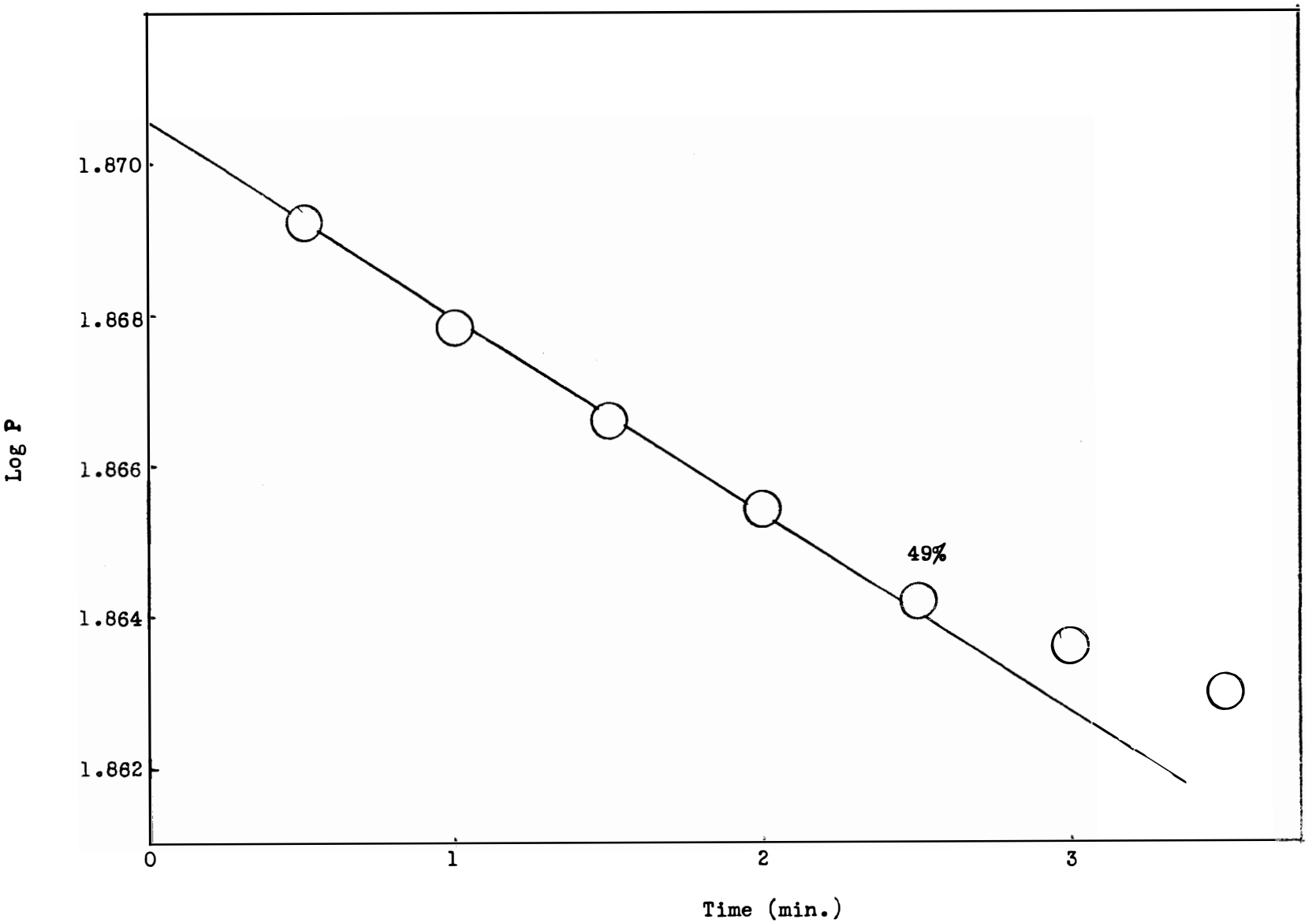


Figure 26. Plot of log P versus time for hydrogenation of 2-nitro-1-butene.

difficult to explain by a first order dependence of acceptor since the concentration is still in the range of zero order dependence, shown in Figure 26. Also by using different ratios of catalyst weight to acceptor weight for other runs, plots were obtained which indicate breaks at one mole (Figure 27) and two moles (Figure 28).

A summary of runs made at 30° is given in Table IX. The runs at different pressures give rate constants indicating that strict first order dependence on hydrogen pressure does not hold. The apparent activation energy for the hydrogenation of 2-nitro-1-butene in the rhodium-acetic acid system is 11,400 cal./mole which is rather high considering the fact that the rate constant ($k_{1.0}$) is higher than the rate constants for the other nitro compounds studied. The activation energy plot is shown in Figure 29.

F. Comparison of Hydrogenation Results

All of the nitro compounds studied showed approximately first order dependence on hydrogen pressure and the first order constants were therefore calculated. Nitroethane and nitromesitylene exhibit first order acceptor dependence at low concentrations and zero order at high concentrations. Nitrobenzene, beta-nitrostyrene, and 2-nitro-1-butene show zero order acceptor dependence for all the concentration ranges studied. The values for the rate constants are given in Table X. Comparison of these constants with those obtained for the platinum-acetic acid system[16e] is given in Table XI. Rather constant ratios are evident. Comparison of the apparent activation energies for the two systems is given in Table XII.

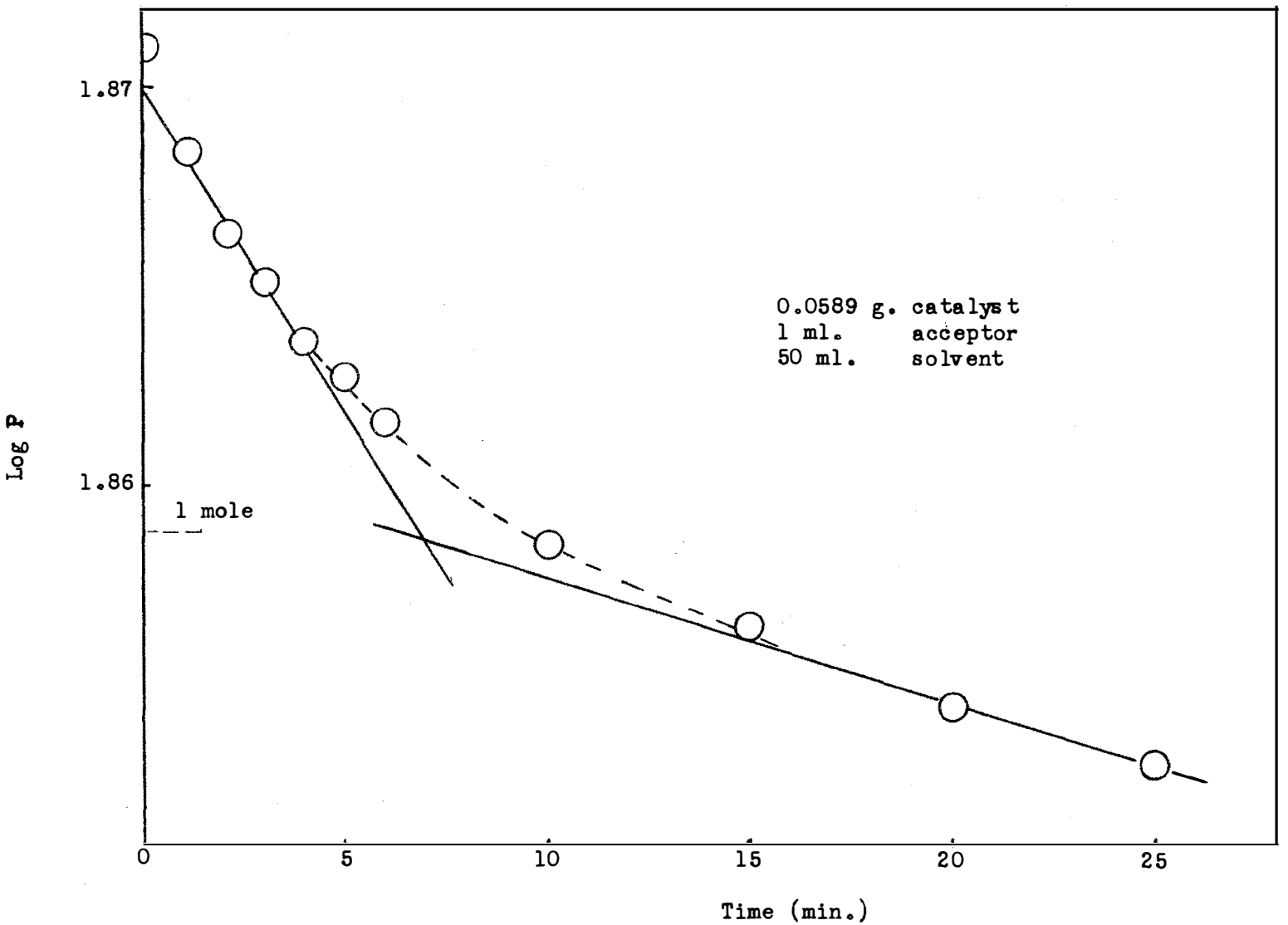


Figure 27. Plot of log P versus time for hydrogenation of 2-nitro-1-butene showing break point at 1 mole of hydrogen.

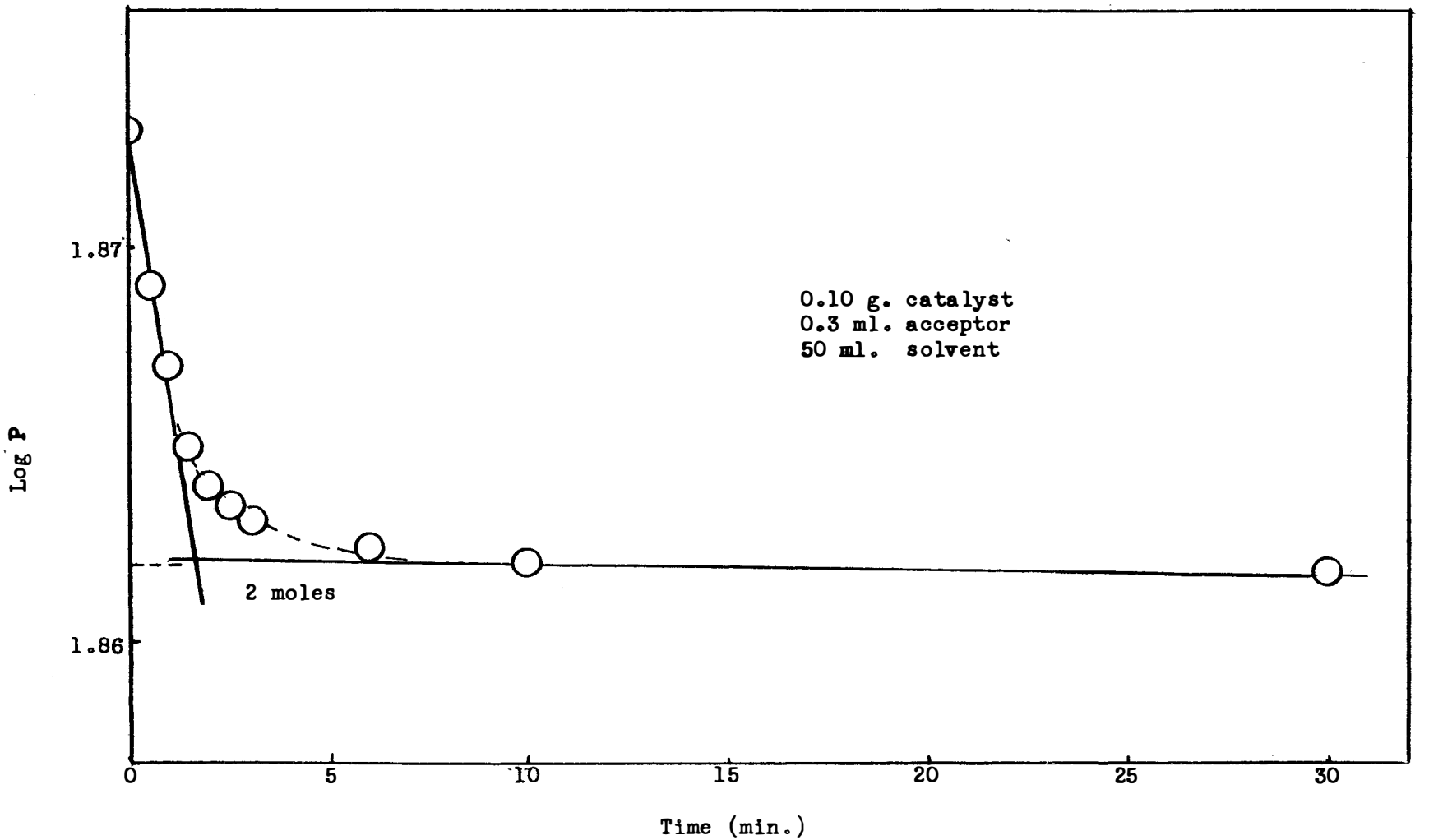


Figure 28. Plot of log P versus time for hydrogenation of 2-nitro-1-butene showing break point at 2 moles of hydrogen.

TABLE IX

HYDROGENATION OF 2-NITRO-1-BUTENE OVER SUPPORTED RHODIUM

Weight of Catalyst (g.)	Initial Conc. (ml./ml. Solvent)	Initial Pressure (p.s.i.a.)	$k_{1.0}$ (l./min. g.)
0.0589	1/50	74.5	0.102
0.0223	.5/50	74.5	0.107
0.0117	.2/50	74.5	0.100
0.0496	.3/50	74.5	0.124
0.0495	.3/50	74.5	0.134
0.0497	.3/50	49.5	0.161
0.0497	.3/50	24.5	0.175

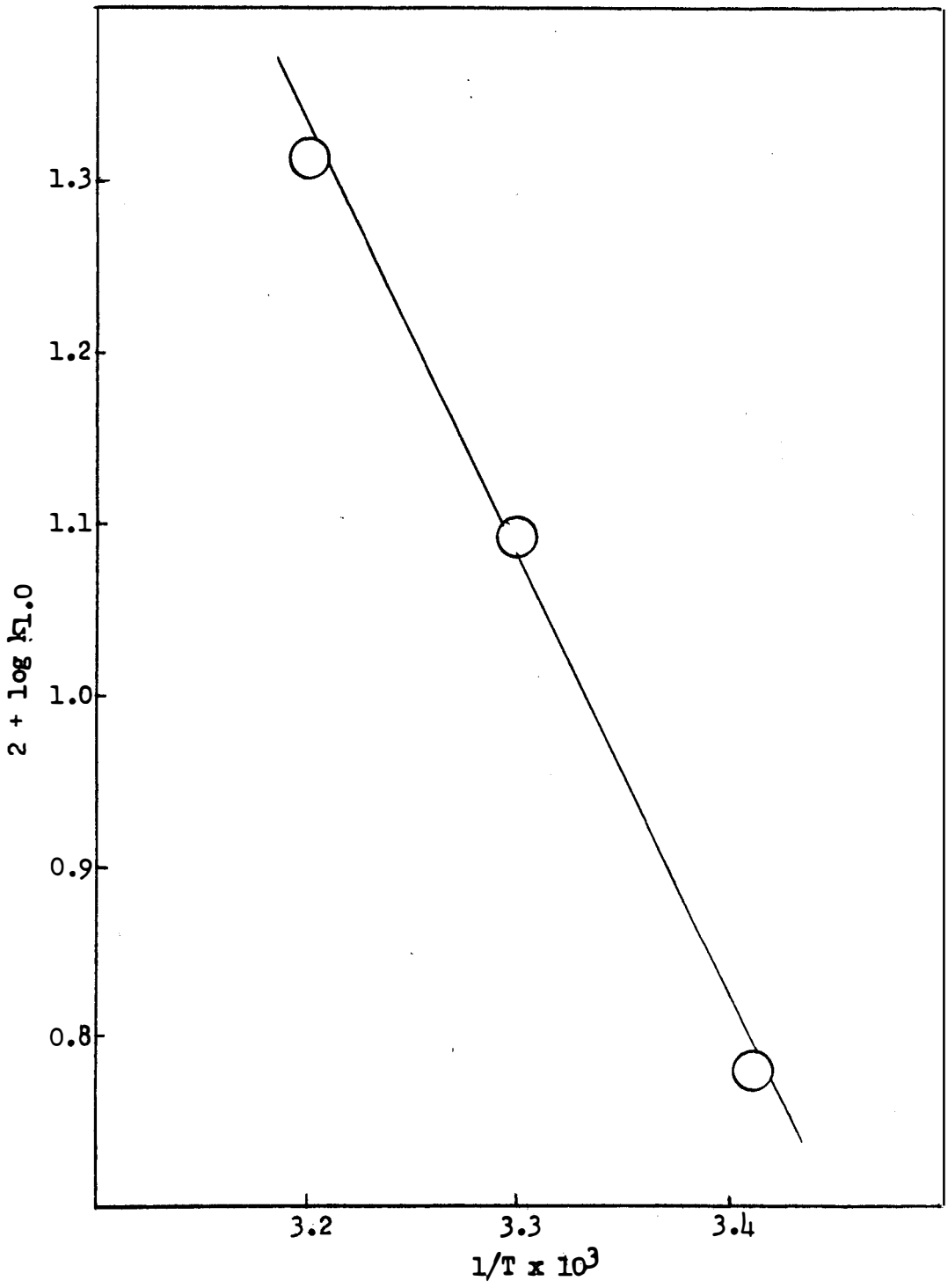


Figure 29. Activation energy plot for the hydrogenation of 2-nitro-1-butene.

TABLE X

SUMMARY OF RATE CONSTANTS FOR HYDROGENATIONS AT 30° OVER SUPPORTED RHODIUM CATALYST

Acceptor	Concentration	$k_{1.0}$ (l./min. g.)
Nitrobenzene	Several	0.115
beta-Nitrostyrene	Several	0.0824[a]
Nitroethane	1 ml./50 ml. Solvent	0.0243
Nitromesitylene	1 g./50 ml. Solvent	0.0180
2-Nitro-1-butene	0.3 g./50 ml. Solvent	0.124

[a]Obtained after very extensive purification of a fresh preparation of acceptor. The rate constant was very low (0.0240) for an older preparation by E. L. McDaniel, Jr., which was recrystallized immediately before use.

TABLE XI

COMPARISON OF RATE CONSTANTS, $k_{1.0}$ (l./min. g.) USING PLATINUM AND SUPPORTED RHODIUM CATALYSTS IN ACETIC ACID AT 30°

Acceptor	Supported Rhodium	Platinum[16a]	$\frac{k_{1.0}\ Pt}{k_{1.0}\ Rh}$
2-Nitro-1-butene	0.124	3.57	28.8
Nitrobenzene	0.115	3.03	26.3
beta-Nitrostyrene	0.0824	2.66	32.3
Nitroethane	0.0243	0.0069[a]	- - -
Nitromesitylene	0.0180	0.585	32.5

[a]The rate for the reduction is first order with respect to acceptor and zero order with respect to hydrogen, while all others are zero order with respect to acceptor and first order with respect to hydrogen.

TABLE XII

COMPARISON OF ACTIVATION ENERGIES (cal./mole) USING PLATINUM AND SUPPORTED RHODIUM CATALYSTS IN ACETIC ACID AT 30°

Acceptor	Supported Rhodium	Platinum[16a]
2-Nitro-1-butene	11,400	4,900
Nitromesitylene	10,700	4,250
Nitroethane	10,300	12,300
Nitrobenzene	9,330	3,700
beta-Nitrostyrene	9,150	4,900

G. Comparison With Deuterium Exchanges

Previous work[21c] using the rhodium-acetic acid system and deuterium has shown that low concentrations of 2-nitro-1-butene, nitrobenzene, and beta-nitrostyrene decrease the exchange of deuterium with acetic acid and completely suppress the exchange at moderate concentrations. This fact indicates that these compounds must be more strongly adsorbed on the catalyst surface than is the solvent.

The present kinetic studies show that these three nitro compounds in the same system give zero order dependence in acceptor concentration. This must be due to strong monomolecular adsorption on the catalyst surface. Thus the deuterium exchange reactions would be decreased or prevented by these layers of solute molecules. Of more interest is the fact that nitromesitylene and nitroethane increased the exchange at low concentrations and gradually decreased the exchange at higher concentrations. From the kinetic results this phenomenon can be partially explained. At low concentrations, the rates of reduction of both compounds showed first order acceptor dependence whereas at higher concentrations zero order dependence was approached.

The nitro compound competes with acetic acid and deuterium for adsorption upon the catalyst. The rate of reduction of the nitro compound will be proportional to the fraction of surface that it covers. If only a small fraction is covered by the nitro compound, more of the surface will be available for acetic acid and deuterium adsorption. Thus a high exchange rate would be expected if the compound only partially covers the surface.

Evidently nitromesitylene and nitroethane or their reduction products can give some special effect with the adsorbed acetic acid, so that the exchange is actually greater than with acetic acid alone. Salt formation with hydroxylamines or amines might occur on the surface so that the hydrogen of acetic acid is more available.

The decrease in exchange at higher concentrations of nitromesitylene and nitroethane is explained by the hydrogenation results. Zero order acceptor dependence was approached at higher concentrations. Thus the fraction of surface covered by acceptor is increasing with an increase in acceptor concentration.

CHAPTER IV

SUMMARY

The kinetics of the catalytic hydrogenation of the nitro group of several compounds have been investigated. The supported rhodium-acetic acid system was employed.

Nitrobenzene, beta-nitrostyrene, nitroethane, nitromesitylene and 2-nitro-1-butene gave kinetic behaviors which were first order with respect to hydrogen pressure. Nitromesitylene and nitroethane exhibited zero order acceptor dependence at high concentrations and first order at low concentrations. Nitrobenzene, beta-nitrostyrene, and 2-nitro-1-butene exhibited zero order dependence for all concentrations studied. Variation of the ratio of catalyst weight to acceptor concentration, in some cases, revealed the stepwise mechanism of the hydrogenation of the nitro group. In some cases the possible intermediates were indicated or identified.

A comparison with deuterium exchange data shows that the exchange effects are paralleled by the hydrogenation data. In general the Langmuir adsorption isotherm explains both the exchange data and hydrogenation data. The special effect of increased exchange in the case of nitromesitylene and nitroethane is discussed.

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PART II

THE EXCHANGE OF DEUTERIUM GAS AND METHANOL IN THE PRESENCE OF RANEY NICKEL

CHAPTER I

INTRODUCTION

A. General Discussion

If two reactants are adsorbed on a catalytic surface, the reaction can proceed between adjacent molecules. This is called the Langmuir-Hinshelwood mechanism.[1,2] To express the rate for this mechanism, one could calculate the surface concentration of reactants using adsorption isotherms. The rate of reaction is then proportional to the fractions of surface covered by each reactant.

If one reactant is adsorbed and another is in the van der Waals layer next to the surface, a reaction can proceed by collisions of the reactant molecules. This is called the Rideal-Eley mechanism.[3,4] It does not have such widespread application as the former mechanism.

Molecules may be adsorbed on a catalytic surface by means of chemical bonds, and high energies are usually associated with the process. There may be an appreciable activation energy of adsorption, in which case the process is called activated adsorption. Physical adsorption is probably not important in the reactions of stable molecules.

If one assumes adsorption to be ideal, there would be no interaction of the adsorbed molecules and the catalyst surface would be homogeneous. For such conditions the amount of chemisorbed substance on the surface is given by the Langmuir adsorption isotherm.[5a]

B. Langmuir Kinetics

In the adsorption isotherm expression, $\theta = \frac{kp}{1 + kp}$, θ is the fraction of the surface covered by gas molecules, k is a constant, and p is the pressure of the gas in equilibrium with the surface. For a strongly adsorbed gas at moderate pressures, the fraction covered is approximately unity. For a weakly adsorbed gas at moderate pressures, the fraction of surface covered is proportional to the gas pressure. The rate of reaction, r, is proportional to θ, i.e., $r = k'\theta$. Thus the rate is given by

$$r = \frac{k'kp}{1 + kp}$$

For a strongly adsorbed gas, kp is much greater than unity and the expression reduces to a zero order rate expression:

$$r = k'$$

For a weakly adsorbed gas, kp is much less than unity and the expression is given by a first order rate expression:

$$r = k'kp$$

For a bimolecular surface reaction involving the Langmuir conditions, the fractions of surface covered by gases A and B are given by the following:

$$\theta_A = \frac{k_A p_A}{1 + k_A p_A + k_B p_B}$$

$$\theta_B = \frac{k_B p_B}{1 + k_A p_A + k_B p_B}$$

For a strongly adsorbed gas A and weakly adsorbed gas B, $k_A p_A$ will be much greater than $1 + k_B p_B$ and the above expressions reduce to

the following:

$$\theta_A \doteq 1$$

$$\theta_B \doteq \frac{k_B p_B}{k_A p_A}$$

The rate of such a bimolecular reaction will be proportional to both fractions covered, i.e., $r = k'\theta_A\theta_B$. Thus one obtains

$$r = \frac{k' k_A k_B p_A p_B}{(1 + k_A p_A + k_B p_B)^2}$$

This reduces to simpler expressions depending upon the relative strengths of adsorption of A and B. Also this expression predicts a maximum in the reaction rate as the pressure of either reactant is increased.

For the Rideal-Eley mechanism, assuming that A is the adsorbed reactant, Langmuir heterogeneous kinetics gives the following expression for the rate:

$$r = \frac{k' k_A p_A p_B}{1 + k_A p_A}$$

In this case an increase in the pressure of the adsorbed reactant results in a limiting value for the rate. This is an experimental characteristic distinguishing the two mechanisms.

Statistical mechanics gives adsorption isotherms of the same type deduced by Langmuir and thus gives theoretical meaning to the constants.[5b]

C. Catalytic Hydrogenations

For many years the kinetics of catalytic hydrogenation of organic compounds in solvents, such as acetic acid and ethanol, have been studied

at these laboratories. In most cases, the experimentally found orders can be explained on the basis of Langmuir kinetics but some of the mechanisms involved remain to be clearly formulated.[6,7,8]

There are many studies reported in the literature concerning the catalytic hydrogenation of nitro compounds on Raney nickel catalyst but most are not kinetic in nature.[9,10] Bedoit[6a] has made a kinetic study of the catalytic hydrogenation of nitro compounds using Raney nickel catalyst and ethanol solvent. The aromatic and aliphatic nitro compounds showed zero order acceptor dependence and first order dependence in hydrogen pressure. For most aliphatic and aromatic compounds, it was postulated that the initial attack occurred on the coordinate-covalent oxygen.

Two reasons for studying hydrogenation and deuteration reactions are that additional evidence for the mechanisms might be obtained and that they might give basic data showing how to utilize kinetic methods for separating hydrogen and deuterium.

Some studies have been made using deuterium, in place of hydrogen, for the reduction of some nitro compounds. The reaction is slower and is complicated by the exchange of deuterium gas with hydrogen of the solvent. Several exchange reactions for various catalyst-solvent systems and the effect of nitro compounds on the exchanges have been examined.[11,12,13]

The present work is a study of the exchange of deuterium with methanol over Raney nickel and the effect of some nitro compounds on the exchange.

D. Catalytic Deuterium Exchanges

Deuterium gas exchanges with practically all hydrogen containing compounds when suitable catalysts and conditions are employed. Deuterium exchanges readily with water, benzene, ethanol, acetone, 2-ethylhexanol, n-butane, and ethyl ether vapors over platinized platinum at room temperature.[14]

With ethanol vapor the exchange was first order in deuterium pressure. Increasing the pressure of ethanol at constant deuterium pressure gave a maximum in the rate of exchange, indicating that a Langmuir-Hinshelwood mechanism was operating. The exchange of ethanol vapor was seven times as rapid as ethanol liquid.

Exchange studies of deuterium with various alcohols over metal films such as platinum, rhodium, and nickel have been made.[15] Nickel was found to be the least active for the exchange. The rate expression for methanol exchange indicates one-half order in deuterium and one-half order in methanol pressure. One-half order dependence would be predicted if deuterium and methanol are adsorbed with dissociation to give reaction and if they are adsorbed with about the same strength.

Studies of deuterium gas exchange with acetic acid over Adams platinum, with methanol over Adams platinum, with acetic acid over supported rhodium, with methanol over supported rhodium, and with methanol over Raney nickel have been carried out in these laboratories.[11,12,13] With the acetic acid-supported rhodium system, first order dependence in deuterium pressure was observed.[13c] With the methanol-Adams platinum system, six-tenths order dependence was observed.[13d]

E. Statement and Purpose of the Research

The kinetic behaviors for the hydrogenation of some nitro compounds over Raney nickel using ethanol solvent have been previously elucidated.[6a] There should be little difference using methanol as a solvent. The effects of nitro compounds upon the exchange of deuterium with methanol over Raney nickel were to be studied and correlated with the hydrogenation kinetics. Also it was hoped that the role of the catalyst in the exchange and the mechanism of the exchange reaction could be better explained.

CHAPTER II

EXPERIMENTAL

A. Preparation of Raney Nickel

Raney nickel was prepared in several batches by a method similar to that given by Bedoit.[16] In a 2-l., three-necked, round-bottomed flask equipped with thermometer and motor-driven glass stirrer were placed 128 g. of c.p. sodium hydroxide and 500 ml. of distilled water. The flask was immersed in a pneumatic trough filled with cold tap water, and equipped with a siphon so that the cooling bath could be regulated. When the temperature of the alkaline solution had subsided to 50°, 50 g. of commercial Raney nickel-aluminum alloy powder was added at such a rate to the rapidly stirred solution that the reaction temperature remained at 50°.

The trough was removed and a Glas-Col heating mantle was placed about the reaction flask. The mixture was digested at 50° for one hour with continued stirring. In some early preparations, the catalyst was then transferred to a 2-l. Erlenmeyer flask with the aid of deaerated distilled water and was washed by decantation with 2-l. portions of deaerated distilled water. After twenty washes the wash solution was neutral to phenolphthalein. Washing was continued ten or fifteen more times using deaerated water. Four washings with 500 ml. portions of deaerated distilled methanol were made. The catalyst was transferred to a 150-ml., glass-stoppered bottle and stored under methanol in a refrigerator. The distilled water and distilled methanol used in the washing

steps were deaerated by bubbling tank nitrogen through the liquids for ten minutes. Later preparations omitted the deaeration steps, which deactivated the catalyst.

Raney nickel catalyst contains some impurities present in the original alloy, occluded aluminum, traces of silicon, and occluded alkali. Immediately following preparation, Raney nickel is saturated with hydrogen, some of which cannot be removed by ordinary heating. The catalytic activity declines as the hydrogen is released, but the two behaviors are not parallel. The hydrogen is probably not simply adsorbed but is combined with the metal in the form of the hydride.

Raney nickel is a dense, black, crystalline powder. Oxides formed on the surface of the metal may join with the nickel to give active centers on the surface.[17] The presence of iron and other metals in the nickel causes crystallization into the face-centered cubic type of lattice. The cubic form of nickel is catalytically active whereas the hexagonal is not.[18]

B. Preparation and Purification of Nitro Compounds

The preparation of the nitro compounds used in this work is described in Part I of this dissertation. The liquid solutes, nitrobenzene, nitroethane, and 2-nitro-1-butene, were redistilled immediately before use. The solid solutes, nitromesitylene and beta-nitrostyrene, were recrystallized immediately before use.

C. Purification of Methanol Solvent

Drum grade synthetic methanol was fractionally distilled in an 8-ft. Vigreux column. Constant-boiling cuts were collected at a reflux ratio of 10:1. A typical cut boiled at 63.8°/740 mm.

D. Preparation of Deuterated Methanol

Ordinary methanol was equilibrated with heavy water of greater than 99.5 per cent purity obtained from Liquid Carbonic Company. After four successive acid-catalysized equilibrations, heavy methanol, CH_3OD, of at least 99.6 per cent purity was obtained. The procedure was as follows:

A mixture of 25.0 ml. of distilled methanol and 25.0 ml. of heavy water containing a trace of sulfuric acid was refluxed for more than twenty minutes in a small still. The still was equipped with a 15-inch Vigreux column, a total-condensation partial take-off head, and a 50-ml. pot heated by an internal wire coil. After refluxing, the methanol was collected at a 2:1 reflux ratio, which required about two and one-half hours. The remaining aqueous portion was removed from the pot.

The collected methanol was then heated with a new 25.0-ml. portion of heavy water for more than twenty minutes. The slow distillation and collection were repeated as before. The procedure was repeated two more times to give 20.0 ml. of CH_3OD of at least 99.6 per cent purity, as determined by calculation using the experimental value, 1.81, for the equilibrium constant.[19]

Each distillation required about two and one-half hours, which was sufficient time for almost complete equilibration. The actual volumes of methanol for each successive equilibration were less than the volumes assumed for the calculations and thus the calculated purity is a minimum value. The methanol behaved like pure CH_3OD when treated with deuterium gas and Raney nickel catalyst for an exchange run. No hydrogen was detected in the sample gas after the exchange.

E. Deuterium and Hydrogen

Deuterium gas of greater than 99.5 mole per cent purity was obtained from the Stuart Oxygen Company of San Francisco. It was passed through a trap cooled with liquid nitrogen immediately before use. Electrolytic hydrogen, obtained from the National Cylinder Gas Company, was used in preliminary runs for testing the effusion system. The hydrogen was also passed through the trap immediately before use, except in a few exchange runs.

F. Reaction Apparatus

1. Reaction Vessels

The reaction vessels consisted of 50-ml. Erlenmeyer flasks sealed at the neck to the side arms of number 6 Pyrex stopcocks 6 cm. below the stopcock housing. To the other arm of each stopcock a socket of a standard ball and socket joint (28/15) was sealed about 7 cm. from the housing. The total volume of the reaction flasks to the stopcock was 63 ml.

The flasks were tested for leaks with a Tesla coil. Cleaning was effected with a nitric acid-sulfuric acid mixture. The flasks were rinsed with tap water five times, distilled water five times, steamed, and dried in an oven at 130°.

2. Shaker

Reactions were carried out by shaking the flask in a controlled-temperature shaker for known times. The shaker was driven by a geared-down Mixmaster motor mounted on an iron base. The jacket for temperature control consisted of a brass can 4 cm. in width and 10 cm. in depth mounted in an outside brass can having a width of 7.5 cm. and depth of 11 cm. An inlet connection was at the base of one side and an outlet connection was at the top of the opposite side. The reaction flask was seated on the bottom of the inside can and held in place by a partially split, one-hole No. 10-1/2 rubber stopper. The flask was surrounded by water up to the rubber stopper. Within the space completely enclosed by the two cans, water from a constant temperature bath was circulated.

With this shaker bath, 10 ml. of methanol in a reaction vessel at room temperature could be brought to a constant temperature of 35° in less than five minutes. In practice, the flask contents were already at the desired temperature before insertion into the jacket. The flask could be shaken at constant speeds from 150 to 340 cycles per minute, with the body of the reaction flask traveling through an arc of about 30 degrees at a distance of 17 cm. from the axis of revolution.

3. Analytical Apparatus

It seems appropriate to mention some unsuccessful attempts to utilize a heat conductivity apparatus for the determination of gas composition. This apparatus, constructed by E. J. Kelly, contained two matched Pyrani tubes and a bridge arrangement. A calibration could be made with hydrogen, deuterium, and their mixtures so that the percentage composition could be read directly from the plot of composition versus galvanometer reading.

This method would be very good if a large number of determinations could be done at one time. With acetic acid as the exchange solvent, it would be easy to keep the reaction mixtures frozen until a large number were ready for the gas analysis. With methanol solvent this would not be feasible.

This analytical method actually required more time than effusiometry when only a few runs were to be made at one time, and it was subject to very large random errors. One source of error noted was an erratic fluctuation due to normal vibration during use. Evidently some of the variable resistors in the bridge need to be isolated from the rest of the apparatus and housed in a special vibration-free environment. Also the response varied with temperature, which was difficult to maintain constant for any length of time when liquid nitrogen was employed for the bath.

The effusiometry apparatus used in this work to determine the amount of hydrogen and deuterium in the mixtures after exchange reactions was basically the same as used by other investigators.[11a,12a] However, a number of modifications were made in order to increase the precision and

to simplify the analytical procedure.

Early work with the platinum pinhole indicated that effusion times were subject to significant variation from run to run, from day to day. The greatest source of difficulty with the system was that a small space between the platinum foil and the stopcock, including the bore, could not be evacuated. Even after fifteen or twenty flushings with the gas being determined, a slight variation in effusion times could be detected. Another great difficulty was caused by the stopcock grease plugging the pinhole. This occurred easily since the pinhole was of necessity very close to the stopcock. It is possible that heating effects (as hydrogen or deuterium is passed through the pinhole) gave some variation in effusion times, and the presence of moisture on the platinum which was in contact with the atmosphere at all times could give some variation.

For each run with this system, the mercury had to be pulled into a lower reservoir and then forced with compressed air into an upper reservoir. The quantity and cleanliness of the mercury would be subject to some variation. Also, the stopcock grease used on a 120°, three-way stopcock at the bottom of the system very readily came to the top of the mercury on both sides of the system. This necessitated frequent cleaning of the entire effusion system. The effusion system contained a three-way stopcock just under the platinum foil and this was subject to leakage after a few runs. The vacuum manifold contained a three-way stopcock which frequently gave difficulties.

The modified apparatus incorporated a glass effusion pinhole bulb which could be completely evacuated. A glass pinhole system for effusiometry has been previously described.[20,21] The pinhole for this work

was obtained by sparking a thin glass bulb with a Tesla coil until a hole was produced, as evidenced by the bright spark through the glass. After several unsuccessful attempts to prepare such a pinhole and etch to the proper size with hydrofluoric acid, it was found that trial and error sparking gave a pinhole of just the right size.

A diagram of the manifold and effusion system is shown in Figure 1. The stopcocks are numbered from 1 to 10. All except the flask stopcock are number 2, two-way stopcocks. Mercury was contained in reservoirs A, B, and C. Reservoirs B and C were connected by 10 mm. Pyrex tubing through a short section of Tygon tubing. This plastic tubing prevented strains on the two sides of the mercury setup and allowed easy disassemblage for cleaning.

All stopcocks, except numbers 1, 8, and 10, were secured with aluminum fasteners. All stopcocks and the ball and socket joint were lubricated with Apiezon T stopcock grease. Water from a constant temperature bath was circulated through the jacket which housed the effusion chamber and mercury reservoir A. The trap between stopcocks 5 and 6 was a U-bend of capillary tubing (8 mm., o.d.; 2 mm. i.d.) which was cooled with liquid nitrogen.

G. Exchange Procedure

The technique for carrying out an exchange reaction was very important. Evacuations and flushings had to be thorough. All glass apparatus used with the catalyst had to be very clean. All reaction vessels and

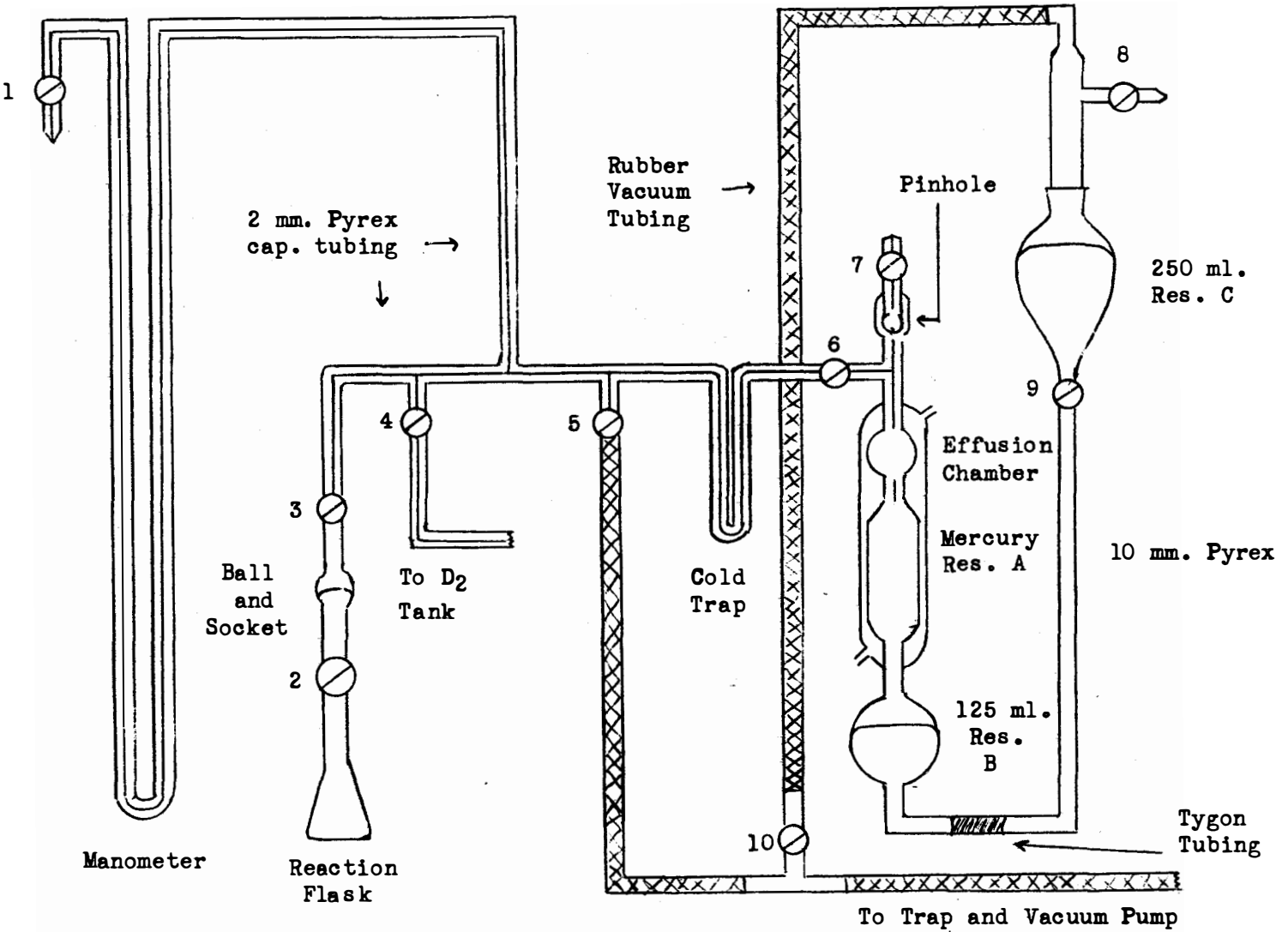


Figure 1. Diagram of manifold and effusion system (not to scale).

glassware used were wiped free of stopcock grease with absorbent tissue and soaked in ethyl ether. After rinsing in pure ether, cleaning with nitric acid-sulfuric acid, and rinsing with tap water and distilled water, the glass was dried in an oven at 130°. The reaction vessels were steam cleaned immediately before drying in the oven.

Raney nickel while wet with methanol was added from a calibrated glass tube. The tube permitted rough control of the amount of catalyst. After the reaction was completed, the nickel was collected upon a fritted funnel, dried by evacuation with a water pump for one hour, and covered with an atmosphere of carbon dioxide, using a special filtration system. Then the funnel was stoppered and weighed.

Solid solutes were weighed in 10-ml., glass-stoppered flasks and dissolved with 5 ml. of methanol. Liquid solutes and solvents were pipetted into a long stem funnel inserted in the reaction flask.

Unless otherwise specified, 10 ml. of solvent and 799 mm. of deuterium were used. The exchanges were run at 35.0 ± 0.2°, with a shaking speed of 270 ± 10 c.p.m., and, in most cases, for ten minutes. The procedure for carrying out the exchange and analysis was as follows:

(a) The stopcock on the reaction flask was lubricated with Apiezon T stopcock grease and assembled while still warm.

(b) The reaction flask was connected to the manifold at the ball and socket joint. The contents were frozen using liquid nitrogen.

(c) The flask stopcock was opened and the flask was evacuated for two minutes using a Hyvac mechanical pump and a liquid nitrogen trap. Stopcocks 6, 9, and 10 must be closed.

(d) The flask stopcock and stopcock 3 were closed and the flask removed from the manifold. The contents were thawed in the constant temperature bath at 35° for two minutes.

(e) The flask was reconnected to the manifold and the contents were frozen.

(f) Stopcock 3 and the flask stopcock were reopened and the flask was evacuated for five minutes.

(g) The flask stopcock and stopcock 3 were closed and the flask was removed from the manifold. The contents were thawed in the constant temperature bath at 35° for five minutes.

(h) The flask was reconnected to the manifold. A beaker of water at 35° was used to maintain the temperature of the flask constant. The space between the flask and manifold stopcocks was evacuated for two minutes.

(i) The deuterium line was opened to the manifold (stopcock 4) and evacuated during the above step. The entire manifold was then flushed with deuterium and evacuated. Flushing and evacuation were repeated twice. Thereafter, stopcock 4 was left open.

(j) Stopcock 5 was closed. The manifold was filled with deuterium to 1000 mm. pressure, the flask stopcock was opened, and the pressure readjusted to 1000 mm.

(k) The flask stopcock and stopcock 3 were closed. The flask was removed from the manifold and placed in the shaker bath which was at 35°. The shaker was turned on and the reaction was run for the desired time.

(l) While the exchange reaction was proceeding, the mercury level was brought to the top of the mercury reservoir B by closing stopcock 8, opening stopcock 6 to the pressure of the system, opening stopcock 10 and finally opening stopcock 9. The mercury was pulled down until it reached the top of reservoir B, then stopcock 9 was closed to lock the mercury at that position. Stopcock 10 was then closed and stopcock 8 was opened. Stopcock 7 was always closed except during effusions.

(m) At the end of the reaction time the shaker was stopped and the dried flask immersed in liquid nitrogen to freeze the contents. The flask was reconnected to the manifold. Evacuation of the entire manifold system and effusion system was carried out for two minutes. For this evacuation stopcocks 3, 4, and 6 must be opened and stopcocks 7 and 9 must be closed. One flushing with deuterium followed by another two-minute evacuation was made.

(n) The vacuum stopcock was closed and the flask stopcock slowly opened to admit the gas into the effusion chamber and mercury reservoir A. Then stopcock 6 was closed and stopcock 9 was opened. This compressed the gas with the mercury to an arbitrary level below the effusion chamber. Pressures to allow the exact amount of gas collection were determined and marked on the two-way manometer.

(o) After five minutes to allow temperature equilibrium, stopcock 7 was opened to allow the gas to effuse through the pinhole. When the rising mercury reached an arbitrary mark on the capillary tubing just below the effusion chamber, the stopwatch was started. When the level reached a mark on the upper capillary tubing, the stopwatch was stopped

and stopcock 7 was closed. The time required for the gas to effuse was measured to the nearest 0.1 second.

(p) For additional samples of gas, stopcock 8 was closed and stopcock 10 was opened. Then stopcock 6 was opened so that gas would be pulled into the effusion system. The procedure after collecting sufficient gas was identical with the above. For most runs three or four samples could be collected.

In case hydrogen is directly liberated, as may happen with active samples of Raney nickel, one must measure the amount liberated. This was done for the deuterium-methanol exchange as follows:

(a') The reaction flask was connected to the manifold at the ball and socket joint. Steps (b) through (j) in the preceding description were repeated.

(b') The flask stopcock was closed. The system up to stopcock 6 was evacuated for two minutes. Then stopcock 5 was closed and stopcock 2 was opened. This gave a pressure due to 53 ml. of deuterium at 799 mm. and 35° expanding into the system. The pressure was measured.

(c') With the flask maintained at 35°, deuterium was readmitted until the manometer read 1000 mm. (799 mm. of deuterium), then stopcock 2 was closed and an exchange run carried out in the usual manner.

(d') After the exchange run, the flask was reconnected and thermostatted at 35°. After evacuation of the system between stopcocks 2 and 6, stopcock 5 was closed and stopcock 2 was opened. The pressure was again measured. Any increase, $P_{H_2(l)}$, from the original measurement with deuterium was due to directly liberated hydrogen. The actual pressure

reading for deuterium must be subtracted from atmospheric pressure. This total pressure was corrected by subtracting the vapor pressure of the methanol at 35° (301 mm.) and was designated $P_{D_2(i)}$. See Section 5 under "Calculations" of this chapter.

H. Calculations

1. Calibration of the Pinhole

The pinhole was calibrated by determining the effusion times for pure liberated hydrogen and tank deuterium. The rate of effusion of a gas is inversely proportional to the square root of its molecular weight. The time of effusion is thus directly proportional to the square root of the molecular weight. For the effusion times of equal volumes of hydrogen and deuterium, one obtains:

$$\frac{t_{D_2}}{t_{H_2}} = \sqrt{1.998} = 1.414$$

Using hydrogen, freshly liberated from acetic acid by sodium, and tank deuterium, a ratio of 1.406 was obtained. This agrees with the ratio obtained previously using the platinum pinhole.[13a] When tank hydrogen was used, a lower ratio of 1.394 was obtained which is probably due to gases such as nitrogen and oxygen in the tank hydrogen. For all calibration and exchange runs, the gases were passed through a trap cooled with liquid nitrogen before effusion.

2. Standardization with Deuterium

By determining the effusion time for deuterium to one part in 1000 before each run, the effusion time for hydrogen could be calculated using the experimental ratio of 1.406. The variation in effusion times for deuterium was generally less than 1 per cent from run to run. Room temperature and atmospheric pressure affect the effusion times slightly. Variation is also due to changes in the condition of the pinhole itself due to adsorbed substances or temperature effects including hysteresis of the glass. Another important factor for obtaining good agreement is that flushing of the deuterium diaphragm valve must be made in order to eliminate the air which could enter when the valve pressure goes down and atmospheric pressure increases. Also impurities may be picked up from the rubber tubing connecting the deuterium line to the tank valve.

3. Calculation of Percentage Hydrogen

Using the experimentally obtained effusion times for deuterium (t_{D_2}), gas mixture (t_{X_2}), and the calculated time for hydrogen (t_{H_2}), the atomic per cent hydrogen was calculated from the following expression:

$$\% \text{ Hydrogen} = \frac{t_{D_2}^2 - t_{X_2}^2}{t_{D_2}^2 - t_{H_2}^2} \times 100$$

This follows from Graham's Law of Effusion.[11b] See Appendix I. The equation has been verified using known mixtures and the agreement is very good. When no hydrogen is liberated directly from the catalyst, the percentage hydrogen is also the percentage exchange.

4. Precision and Accuracy

The uncertainty in effusion times was less than ± 0.1 second, which gave an absolute error of ± 0.2 per cent exchange. Thus for 20 per cent exchange, the relative error was ± 1.0 per cent. The relative error would be more for exchanges of less than 20 per cent.

Accuracy was affected by the calibration and by the standardization effusion runs. Also a slight error was due to the fact that the deuterium in the stopcock bore of the reaction flask was not utilized in the exchange reaction. For the second sample the absolute error was very small, but for the first sample the absolute error was found to be about 1 per cent.

5. Calculation of Percentage Exchange

When hydrogen is liberated directly from the catalyst, more data are required for a calculation of percentage exchange. The difference in pressure readings before and after the exchange run is measured. This can be denoted $P_{H_2(l)}$. Any increase in pressure must be due to directly liberated hydrogen. The final pressure reading then will always be the sum of $P_{D_2(i)}$, the initial deuterium pressure reading, and $P_{H_2(l)}$, the increase in pressure. All readings must be taken for the same volume and temperature.

The expression for calculation of percentage exchange, as derived in Appendix II, is as follows:

$$\% \text{ Exchange} = 100 - \left[100 - \% H_2\right]\left[1 + \frac{P_{H_2(l)}}{P_{D_2(i)}}\right]$$

where

$$\% H_2 = \frac{t_{D_2}^2 - t_{X_2}^2}{t_{D_2}^2 - t_{H_2}^2} \quad (100)$$

6. Calculation of Exchange Order

From exchange results using various pressures of deuterium gas, the order with respect to deuterium gas pressure can be calculated. The equation of van't Hoff:[22]

$$n_b = \frac{\log \left[\frac{dx}{dt}\right]_1 - \log \left[\frac{dx}{dt}\right]_2}{\log (B)_1 - \log (B)_2}$$

where dx/dt, the differential change in concentration with time, is replaced by $\Delta x/\Delta t$ for the initial rate, gives with appropriate substitutions, the following expression:

$$n_{D_2} = \frac{\log \left[\frac{P_o(\%\ \text{Ex. g.}^{-1}\ \text{min.}^{-1})}{100}\right]_1 - \log \left[\frac{P_o(\%\ \text{Ex. g.}^{-1}\ \text{min.}^{-1})}{100}\right]_2}{\log (P_o)_1 - \log (P_o)_2}$$

where n_{D_2} is the order with respect to deuterium gas, P_o is the corrected initial deuterium pressure, and % Ex. $g.^{-1}$ $min.^{-1}$ is the calculated exchange for the initial part of the reaction.

7. Calculation of Rate Constants

For an exchange reaction that is zero order with respect to deuterium pressure, the expression for the rate constant becomes:

$$k = \frac{P_{H_2}}{t}$$

where P_{H_2} is the pressure of hydrogen and t is the time. Using the exchange data, the expression becomes:

$$k_{1.0} = \frac{P_o \cdot \%\ \text{Ex. g.}^{-1}}{100 \cdot t}$$

where P_o is the corrected initial deuterium pressure and % Ex. $g.^{-1}$ is the calculated exchange found after time, t, for the given initial pressure. The derivation is given in Appendix III.

CHAPTER III

RESULTS AND DISCUSSION

A. Catalyst Weight

The effect of catalyst weight on the exchange reaction of deuterium gas with liquid methanol was studied using four batches of Raney nickel. It was found that deaeration of wash liquids for the first three preparations gave a Raney nickel of rather low activity. A higher activity was obtained by using untreated wash liquids.

As shown in Figure 2, the catalyst activity declined after preparation. It remained fairly constant after three weeks of aging. For the deaerated catalyst, it is probable that the surface hydrogen was removed quickly. Also some poisoning probably occurred.

The standard catalyst adopted for this work was based on seven runs made with catalyst batch 4 after being aged several weeks. By definition it was taken to be a Raney nickel catalyst which would give an activity of 7.11 per cent exchange per gram per minute, for deuterium-methanol exchanges at 35° using 53 ml. of deuterium at 799 mm. and 10 ml. of methanol. An equilibrium shaking rate is necessary and the per cent exchange must be linear with catalyst weight. Equilibrium catalyst weights were below about 0.35 g. for batch 4. All runs listed in Table I were made with 10 ml. of methanol at 35° for ten minutes with a shaking rate of 270 ± 10 c.p.m. and at a deuterium pressure of 799 mm. Hg. It is apparent that Raney nickel is a very weak catalyst for the exchange reaction as shown in Table II.

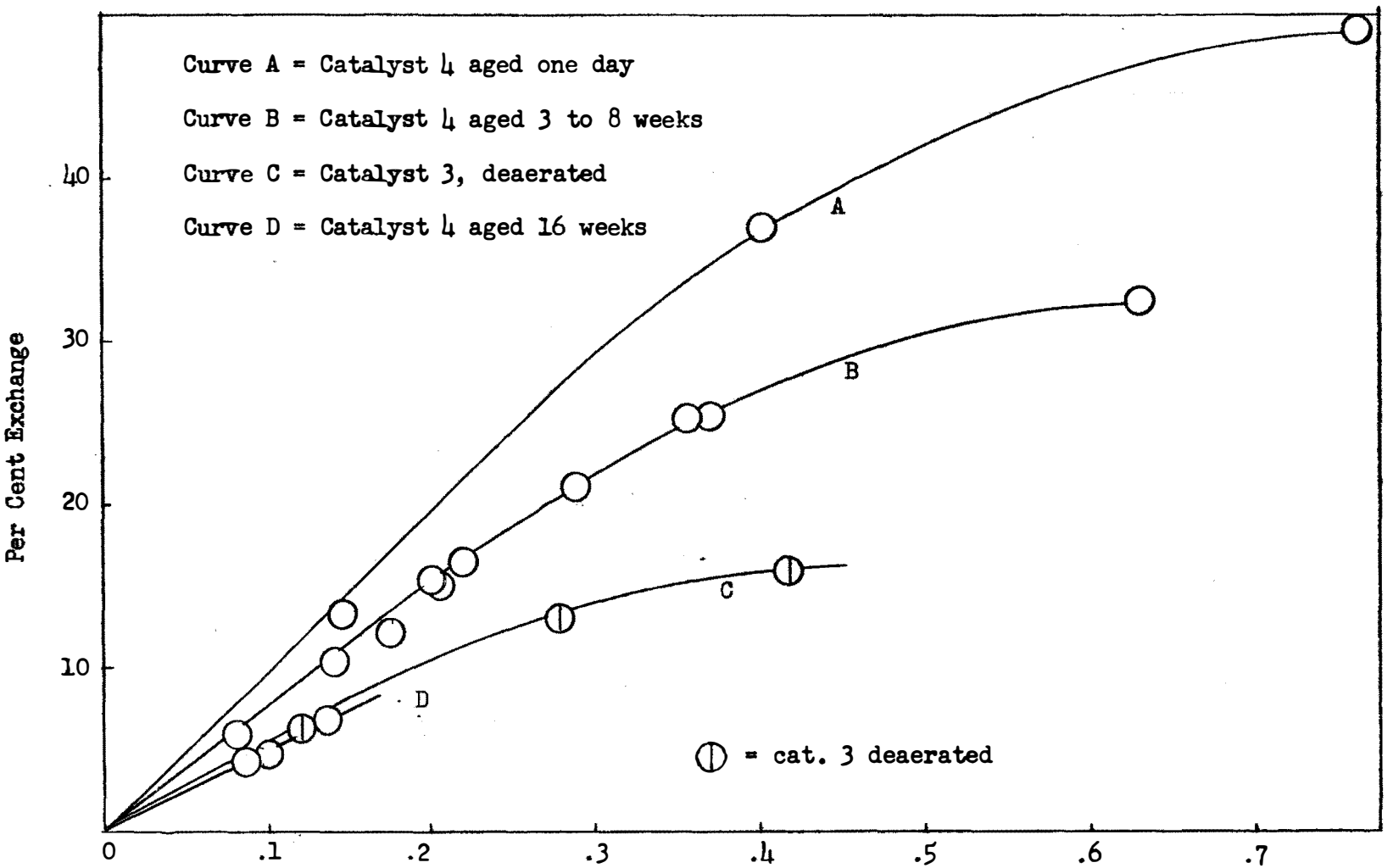


Figure 2. The effect of catalyst weight, method of washing, and aging upon the exchange of deuterium with methanol.

TABLE I

CATALYST WEIGHT RUNS FOR DEUTERIUM METHANOL EXCHANGE

% Exchange	Catalyst Weight (g.)	% Ex. $g.^{-1}$ $min.^{-1}$
55.75	0.8219	6.78
52.06	0.8367	6.22
49.64	0.7578	6.55
21.06	0.2926	7.20
5.73	0.0860	6.66
10.37	0.1361	7.62
25.48	0.3703	6.88
16.71	0.2206	7.57
11.78	0.1760	6.69
16.76	0.2334	7.18
	Average	7.11[a]

[a]Omitting first three values. Standard deviation is ± 0.39.

TABLE II

COMPARISON OF CATALYSTS FOR THE DEUTERIUM-METHANOL EXCHANGE REACTION

Catalyst	Catalyst Weight (mg.)	Reaction Time (min.)	Per Cent Exchange	Per Cent Exchange ($mg.^{-1}$ $min.^{-1}$)
Adams platinum	2	5	30.2	3.02[a]
Five per cent rhodium on alumina	25	5	23.2	0.186[a]
Raney nickel	111	5	13.5	0.0243[a]
Raney nickel	327	10	74.1	0.0227[b]
Raney nickel	All less than 371	10	From 5 to 25	0.00711[c]

[a]Previous work.[13]

[b]Present work with a very active sample. This is probably due to some directly liberated hydrogen.

[c]Adopted average value of seven determinations for the standard catalyst activity.

B. Shaking Rate

In order to eliminate either of the diffusion steps from being slow (rate determining), it was necessary to determine the minimum shaking rate for which equilibrium conditions were still met. As shown in Figure 3, a shaking rate of about 270 c.p.m. eliminated diffusion from being rate controlling. These runs were made with 10 ml. of methanol at 35° for ten minutes and at 799 mm. Hg pressure of deuterium. Catalyst weights were less than 0.35 g.

C. Effect of Deuterium Pressure

In order to determine the order with respect to deuterium pressure, several runs at various pressures were carried out as shown in Figure 4. The per cent exchange per gram per minute decreases linearly with an increase in deuterium pressure above about 400 mm. Hg. This represents an increase in the measured amount of deuterium after the exchange runs but it must be remembered that more deuterium gas was present at the higher pressures.

Using the equation of van't Hoff, the order with respect to deuterium was calculated. Taking two points on the straight line for the values of P_o (the corrected initial deuterium pressure) and for the values of % Ex. $g.^{-1}$ $min.^{-1}$, the equation gives zero for the order with respect to deuterium, n_{D_2}. The values substituted are given below:

$$n_{D_2} = \frac{\log .505\ (1000) - \log 1.01\ (500)}{\log 1000 - \log 500}$$

$$n_{D_2} = 0$$

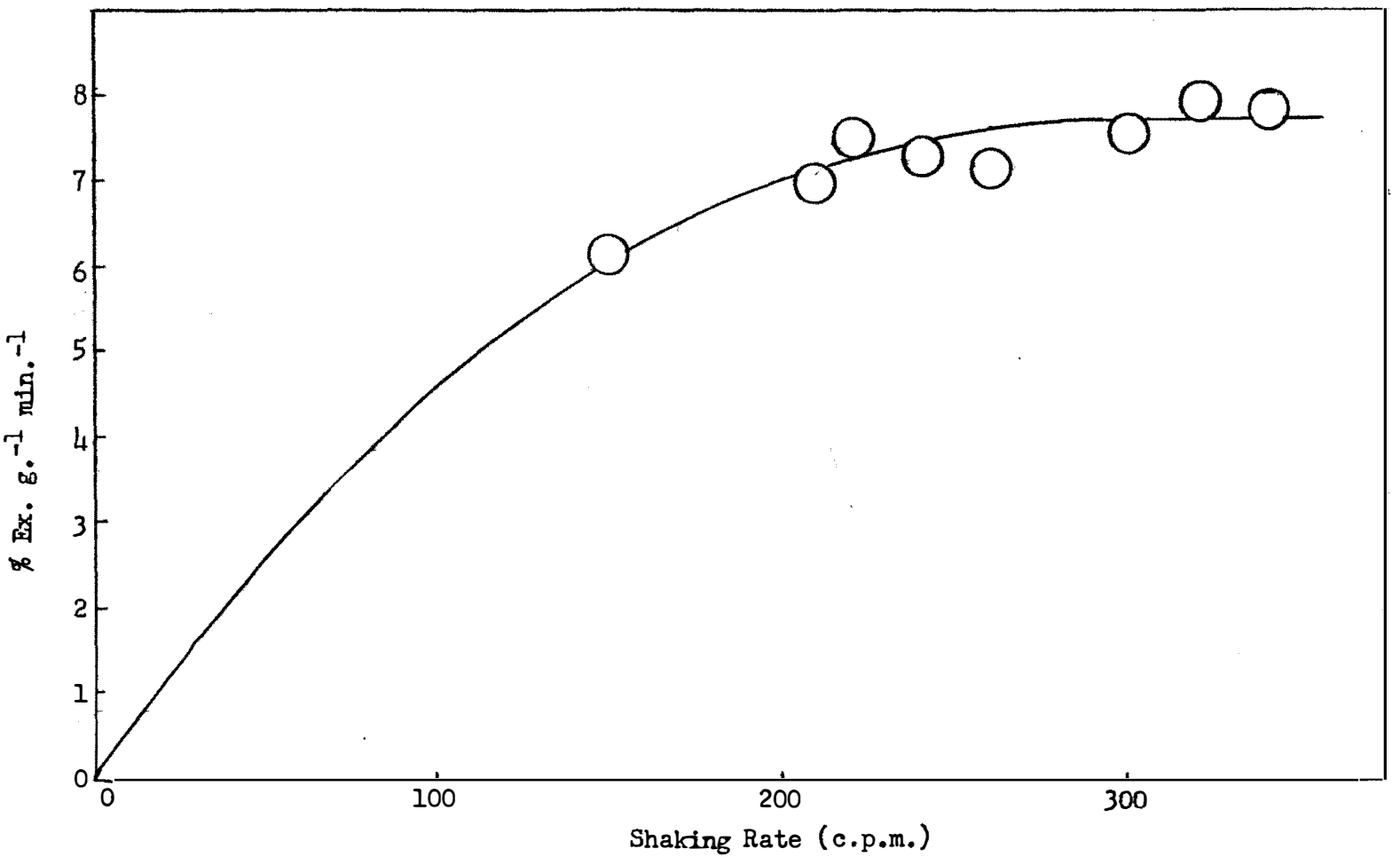


Figure 3. Effect of shaking rate upon the methanol-deuterium exchange.

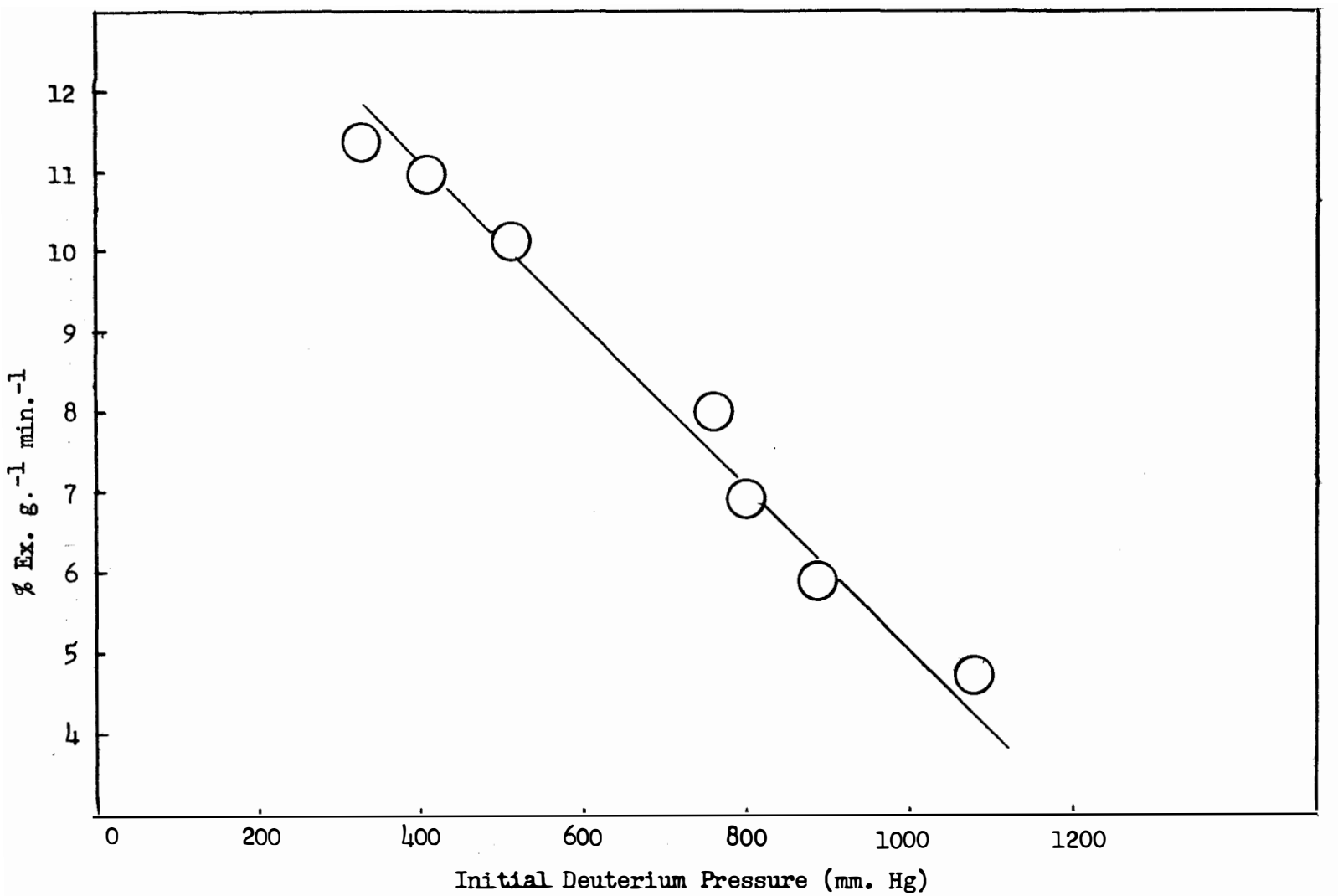


Figure 4. The effect of initial deuterium pressure upon the methanol-deuterium exchange reaction.

Since methanol was present in such a large excess, the concentration changed less than 1 per cent during a run and may be regarded as remaining constant. The order could be determined using various concentrations of methanol in some non-exchanging solvent such as cyclohexane. It would be interesting to know the actual order with respect to methanol. In the present work, it would be pseudo-zero order.

The zero order rate constants at each pressure were calculated with the expression:

$$k_{1.0} = \frac{P_{H_2}}{t} = \frac{P_o \cdot \% \text{ Ex. } g.^{-1}}{100 \cdot t}$$

where P_o is the corrected deuterium pressure, % Ex. $g.^{-1}$ is the calculated exchange for the given P_o, and t is the time in minutes. Table III shows that the zero order constants are fairly constant above P_o = 507 mm. Hg. Below this pressure there is probably insufficient deuterium to give equilibrium surface coverage of the catalyst. The average value neglecting the first two points is 54.5 mm. $min.^{-1}$ $g.^{-1}$.

The zero order constant should be corrected for the volume of gas in the system (53 ml.) in order to make a comparison with other constants obtained with a different system. Thus the value 54.5 mm. $min.^{-1}$ $g.^{-1}$ would become 2.9 l. mm. $min.^{-1}$ $g.^{-1}$.

Apparently the deuterim-methanol reaction under the conditions of the present work has a Rideal-Eley mechanism, which considers one reactant adsorbed and one reactant in the van der Waals layer next to the surface. A characteristic of this mechanism is a limiting value for the rate as the pressure of the adsorbed reactant is increased. This was found true for deuterium in the present work.

TABLE III

ZERO ORDER RATE CONSTANTS FOR DEUTERIUM-METHANOL EXCHANGE AT 35°

P_{D_2} (mm. Hg)	P_o (mm. Hg)	% Ex. $g.^{-1}$	P_{H_2} (mm. Hg)	t (min.)	$k_{1.0}$ (mm. $min.^{-1}$ $g.^{-1}$)
524	323	113.5	366.6	10	36.7
604	403	110.7	446.1	10	44.6
708	507	102.1	517.6	10	51.7
962	761	80.5	612.6	10	61.3
1000	799	69.4	554.5	10	55.5
1098	897	58.2	522.1	10	52.2
1282	1081	48.6	525.4	10	52.5
				Average	54.5[a]

[a]Neglecting first two values.

Zero order dependency of the deuterium pressure indicates strong adsorption of deuterium. The mechanism could be represented as follows:

$$D_2 + \text{-M-M-} \rightleftharpoons \overset{D}{\text{-M}}\text{-}\overset{D}{\text{M-}}$$

$$\overset{D}{\text{-M}}\text{-}\overset{D}{\text{M-}} + CH_3OH \longrightarrow \text{-M-M-} + HD + CH_3OD$$

It might be of interest to measure the actual surface coverage to determine if the entire surface is saturated with deuterium and hydrogen.

D. Effect of Time

As shown in Appendix III, the zero order expression for the exchange reaction predicts a straight line when $P_o - P_{H_2}$ is plotted <u>versus</u> reaction time. P_o is the corrected deuterium pressure and P_o is the pressure. P_{H_2} is given by:

$$P_{H_2} = \frac{\%\ Ex.\ g.^{-1}}{100}\ P_o$$

Figure 5 shows that the plot is linear for the exchange to 42 per cent reaction. The points represent individual runs for the given times. A single run cannot be followed since the gases are lost upon analysis.

E. Effect of Temperature

Runs were made at four temperatures to determine the apparent activation energy. The rate constants for these temperature are given in Table IV. A plot of log $k_{1.0}$ <u>versus</u> 1/T is shown in Figure 6. The activation energy is 3.47 kcal./mole which seems low compared to 5.5 kcal./mole for the deuterium-methanol exchange over Adams platinum.[13e] With

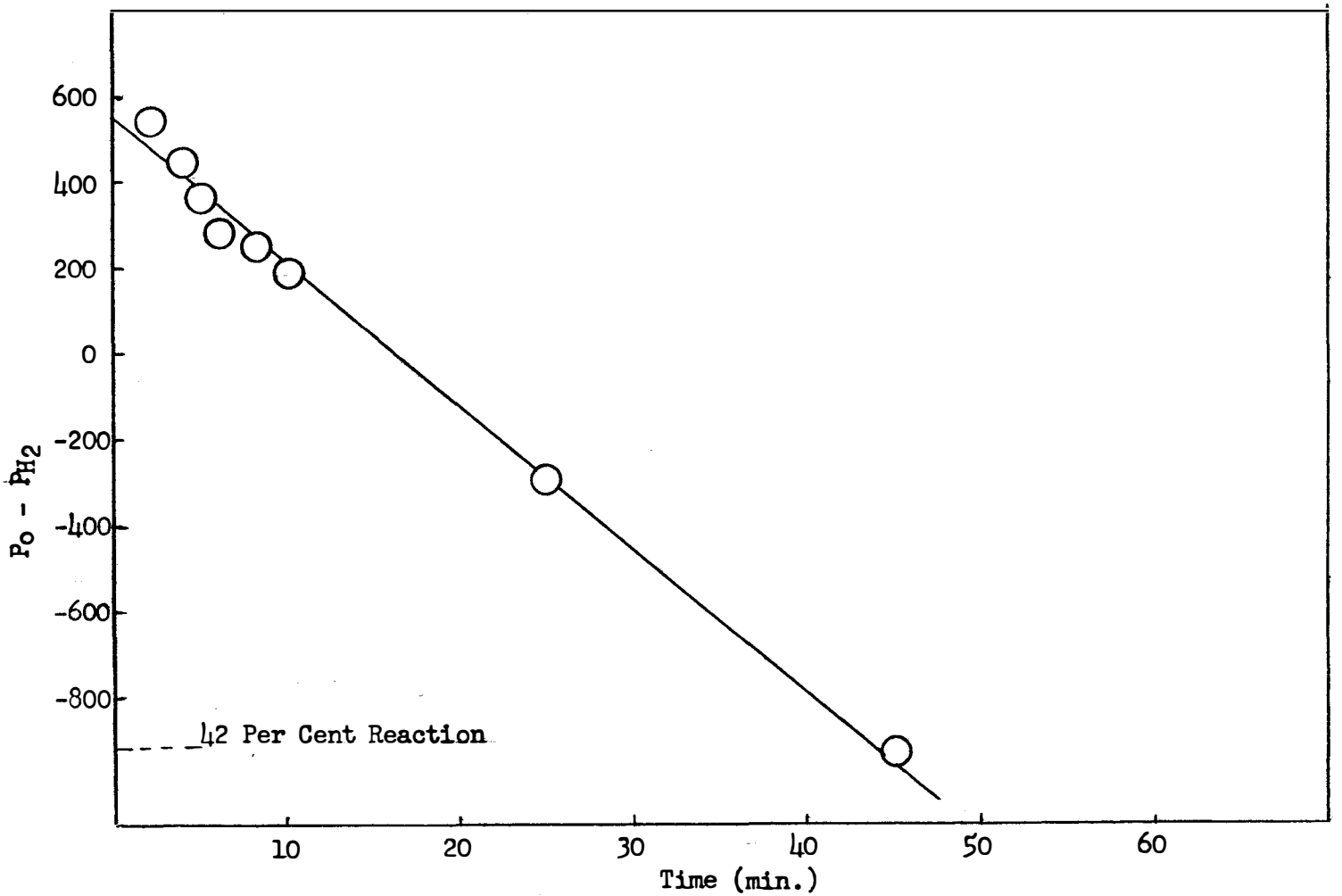


Figure 5. Zero order plot for deuterium-methanol exchange.

TABLE IV

RATE CONSTANTS AT VARIOUS TEMPERATURES FOR DEUTERIUM-METHANOL EXCHANGE

$k_{1.0}$ (mm. $min.^{-1}$ $g.^{-1}$)	log $k_{1.0}$	t (^{o}C)	$\frac{1}{T}$ ($^{o}K^{-1}$)
62.9	1.799	39.9	.00319
55.5	1.744	35.0	.00325
50.0	1.699	29.0	.00331
46.1	1.663	23.6	.00337

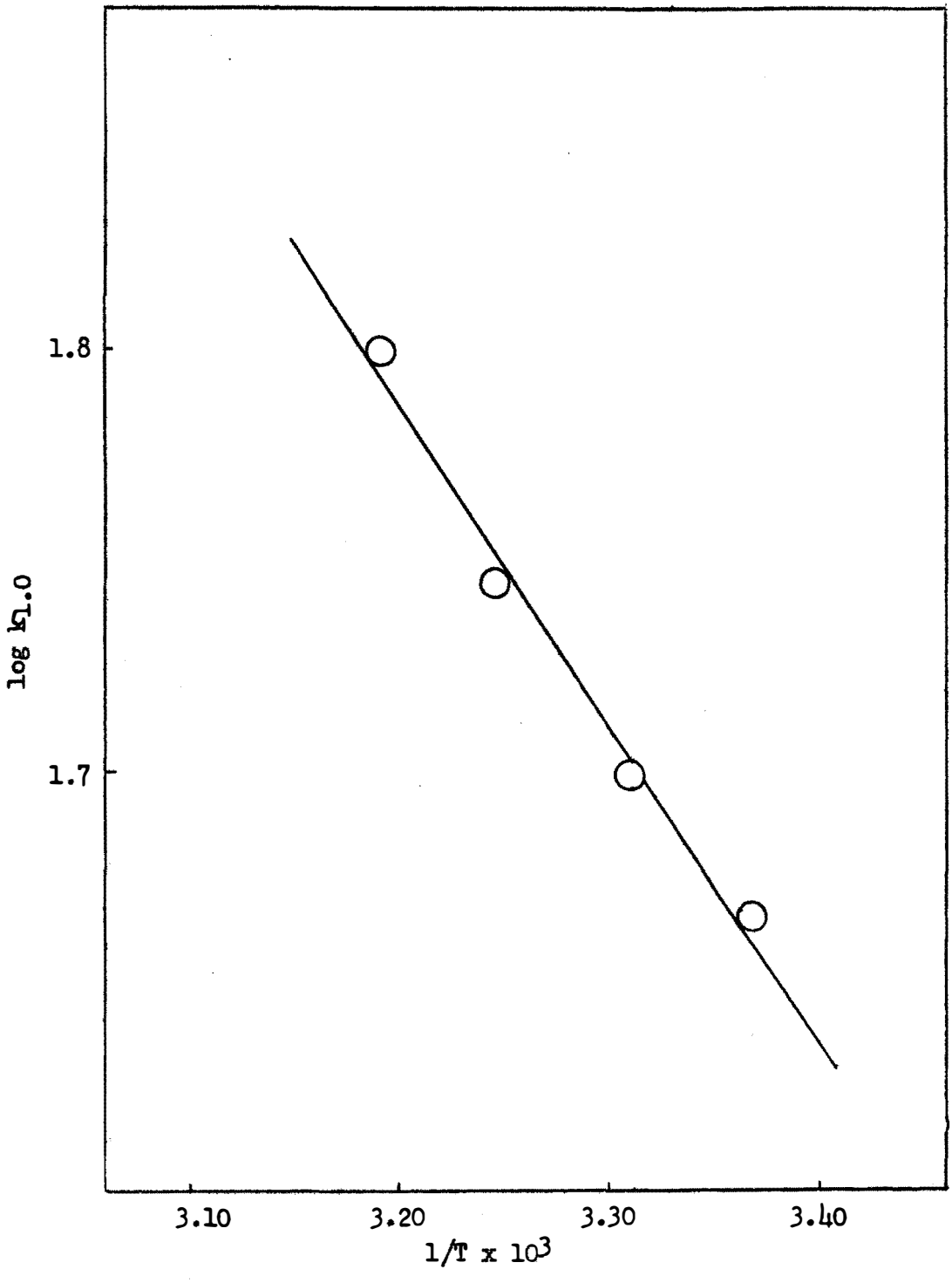


Figure 6. Activation energy plot for deuterium-methanol exchange.

platinum, however, there was a considerable scattering of the points and the value may be too high.

F. Effect of Nitro Compounds

Various concentrations of nitromesitylene, nitroethane, beta-nitrostyrene, nitrobenzene, and 2-nitro-1-butene were used to determine their effect upon the deuterium-methanol exchange. The reactions were run for ten minutes at 35.0°C, with an initial deuterium pressure of 799 mm. Catalyst weights were generally less than 0.35 g. The data are given in Tables V and VI. Plots are given in Figures 7 and 8.

All of the nitro compounds decreased the exchange at low concentrations. This effect was noted also using Adams platinum for the deuterium-methanol exchange.[13f] The relative order of the effect is the same as for the platinum results.

The kinetics of catalytic hydrogenation of the nitro compounds in ethanol over Raney nickel are zero order in acceptor, indicating strong adsorption of the nitro compounds on the catalyst.[6b,6c] It is expected that the same kinetic results would be obtained using methanol solvent with possibly a shift in the rates of hydrogenation for all compounds. The exchange results also indicate strong adsorption of all acceptors except for nitromesitylene.

Of interest is the fact that with nitromesitylene an exchange value almost equal to that with pure methanol was obtained. There was no significant decrease for concentrations as great as 0.27 moles per liter. Some early

TABLE V

THE EFFECT OF NITROMESITYLENE UPON THE EXCHANGE OF DEUTERIUM WITH METHANOL OVER RANEY NICKEL AT 35° FOR TEN MINUTES

Solute	Concentration Moles/Liter	% Ex. $g.^{-1}$
None		71.1
Nitromesitylene	0.0134	40.4
	0.0474	96.1[a]
	0.1723	82.8[a]
	0.0454	65.6
	0.0454	63.7
	0.0705	64.5
	0.0992	57.5
	0.2710	63.7
	0.2710	67.2
	0.2710	63.2
	0.0198	48.1[b]
	0.0935	60.8[b]
	0.1674	60.8[b]

[a]Minimum values.

[b]Corrected to standard catalyst activity.

TABLE VI

THE EFFECT OF SOME NITRO COMPOUNDS UPON THE EXCHANGE OF DEUTERIUM WITH METHANOL OVER RANEY NICKEL AT 35° FOR TEN MINUTES

Solute	Concentration Moles/Liter	% Ex. $g.^{-1}$
None		71.1
Nitroethane	0.0340	35.3
	0.0680	19.4
	0.1020	4.34
	0.1360	0
beta-Nitrostyrene	0.0129	47.8
	0.0587	14.1
	0.0971	7.36
	0.1553	0
	0.2279	0
Nitrobenzene	0.0257	17.7
	0.0514	11.5
	0.0771	0
	0.1285	0
2-Nitro-1-butene	0.0169	19.2
	0.0338	0
	0.0676	0

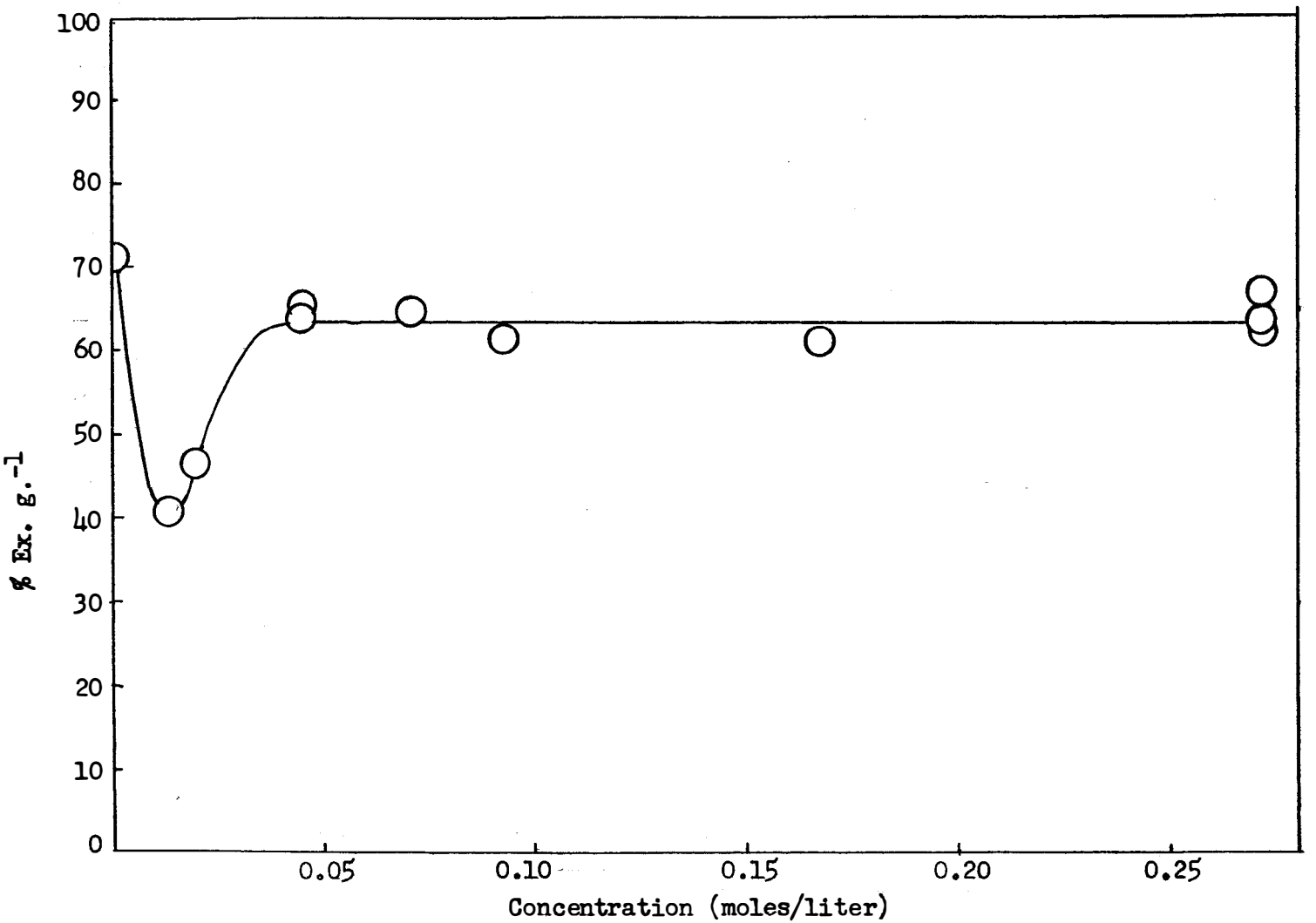


Figure 7. Effect of nitromesitylene upon the exchange of deuterium with methanol.

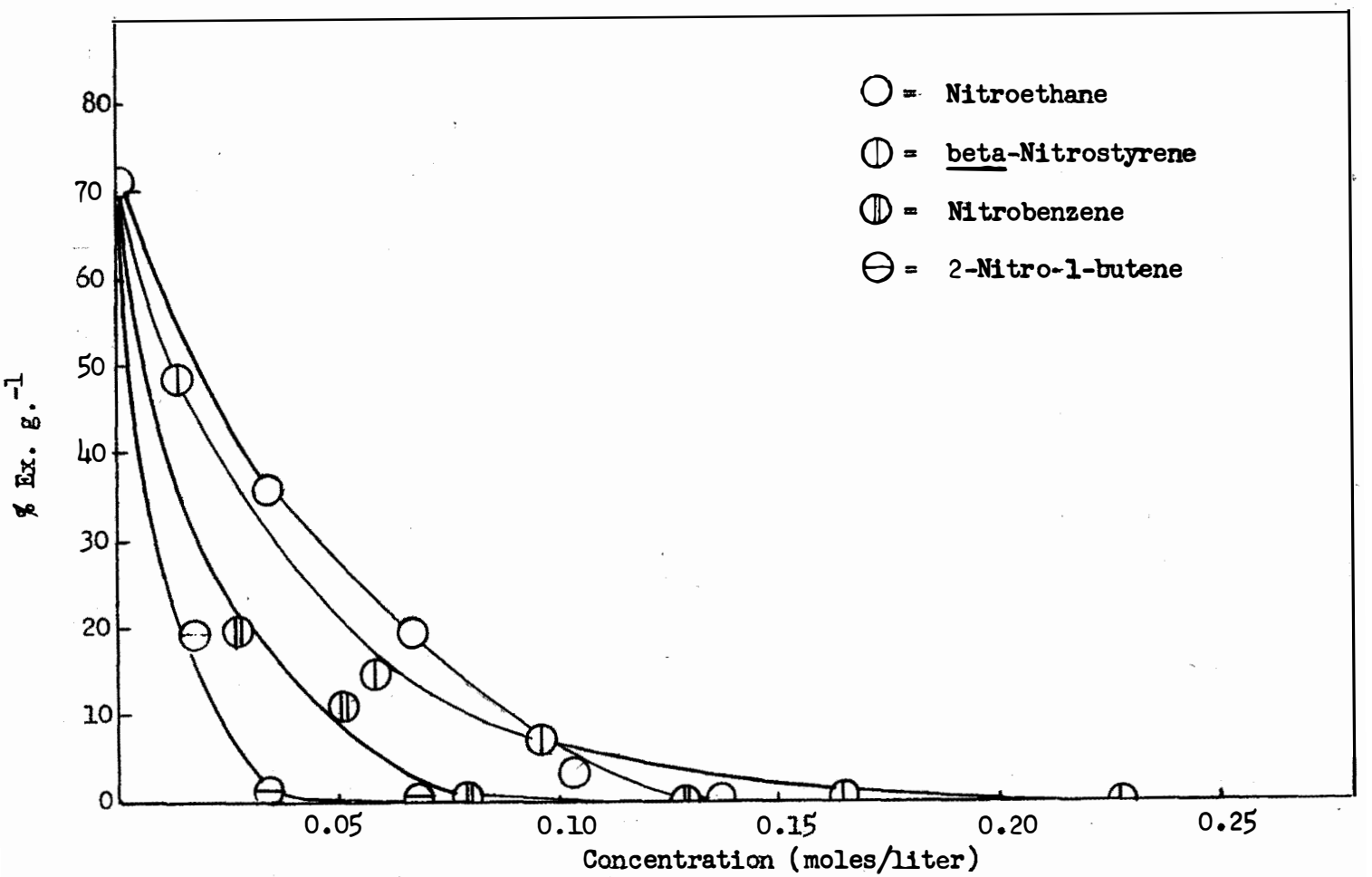


Figure 8. Effect of some nitro compounds upon the exchange of deuterium with methanol.

runs with nitromesitylene and one with beta-nitrostyrene gave much higher apparent exchanges. The calculated exchanges for two runs with nitromesitylene were much greater than for methanol alone. Less active catalyst samples did not give this effect. When these high exchange runs were carried out, a great evolution of gas was observed during the freezing and thawing steps. Thus it was concluded that, in those cases at least, the values for exchange higher than solvent alone were due to directly liberated hydrogen. This may be a special effect with very active catalyst brought about by nitromesitylene which is weakly adsorbed above a concentration of 0.04 moles per liter. A possibility that has not been previously suggested is that freezing and thawing of the mixtures containing these solutes tends to pulverize the catalyst due to expansion-contraction when the solute was precipitated and dissolved. Either greater activity due to smaller catalyst particles or occluded hydrogen freed directly from the interior of some particles could account for this increase in per cent hydrogen.

Even though it was observed only with nitromesitylene and beta-nitrostyrene, it might have been due to hyperactive portions of the catalyst, randomly sampled. Variation of catalyst activity from sample to sample was a great source of difficulty with all exchange runs.

Such increased exchange effects for the deuterium-acetic acid system using supported rhodium catalyst have been previously attributed to intermediates which might have active hydrogens to participate in the exchange reactions.[13g]

One normal exchange run was tested for liberation of hydrogen by the method previously described. Within experimental error, no hydrogen was liberated. A method of magnifying the pressure change and controlling very precisely the temperature of the apparatus might have shown a slight contribution due to directly liberated hydrogen. When the liberation is very great the present method will work very well.

G. Exchange of Heavy Methanol

Experiments were made to establish that the hydroxyl hydrogen of ordinary methanol was actually involved for the exchange reactions. For a single exchange run, less than 1 per cent of the methanol would be deuterated and thus an analysis of the methanol would be rather difficult.

An exchange run using 10 ml. of heavy methanol (CH_3OD) and 53 ml. of deuterium at 799 mm. for ten minutes and at 35° gave no exchange. This is direct evidence that the hydrogen originates neither from the catalyst nor from the hydrogen attached to the carbon of methanol.

Another run was carried out using 10 ml. of heavy methanol (CH_3OD) and 53 ml. of hydrogen at 799 mm. for ten minutes and at 35°. The exchange (9.99 % Ex. $g.^{-1}$ $min.^{-1}$) was comparable to that obtained (7.11 % Ex. $g.^{-1}$ $min.^{-1}$) using ordinary methanol with deuterium.

To insure that the tank hydrogen did not contain sufficient oxygen or other impurities to affect the effusion time of the exchange mixture, two runs were made using 10 ml. of ordinary methanol and 53 ml. of hydrogen at 799 mm. for ten minutes and at 35°. Both runs gave essentially

the same result. No significant impurities were present in the gas mixtures as shown by effusiometry analysis. Both samples contained hydrogen which effused with the same rate as tank hydrogen. The ratio of effusion times for deuterium and tank hydrogen was 1.394 which agreed exactly with some earlier calibrations. The ratio of effusion times for deuterium and sample hydrogen was 1.393 for one run, and 1.394 for another. Thus, it was concluded that the calculated exchange of hydrogen with heavy methanol was a good value. Also it was concluded that the hydroxyl hydrogen of methanol is involved in the exchange reaction with deuterium.

CHAPTER IV

SUMMARY

An improved effusiometry apparatus for analyzing hydrogen and deuterium mixtures was constructed and utilized to study the exchange reaction of deuterium with methanol over Raney nickel catalyst.

The exchange reaction was zero order with respect to deuterium pressure and pseudo-zero order with respect to methanol concentration. The apparent activation energy was found to be 3.5 kcal./mole. The specific reaction rate constant was 2.9 l. mm. $min.^{-1}$ $g.^{-1}$.

The effects of nitro compounds upon the exchange of deuterium with methanol over Raney nickel were studied. All of the compounds decreased the exchange at very low concentrations and all, except nitromesitylene, prevented the exchange at higher concentrations. Except for nitromesitylene, the effects paralleled the kinetics of catalytic hydrogenation of these nitro compounds under similar conditions.

Since Raney nickel can liberate hydrogen directly, a method for determining per cent exchange in its presence was developed. It was shown that the exchanged hydrogen did originate from the hydroxyl hydrogen of methanol.

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APPENDICES

APPENDIX I

DERIVATION OF EFFUSION EQUATION

From Graham's Law of Effusion in terms of the densities and noting that the volumes are the same, one can obtain:

$$t_{D_2}^2 \, g_{H_2} = t_{H_2}^2 \, g_{D_2} \tag{1}$$

and

$$t_{D_2}^2 \, g_{X_2} = t_{X_2}^2 \, g_{D_2} \, . \tag{2}$$

Also

$$t_{D_2}^2 \, g_{D_2} \equiv t_{D_2}^2 \, g_{D_2} \tag{3}$$

Appropriate substractions and divisions give:

$$\frac{t_{D_2}^2 - t_{X_2}^2}{t_{D_2}^2 - t_{H_2}^2} = \frac{g_{D_2} - g_{X_2}}{g_{D_2} - g_{H_2}} \tag{4}$$

Consider two different volumes of gas to be analyzed. The first is a mixture of hydrogen and deuterium, and the weight of the mixture (g_{X_2}) is the sum of the weight of hydrogen (g_{H_2}) and the weight of deuterium (g_{D_2}):

$$g_{X_2} = g_{H_2} + g_{D_2} \tag{5}$$

Thus the numerator for the right side of equation (4) becomes $- g_{H_2}$, which should be denoted $- g'_{H_2}$ where the prime refers to sample hydrogen.

The second volume is pure hydrogen, and the weight of deuterium is zero. Thus the denominator of equation (4) becomes $- g_{H_2}$. Equation (4) reduces to:

$$\frac{t_{D_2}^2 - t_{X_2}^2}{t_{D_2}^2 - t_{H_2}^2} = \frac{g'_{H_2}}{g_{H_2}} = \frac{n'_{H_2}}{n_{H_2}} \qquad (6)$$

The number of moles of hydrogen, n_{H_2}, for a given volume of 100 per cent hydrogen is equal to the sum of the number of moles of sample hydrogen, n'_{H_2}, and deuterium, n'_{D_2}, at the same given volume, temperature, and pressure. In symbols,

$$n_{H_2} = n'_{H_2} + n'_{D_2} \qquad (7)$$

Therefore by substitution of equation (7) into equation (6), one has

$$\text{Mole per cent hydrogen} = \frac{n'_{H_2}}{n'_{H_2} + n'_{D_2}} 100 = \frac{t_{D_2}^2 - t_{X_2}^2}{t_{D_2}^2 - t_{H_2}^2} 100 \qquad (8)$$

Mole per cent hydrogen can be abbreviated % H_2, and mole per cent exchange can be abbreviated % Ex.

APPENDIX II

DERIVATION OF EXCHANGE EQUATION FOR HYDROGEN DIRECTLY LIBERATED

By definition:

$$\text{Mole percentage } H_2 = \frac{n_{H_2}}{n_{H_2} + n_{D_2}}(100) = \frac{P_{H_2}}{P_{H_2} + P_{D_2}}(100) \qquad (1)$$

Also, as derived in Appendix I, one has:

$$\text{Mole percentage } H_2 = \frac{t_{D_2}^2 - t_{X_2}^2}{t_{D_2}^2 - t_{H_2}^2}(100) \qquad (2)$$

All of the above symbols refer to actual quantities or readings for the components of any mixture. The following must be true for any exchange run:

$$P_{H_2} = P_{H_2(e)} + P_{H_2(l)} \qquad (3)$$

where the subscripts (e) and (l) refer to exchanged and liberated hydrogen. Also the following will be true:

$$P_{D_2(i)} = P_{D_2} + P_{H_2(e)} \qquad (4)$$

where the subscript (i) refers to the initial deuterium pressure. By substitution:

$$P_{H_2} = P_{D_2(i)} - P_{D_2} + P_{H_2(l)} \qquad (5)$$

Therefore:

$$\text{Mole percentage } H_2 = \frac{P_{D_2(i)} - P_{D_2} + P_{H_2(l)}}{P_{D_2(i)} + P_{H_2(l)}}(100) \qquad (6)$$

Solving for P_{D_2}:

$$P_{D_2} = \left[1 - \frac{\% H_2}{100}\right] \left[P_{D_2(i)} + P_{H_2(l)}\right] \qquad (7)$$

Also:

$$\% \text{ Ex.} = \frac{P_{H_2(e)}}{P_{H_2(e)} + P_{D_2}} (100) = \frac{P_{D_2(i)} - P_{D_2}}{P_{D_2(i)}} (100) \qquad (8)$$

Substituting equation (7) into equation (8), one obtains:

$$\% \text{ Ex.} = \frac{\left\{P_{D_2(i)} - \left[\frac{100 - \% H_2}{100}\right] \left[P_{D_2(i)} + P_{H_2(l)}\right]\right\} 100}{P_{D_2(i)}} \qquad (9)$$

Simplification gives the following:

$$\% \text{ Ex.} = 100 - \left[100 - \% H_2\right] \left[1 + \frac{P_{H_2(l)}}{P_{D_2(i)}}\right] \qquad (10)$$

where $\% H_2 = \frac{t_{D_2}^2 - t_{X_2}^2}{t_{D_2}^2 - t_{H_2}^2}(100)$

$P_{H_2(l)}$ = measured increase in pressure for expansion into a fixed volume, before and after exchange reaction.

$P_{D_2(i)}$ = corrected pressure for expansion of initial deuterium into same fixed volume.

Several special conditions have been examined to check the equation:

(1) No liberated hydrogen but some exchanged hydrogen.

(2) No liberated or exchanged hydrogen.

(3) No exchanged hydrogen but some liberated hydrogen.

(4) Both liberated and exchanged hydrogen.

The equation gives the exact answers for each of these conditions.

APPENDIX III

DERIVATION OF RATE EXPRESSION

The rate of the exchange reaction of deuterium with methanol is given by:

$$\frac{dP_{H_2}}{dt} = kP_{D_2}^{n} \tag{1}$$

where P_{H_2} is the pressure of hydrogen formed in the exchange, P_{D_2} is the pressure of deuterium, k is the specific reaction rate constant, and n is the order of the reaction with respect to deuterium.

A hydrogen molecule arises for every deuterium molecule used in the exchange. Thus the deuterium pressure at any time is:

$$P_{D_2} = P_o - P_{H_2} \tag{2}$$

where P_o is the initial deuterium pressure. P_{H_2} is given by:

$$P_{H_2} = \frac{\% H_2 \cdot P_o}{100} \tag{3}$$

where $\% H_2$ is the mole per cent hydrogen. The following is obtained by substitution of (2) into (1):

$$\frac{dP_{H_2}}{dt} = k (P_o - P_{H_2})^{n} \tag{4}$$

Also

$$\frac{dP_{H_2}}{(P_o - P_{H_2})^{n}} = kdt \tag{5}$$

when $n \neq 1$, the integrated solution to equation (5) is as follows:

$$\frac{(P_o - P_{H_2})^{1-n}}{-(1 - n)} = kt + C \tag{6}$$

At $t = 0$, $P_{H_2} = 0$; at $t = t$, $P_{H_2} = P_{H_2}$. Therefore,

$$\frac{P_o^{(1-n)} - (P_o - P_{H_2})^{(1-n)}}{(1 - n)} = kt \tag{7}$$

When $n = 0$, this becomes:

$$P_{H_2} = kt$$

$$k = \frac{P_{H_2}}{t} \tag{8}$$

A plot of $P_o - P_{H_2}$ <u>versus</u> t should give a straight line having a slope of -k. Direct calculation from a single run can be made from the following expression:

$$k_{1.0} = \frac{P_o \cdot \% \text{ Ex. g.}^{-1}}{100\ t}$$

VITA

Burch Byron Stewart was born in Chattanooga, Tennessee, on May 7, 1929. He received his elementary and high school education in Fountain City, Tennessee. He attended the University of Tennessee from June, 1947 until December, 1948 on a scholarship sponsored by the Westinghouse Science Talent Search for 1947. In December of 1950 he entered the Navy for two years during the Korean War. In January, 1953, he returned to the University of Tennessee to complete his undergraduate work and begin graduate work.

He was employed in the Rhenium Research Laboratory of the University of Tennessee Department of Chemistry from May, 1953 to September, 1954, on a part-time basis. In the fall of 1954 he was granted a graduate assistantship, and in September, 1956, he was granted a research assistantship sponsored by the Atomic Energy Commission. He received the Bachelor of Science in Chemistry degree in March, 1955, and the Master of Science degree in chemistry in March, 1957.

He was awarded the Student Award of the East Tennessee Section of the American Chemical Society for 1954 and the Merck Index Award for 1954. He is a member of the Society of the Sigma Xi, the American Chemical Society, and the Alpha Chi Sigma chemical fraternity.

He is married to the former Lois M. Speaker of Neptune, New Jersey, and has one daughter, Leslie Elizabeth.