

CATALYTIC DIMERIZATION OF PROPYLENE
IN A PRECISION MICROREACTOR

by

Thomas P. Shackelford

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SIGNED: Thomas P. Shackelford

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

J. W. Hall
J. W. Hall
Associate Professor of
Chemical Engineering

Nov. 8, 1965
Date

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ABSTRACT

The dimerization of propylene to 1-hexene over a silica-alumina fluid cracking catalyst has been studied. The kinetics of this reaction were defined by determination of the activation energy of the reaction and the order of the reaction. In addition, the magnitude of diffusional effects and the aging characteristics were determined.

Kinetic data were taken using a newly constructed precision microreactor. A reactor of less than one cubic centimeter volume could be immersed in a fluidized sand constant temperature bath. Gaseous feed metered through mass flowmeters at a rate of 20 to 60 cc/min was preheated in the sand bath before it reached the microreactor. The effluent from the microreactor was sampled by a solenoid switch valve and analyzed by a gas chromatograph.

The ability of this microreactor apparatus for measuring the kinetics of the dimerization of propylene has been demonstrated. By precise analysis procedures and unique treatment of data, it was possible to single out one of several simultaneous reactions for study.

The activation energy for the dimerization of propylene was calculated to be 9.2 kcal/g-mole. A reaction order of three was determined.

I. INTRODUCTION

Since the discovery of catalytic phenomena, interested investigators have had many difficulties in studies involving catalytic reactions. It was necessary to surmount major problems of inefficient, awkward equipment and imprecise analytical techniques. In recent years, great strides forward in precise analytical instruments, many of them entirely automatic, have helped the researcher in catalysis to better define and solve analytical problems. In addition, new knowledge of catalysts and techniques made more and more sophisticated have combined with better equipment to make catalysis and kinetic studies more accurate and more satisfying. In the present study, these recent developments were combined to produce a precision microreactor system.

Kokes, Tobin, and Emmett (9) were the first to combine the usefulness of chromatographic analysis precision with the advantages of a differential reactor. These investigators found that by attaching a reactor unit to the inlet of a chromatograph column, one could inject small quantities of reactant into a suitable carrying gas, pass the mixture over a catalyst and analyze the exit gas from the reactor by passing it directly into the chromatographic

column. The reaction used to demonstrate the apparatus was the decomposition of 2,3-dimethylbutane over cracking catalyst.

Later, Emmett and W. K. Hall (3) expanded on Emmett's previous work by showing the utility and reproducibility of the equipment. The previous arrangement had two major drawbacks: 1) the reproducibility was limited by the accuracy by which gases or extremely small samples of liquid can be measured and transferred in hypodermic syringes; and 2) in studies over reduced metal catalysts (particularly of low surface areas) oxygen diffusing in through the serum cap could irreversibly poison the catalyst. Emmett and Hall described techniques for circumventing these problems. In addition, a method was devised for synthetic blends that could be used in calibration or in the actual catalytic study. This involved metering of reactant gases in a closed system and taking constant volume samples mechanically.

In the course of this experimentation, certain additional advantages were discovered:

- 1) With this new technique, the reaction vessels became nearly isothermal reactors.
- 2) Information obtained from one slug of reactant gas could be used immediately to establish conditions for the next.

- 3) The technique was useful for studies involving changes in catalytic activity.
- 4) The technique was useful for determining the effects of small amounts of poisons.
- 5) Employing a "tail-gas" technique, where samples of a continuous reactor effluent could be taken, steady-state reactions could be studied.

W. K. Hall, MacIver, and Weber (6), employing Hall's more sophisticated apparatus, studied the polymerization of propylene and cracking of 2,3-dimethylbutane over silica-alumina cracking catalysts. Useful information with satisfactory precision was obtained by combining both the original "slug" technique and the "tail-gas" technique.

Harrison, J. W. Hall and Rase (7), with the benefit of the discoveries of the above authors, developed a completely automatic precision microreactor. Utilizing this new automatic microreactor apparatus, J. W. Hall and Rase (5) examined the effect of dislocations on the catalytic activity of LiF crystals. The design for the microreactor used in the present study came largely from this work.

The newly constructed microreactor apparatus and development of new analytical procedures enabled the author to single out and study one of the 15 observed products

of the polymerization of propylene on silica-alumina cracking catalyst. The kinetics of the dimerization of propylene to 1-hexene has received very little attention by previous investigators. With the present high interest in biodegradable detergents, whose manufacture is based on long straight-chain olefins, 1-hexene may soon be of great importance.

Borisova, Dizisko, and Cherednik (2) studied the relation between the acidity of oxide catalysts and their activity with respect to the dimerization of propylene. The reaction was investigated in a closed circuit apparatus at constant pressure over a number of catalysts of varying composition. These investigators reported an activation energy for the reaction of 2-3 kcal/mole, but admitted that many difficulties hindered accurate determination of the activation energy of their reaction.

A catalyst for the dimerization of propylene was developed by Alderson, Hambling and Yeo (1). The catalyst was prepared by thorough stirring of molten sodium or lithium with finely divided potassium carbonate. The dimerization took place in an autoclave at 1700 lb/in² and 160°C. Distillation of the product yielded 95 per cent conversion to hexenes, but only 2.2 per cent of that was 1-hexene. No reaction kinetics were reported.

Schramm (13) developed essentially the same process, but operated at 100 atmospheres pressure and 300^oF to produce 20 per cent hexenes. Again, no reaction kinetics were reported.

It was the goal of this research to illustrate the precision and usefulness of a newly constructed microreactor apparatus by determining the kinetics of the reaction of propylene to 1-hexene over a silica-alumina catalyst.

II. THEORY

Where accurate methods of chemical analysis are available, rate equations are best established from direct rate measurements in a differential reactor containing a bed of catalyst so small that relatively small changes of composition are obtained. Such an apparatus should be designed to produce the smallest conversion that permits accurate evaluation of the rate with the available analytical methods. Because of the exponential influence of temperature in the Arrhenius equation;

$$k = A e^{-E/RT} \quad (\text{II-1})$$

where: k = reaction velocity constant;
liters/(g-mole)(sec)

A = proportionality factor characteristic of the system and termed the frequency factor.

E = the molal energy of activation,
cal/g-mole

R = the universal gas constant, 1.987
cal/(g-mole)(°K)

T = temperature, °K,

it is desirable that the differential bed be at uniform temperature. This requires a small-diameter reactor with good heat-transfer at the wall. A versatile differential reactor apparatus also permits wide variation of feed rates and depths of catalyst bed.

A differential reactor is defined as one in which the rate is constant at some average value throughout the reactor. Since reaction rates are concentration dependent, the assumption of constant rate is reasonable when conversion in the reactor is small.

Differential reactors have the advantage of furnishing a direct measure of reaction rate. A material balance for a differential element of the catalyst charge is

$$r \, dA_s = F \, dx \quad (\text{II-2})$$

where: dA_s = surface area of catalyst in the differential volume; cm^2

F = feed rate, amount per unit time; cc/min .

dx = fractional conversion, amount converted in the differential element per unit of feed; cc/cc

r = rate of reaction; $\text{cc}/(\text{min})(\text{cm}^2 \text{ of catalyst surface area})$.

In a differential reactor the fractional conversion is small, and the differentials in Eq. (II-2) can be treated as the actual change. Thus,

$$r = \frac{(F)(\Delta x)}{A_s} \quad (\text{II-3})$$

where: A_s = the surface area of the catalyst charge in the differential reactor; cm^2

Δx = fractional conversion in the differential reactor, the analysis of the product divided by the analysis of the feed; $\text{mol}\%/\text{mol}\%$.

With a knowledge of the reactor effluent, the feed rate, and amount of catalyst, the rate of reaction may be calculated directly.

An additional point in favor of differential reactors is that they are easier to operate isothermally because of the low conversion. If an energy balance is applied to a differential element of the catalyst charge, it gives

$$G C_p \frac{dT}{dz} = \Delta H_R A_x r + U A_c (T_B - T_A) \quad (\text{II-4})$$

where: G = mass flow rate of the reaction gas;
 $\frac{(\text{g-mole})(\text{cm})}{\text{min}}$

C_p = the heat capacity of the reaction gas; $\text{cal}/(\text{g-mole})(^\circ\text{C})$

$\frac{dT}{dz}$ = the change in reaction gas temperature with bed length, z ; $^\circ\text{C}/\text{cm}$

ΔH_R = heat of reaction to products;
 cal/cc

A_x = cross-sectional area of the catalyst bed at any point, z ; cm^2

U = over-all heat transfer coefficient from the catalyst bed to the heat transfer medium outside the catalyst container; $\text{cal}/(\text{min})(\text{cm}^2)(^\circ\text{C})$

A_c = catalyst bed container wall area available for heat transfer; cm^2

T_B = temperature of the catalyst bed at a point; $^\circ\text{C}$

T_A = temperature of the heat transfer medium outside of the catalyst container; $^\circ\text{C}$.

The worst case of non-isothermal conditions through the catalyst bed would be an adiabatic system where there was no heat transferred through the walls of the container, or

$$U A (T_B - T_A) = 0 .$$

If this were the case, Eq. (II-4) would become

$$\frac{dT}{dz} = \frac{\Delta H_R A_x r}{G C_p} , \quad (\text{II-5})$$

$$\text{but } r = \frac{(F) (\Delta x)}{A_s} , \quad (\text{II-3})$$

$$\text{therefore, } \frac{dT}{dz} = \frac{\Delta H_R A_x F \Delta x}{G C_p A_s} . \quad (\text{II-6})$$

The conversion in differential reactors is very small and the catalyst surface area, in general, is rather large. The combination of these two factors makes the change in temperature through the catalyst bed so small as to be considered negligible. For the microreactor system used in this study, this change was found to be approximately 0.2°C and this was considered negligible in the temperature range of $300\text{-}400^{\circ}\text{C}$ used in this study.

SOLID SURFACE REACTIONS

By definition, a catalyst is a substance which influences the rate of a reaction but is not one of the original reactants or final products. The catalyst must

participate in intermediate steps in such a manner as to facilitate the over-all course of the reaction. The activity of a catalytic surface is proportional to the number of "active sites" per unit area.

The catalyst increases the rate of reaction through its ability to adsorb the reactants in such a form that the activation energy is reduced far below the value for the uncatalyzed reaction.

Hougen and Watson (8) suggest the following steps as necessary in a solid catalyzed liquid- or gas-phase chemical reaction:

- 1) The mass transfer of reactants and products to and from the gross exterior surface of the catalyst particle and the main body of the fluid.
- 2) The diffusional and flow transfer of reactants and products in and out of the pore structure of the catalyst particle when reaction takes place at interior surfaces.
- 3) The activated adsorption of reactants and the activated desorption of adsorbed products.
- 4) The surface reaction of adsorbed reactants to chemically adsorbed products.

When a reaction is catalyzed by a solid it is presumed that the actual combination of the reactants

occurs on the surface of the solid. Such surface reactions may take place either between adsorbed reactant molecules and molecules in the fluid phase, or between adsorbed molecules on adjacently situated active sites.

Hougen and Watson developed reaction rate equations for solid catalyzed gaseous reactions based on Langmuir-Hinshelwood models. These equations take into account the ability of a reactant to adsorb to a catalyst, the number of active sites on the catalyst surface where reaction could take place, the activity of the reacting gas and all its products, a reaction driving force of activity differences, and the reaction velocity constant. For the reaction examined in the present study, the polymerization of propylene over silica-alumina cracking catalyst, such an equation would have the form,

$$r = \frac{k K L}{(1 + a_P K_P + a_A L_A + a_I K_I + \dots)} \left(a_P - \frac{a_A}{K} \right) \quad (\text{II-7})$$

where: L = number of active sites

a_P, a_A, a_I, \dots = activities of propylene, reaction products, and inerts; dimensionless

K_P, K_A, K_I, \dots = adsorption equilibrium constants for propylene, products, and inerts; dimensionless

k = reaction velocity constant,
cc/(min)(gram of catalyst)

K = overall equilibrium reaction constant,
dimensionless

γ = constant indicating the type of catalytic site mechanism involved in the reaction.

To determine the rate of propylene polymerization from Eq. (II-7) would require knowing the activities and adsorption equilibrium constants for propylene, all the 15 or more products, and any inerts in the feed. Also, the number of active sites and the overall equilibrium constant would have to be known. To simplify Eq. (II-7) to a more easily applied form, the term

$$\frac{L K}{(1 + a_P K_P + a_A K_A + a_I K_I + \dots)^{\gamma}}$$

was assumed to be essentially constant and was lumped into one term, B. The activities were expressed in terms of the surface concentrations. Thus, Eq. (II-7) became

$$r = k B (C_P - (C_A/K)) \quad (\text{II-8})$$

Since the apparatus employed in this study was a micro-reactor, differential conversion was obtained in a single pass of reaction gas over the catalyst bed. This meant that there would be a negligible reverse reaction, so that it could be said that

$$r = k B (C_P)^{\alpha} \quad (\text{II-9})$$

This is exactly the homogeneous reaction rate equation

$$r = k (C_P)^{\alpha} \quad (\text{II-10})$$

with B incorporated into the constant k, and the order of

the reaction, α , equal to 1.0. At this point, the method of initial reaction rates was applied which requires that pure reaction gas pass over the catalyst. In the present case the reaction gas was 99.5 mole per cent propylene and was considered to be pure. Therefore, no matter what the order of the reaction, α , C_p^α was 1.0 and

$$r = k \quad (\text{II-11})$$

The simplifications applied to Eq. (II-7) resulted in an expression of reaction rate equal to the reaction velocity constant. But from Eq. (II-1),

$$k = A e^{-E/RT} \quad (\text{II-1})$$

or, now

$$r = A e^{-E/RT} \quad (\text{II-12})$$

The activation energy for the reaction may be obtained by taking the logarithm of both sides of Eq. (II-12)

$$\ln r = \ln A - E/RT \quad (\text{II-13})$$

and plotting log rate versus $1/T$. The slope of such a linear plot would be $-E/R$. The constant A , the frequency factor, would serve only to displace the line produced by the plot, but would not change the slope, $-E/R$.

The above is a considerable simplification of the complex rate equations proposed by Hougen and Watson, but such complex equations were not necessary in the present

study. Lapidus and Peterson (10) support such a simplification in a study of heterogeneous catalytic reactions by nonlinear computer estimation. These investigators found degeneracy of the heterogeneous rate equations and comparatively large errors in measurement to be obscuring factors in determining whether the Langmuir-Hinshelwood models were more valid than the simpler homogeneous forms. They found it doubtful that they were.

DIFFUSION

Reaction rates are functions of activities or partial pressures of the reacting components at the surface of the catalyst. These interfacial activities may be significantly different from the activities in the main fluid stream because of the gradients required for the diffusion of reactants toward and products away from the interface. There are two types of diffusion phenomena that may be present in a solid catalyzed gaseous reaction: 1) pore diffusion, and 2) film diffusion.

In chemical reactions catalyzed by solid surfaces the reaction rate per unit mass of catalyst is influenced by the size and shape of the catalyst particle. In general, for a porous catalyst, an increase in external surface area or decrease in particle size for given surface conditions of temperature and component activities increases the

rate of reaction. For a completely impervious catalyst the reaction is confined to the external surface, and the rate is hence directly proportional to the external surface area. Thus, it is clear that the importance of pore diffusion may be examined by varying the size or shape of the reaction catalyst.

The catalyst used in the present study had an average particle diameter of 58 microns. The catalyst particles were so fine that they displayed what was considered to be a maximum exterior surface area to the reaction gas. It was assumed that this situation reduced the effect of pore diffusion to a minimum and made it unimportant.

Film diffusion concerns the effect of a stagnant film which surrounds the catalyst particles. Even under conditions of turbulent flow of feed there is always a layer of fluid at the interface in which laminar flow is maintained. The thickness of this laminar layer, or "film", depends on the conditions of flow, and becomes less as the velocity is increased. The term film as used here should not be confused with adsorbed films which may be only a single molecule in thickness.

Mass transfer is considered as resulting from molecular diffusion across the effective film under the influence of a concentration gradient. Clearly, to study

the effect of film diffusion in a solid catalyzed system, the thickness of the film must be varied. This was done in the present study by varying the velocity of the reaction gas over the catalyst particles. If experimental runs are made at constant catalyst weight to feed rate ratio, W/F , where gas film resistance is important, conversion will vary with changing gas flow rate.

ORDER OF REACTION

The order of a reaction is the value of α in the equation

$$r = k C^{\alpha} \quad (\text{II-10})$$

This value is 1.0 for a first-order reaction, 2.0 for a second-order reaction, and 3.0 for a third-order reaction. In reactions of simple order the exponent of the concentration term in the fundamental rate equation is equal to the minimum number of reactant molecules which must simultaneously combine in order to effect the reaction. This minimum number of combining molecules is termed the molecularity of the reaction (8).

To ascertain the order of a reaction, natural logarithms are taken on both sides of Eq. (II-10) giving

$$\ln r = \ln k + \alpha \ln C. \quad (\text{II-14})$$

Since the reaction velocity constant is temperature

dependent, it is held constant by holding the temperature constant. Thus, a plot of log rate versus log concentration as mole fraction gives a straight line with a slope of α . The reaction order of the dimerization of propylene to 1-hexene over silica-alumina catalyst was determined in this way.

III. EXPERIMENTAL EQUIPMENT

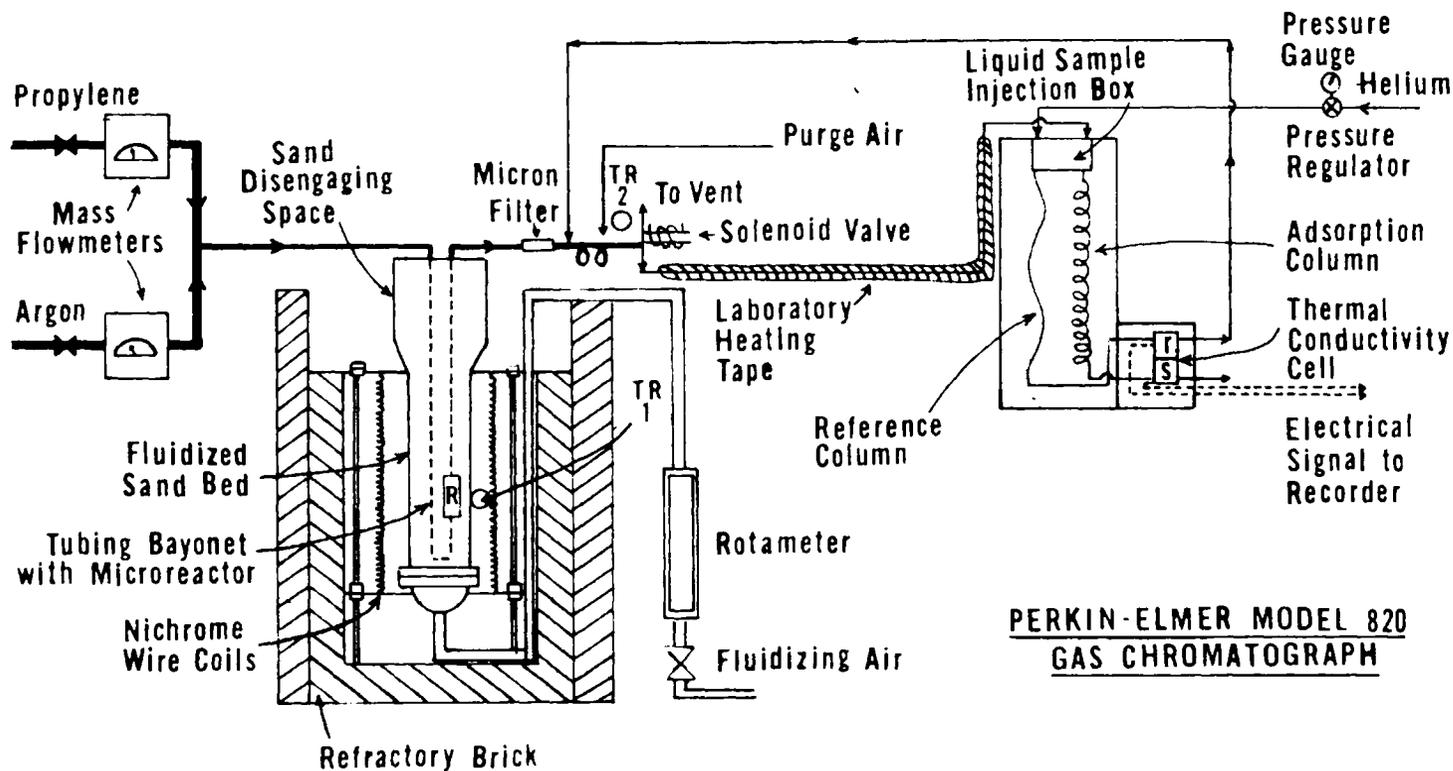
Kinetic data were taken using a newly constructed precision microreactor. A reactor of less than one cubic centimeter volume could be immersed in a fluidized sand constant temperature bath. Gaseous feed metered through mass flowmeters at a rate of 20 to 60 cc/min was preheated in the sand bath before it reached the microreactor. The effluent from the microreactor was sampled by a solenoid operated switch valve and analyzed by a gas chromatograph.

GENERAL ARRANGEMENT

There were six major equipment items involved in the apparatus. These were mass flowmeters, a fluidized sand bed, Variacs, a microreactor, a sampling valve, and a gas phase chromatograph. The general arrangement is shown in Figure 1.

There were two separate feed systems arranged in parallel so that they could be operated independently. Two mass flowmeters employing thermal conductivity cells metered feed gas into the reaction system. Feed concentrations were varied in this manner.

The feed gas passed into a 1/8 in. OD stainless steel tubing bayonet which held a microreactor of less than



**PERKIN-ELMER MODEL 820
GAS CHROMATOGRAPH**

- TR - Temperature Recorder
1 at point No.1, etc.
- R - Microreactor
- r - Reference Cell
- s - Sensing Cell

FIGURE 1 GENERAL FLOW ARRANGEMENT FOR MICROREACTOR

one cubic centimeter volume and extended down into the fluidized sand bed. The sand bed was contained in an electrically heated furnace. The temperature was controlled by two Variacs and was capable of reaching 1000°C . The feed reached the temperature of the sand bed before entering the microreactor. A thermocouple was installed in the entrance of the microreactor early in the experimentation to measure the temperature of the gaseous feed. When it was certain that the feed vapor reached the temperature of the sand bed, the thermocouple was removed for the remainder of the research.

The effluent from the microreactor went to a solenoid operated switch valve which was kept at constant temperature and pressure. The valve was a two-position valve with the microreactor effluent vented to the atmosphere through a different path in each position. Both paths consisted of equal lengths of coiled $1/8$ in. OD stainless steel tubing. In the normal position, the microreactor effluent went through one coil and the helium carrying gas went through the other. When the valve was switched, the microreactor effluent went through the other coil and the helium entered the valve and returned directly to the chromatograph. The valve was then switched to its original position trapping a sample of effluent in the second coil which was purged by the helium into the

chromatograph. Constant volume samples were taken. The sample line from the sampling valve to the chromatograph was heated with laboratory heating tape to keep reaction products from condensing in the line.

The gas chromatograph was equipped with a 1/4 in. OD by 16 ft. long adsorption column packed with granular firebrick coated with DC 200/500 Silicone oil. At 30°C and 20 psig helium carrier gas pressure, this instrument gave an analysis of the microreactor effluent in approximately 24 minutes.

MASS FLOWMETERS

Two Hastings-Raydist Mass Flowmeters, Model LF 300, were employed to accurately meter the feed gas stream. These flowmeters were arranged in parallel in order that two streams could be metered separately before being combined into the microreactor.

The feed stream passed through a Hastings-Raydist Flow Transducer Type F-300 which was the primary element. The meter had a working range of 0 to 300 std. cc/min. in air with approximately 2 millivolts d-c output. The flowmeter was accurate to ± 0.50 cc/min. The transducer had a working pressure of from 1 mm Hg to 200 psig. The transducer could operate up to a gas flow temperature of

220°C and had a response time of approximately 5 seconds. There was no correction necessary over wide ranges of temperature and pressure.

The transducer consisted of an electrically heated tube and an arrangement of thermocouples to measure the differential cooling caused by gas passing through a tube. Thermo-electric elements generated a d-c voltage proportional to the rate of mass flow of gas through the tube. The design depended only on the mass flow and specific heat of the particular gas and was, therefore, almost insensitive to pressure and temperature changes.

SAND BATH

The microreactor was immersed and heated in a constant temperature fluidized sand bath. The fluidized sand was contained by a 13 in. long section of 3-1/4 in. ID stainless steel pipe. At the top of the sand bed, a 6 in. long section of 5-1/4 in. ID stainless steel pipe formed a sand disengaging space. A stainless steel concentric reducer was welded between the fluidized sand section and the sand disengaging section. The bottom of the fluidized sand section was fitted with a flange which held a piece of 100 mesh stainless steel screen. The screen passed the fluidizing air, but retained the sand. The depth of the sand when not fluidized was 9 inches.

The fluidized depth was approximately 11 inches. The sand was light sand from the Mojave Desert near Yuma, Arizona and was screened for uniformity through 60 mesh screen onto 80 mesh screen.

Surrounding the fluidized sand bed was a furnace lined with refractory brick. The outside dimensions of the furnace were 20 in. X 20 in. X 36 inches. Two layers of refractory brick were used reducing the actual heating space to 10 in. X 10 in. X 20 inches. This space was situated about the fluidized sand section. The refractory brick was Babcock and Wilcox Insulating Firebrick No. K-20.

Resting atop one layer of the refractory brick was a 15 in. square piece of Transite board. This board, along with a 10 in. square piece at the bottom of the furnace were used to suspend electrical heating coils in a circle around the sand bed. There were two sets of 8 heating coils. Each coil was made of 7-1/2 feet of 16 gage Nichrome IV heating wire. The two sets of coils were arranged in the circle around the sand bed in such a way that every other coil was part of the same set. Thus, the sand bed was surrounded by a total of 16 heating coils with alternate coils connected in series to make two complete sets of eight coils. Each set of 8 coils was connected in series to a 20 amp, 130 volt Variac. The power to each set of coils was varied independently with one set ordinarily

providing 80-90 per cent of the heat required and the other set making up the difference to reaction temperature. This procedure minimized the time necessary to reach a constant sand bath temperature.

The temperature of the sand bath was measured by a chromel-alumel thermocouple attached to a Leeds & Northrup Company Millivolt Potentiometer No. 8690. The maximum change in temperature from the bottom to the top of the sand bed was found to be 5°C. The thermocouple was arranged in the bed to read the temperature of the bed at the point where the microreactor was situated.

A thermocouple was installed in the entering gas stream to the microreactor early in the experimentation to determine the temperature of the gaseous feed. When it was certain that the feed vapor reached the temperature of the sand bed, the thermocouple was removed for the remainder of the research.

A rotameter was used to meter the sand fluidizing air. The best rotameter setting for the flow was determined by observing the action of the fluidized sand in the bed. The air passed through a 20 in. length of 1/2 in. Schedule 40 stainless steel pipe before entering the bottom of the fluidized sand bed. This pipe was enclosed in the furnace area which surrounded the sand bed. Thus, the fluidizing air was well preheated before entering the

sand bed. This minimized the change in the temperature from the bottom to the top of the sand bed.

VARIACS

The power to the heating coils was varied manually with two 20 amp, 130 volt Variacs, Type W20M. Variac is a trade name for variable output transformers made by the General Radio Company of Concord, Massachusetts. Each Variac was connected in series to a set of 8 heating coils surrounding the fluidized sand bed.

MICROREACTOR

The microreactor is illustrated in Figure 2. The design used in this study was essentially the same as that employed by Pozzi and Rase (12). This very versatile design provides a convenient means of varying the size and relative dimensions of the microreactor.

The microreactor consisted of a length of $1/4$ in. OD 316 stainless steel tubing connected to $1/4$ in. X $1/8$ in. Swagelok reducing unions on each end. The reducing unions allowed the microreactor to be attached to $1/8$ in. OD 316 stainless steel tubing which was shaped into a bayonet and was inserted into the sand. A choice of different reducing unions afforded wide variations in microreactor sizes.

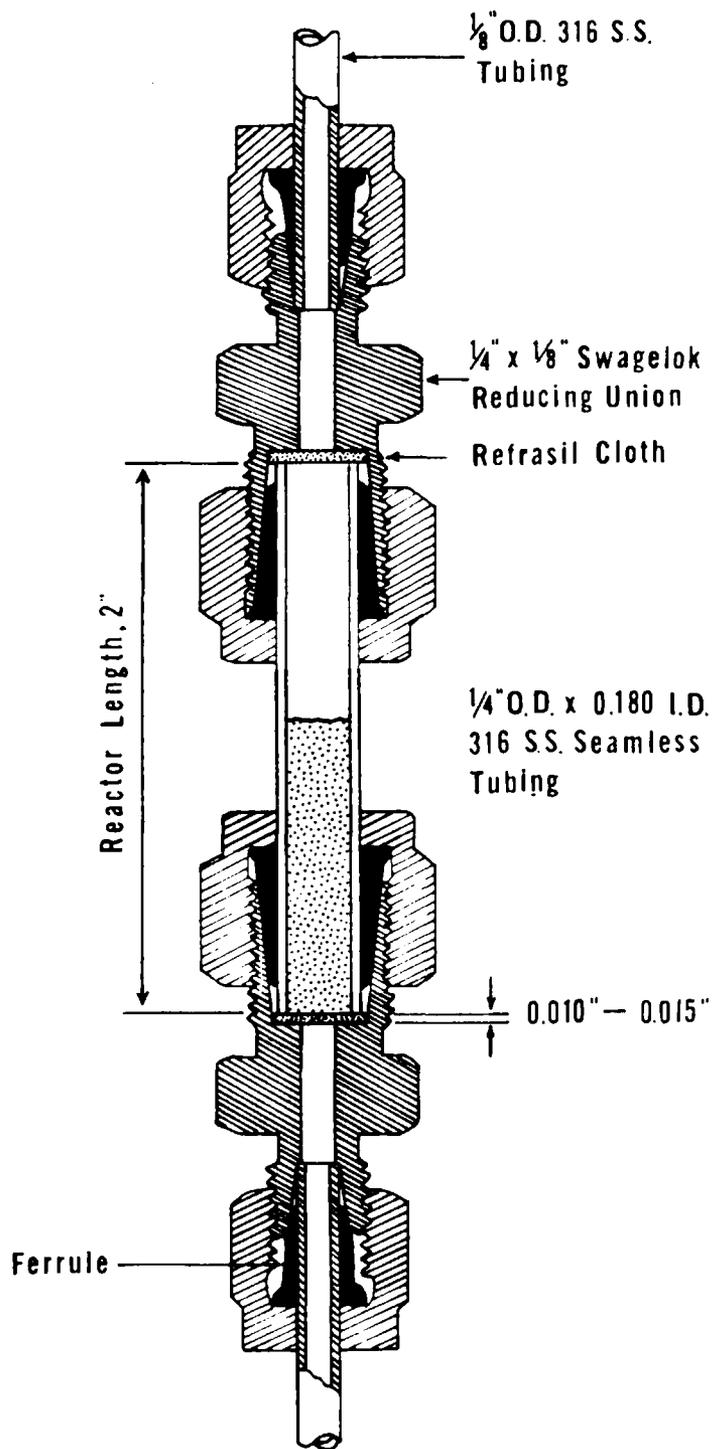


FIGURE 2 MICROREACTOR DETAIL

To contain the catalyst charge, pieces of Refrasil cloth were held in place at the ends of the tubing by the Swagelok reducing unions.

The reactor was prepared by first cutting a piece of tubing to the desired length. A piece of 0.015 in. thick stainless steel screen was placed against the shoulder in the Swagelok fitting to act as a spacer. Hall and Rase (5) reported 0.010-0.015 in. clearance to be desirable in such a 1/4 in. fitting.

The microreactor tube was inserted into the fitting against the screen and the nut on the fitting tightened to set the ferrule. This procedure set the fitting in such a way that clearance was left between the shoulder of the fitting and the end of the tube to accommodate the Refrasil retaining cloth.

The microreactor used in this work was 1/4 in. OD by 2 in. long. This made a volume of 0.905 cubic centimeters.

SAMPLING VALVE

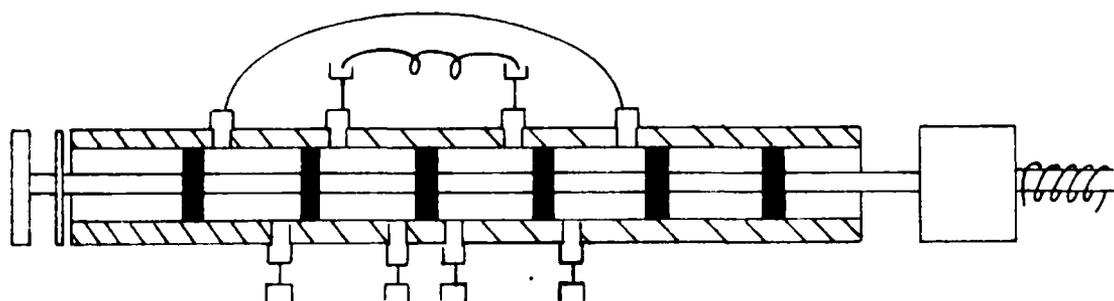
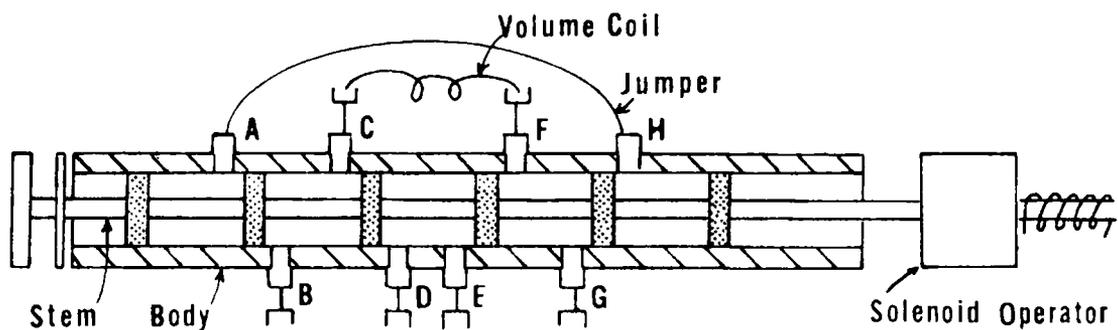
It was necessary to take constant-volume samples of the product gas during each experimental run. To do this, a Loenco Multi-port Instrument Switch Valve Model L-208-8V was employed. The valve was operated with a 115 volt, 60 cycle A.C. solenoid pilot using nitrogen cylinder gas.

There were two positions of the valve, a "pick-up" position and an "inject" position. These positions are shown in Figure 3.

In the "pick-up" position, the solenoid was energized and 20 pounds nitrogen pressure was applied. The product gas flowed through the volume loop and the carrier gas passed into the valve body and directly out.

In the "inject" position, the solenoid was de-energized and the nitrogen pressure was released. The product gas passed through the by-pass loop and the sample gas trapped in the volume loop was swept out by the carrier gas. The carrier gas then delivered the sample to the chromatograph where it was separated into the products of the reaction and what remained of the reaction gas. The valve was at rest in this position.

The "O"-rings on the valve stem were made of "Viton-A" Fluorocarbon elastomer and could be operated at temperatures up to 160°C. The valve was placed just above the furnace area to insure the sample loop always being above the condensation temperature of the reaction products. To keep the valve below the maximum operating temperature of the "O"-rings, a stream of air at room temperature was directed onto the valve at all times. This generally kept the valve at 70-80°C, depending on the furnace operating temperature.



NORMAL CONNECTIONS

B and G — Sample Gas
D and E — Carrier Gas

█ Pick-up Position
█ Inject Position

FIGURE 3 POSITIONS OF SAMPLING VALVE

The 1/8 in. OD Swagelok fittings, stem, and valve body were all 18-8 stainless steel. The port diameters were 0.040 inches so that small pieces of foreign material would not easily clog the valve. To control foreign particles entering the valve and being carried to the chromatograph, however, a Hoke 316 stainless steel No. 2231 filter element was inserted into the sample gas line directly before the sampling valve. The Hoke filter was designed to retain all particles above 2-5 microns in diameter.

Typical flow resistance between any two ports is shown by Figure 4.

CHROMATOGRAPH

The gas chromatograph used in this study was a Perkin-Elmer Model 820 which is a highly sensitive instrument designed expressly for chromatographic analysis utilizing a hot wire detector. The chromatograph was arranged as shown in Figure 1.

Helium was employed as the carrier gas and was piped from the reference thermal conductivity cell to the sampling valve, back to the heated liquid sample injection block and through the adsorption column to the sensing thermal conductivity cell.

The adsorption column used was a Consolidated Electric Corporation (CEC) Column No. 1304080-468. The

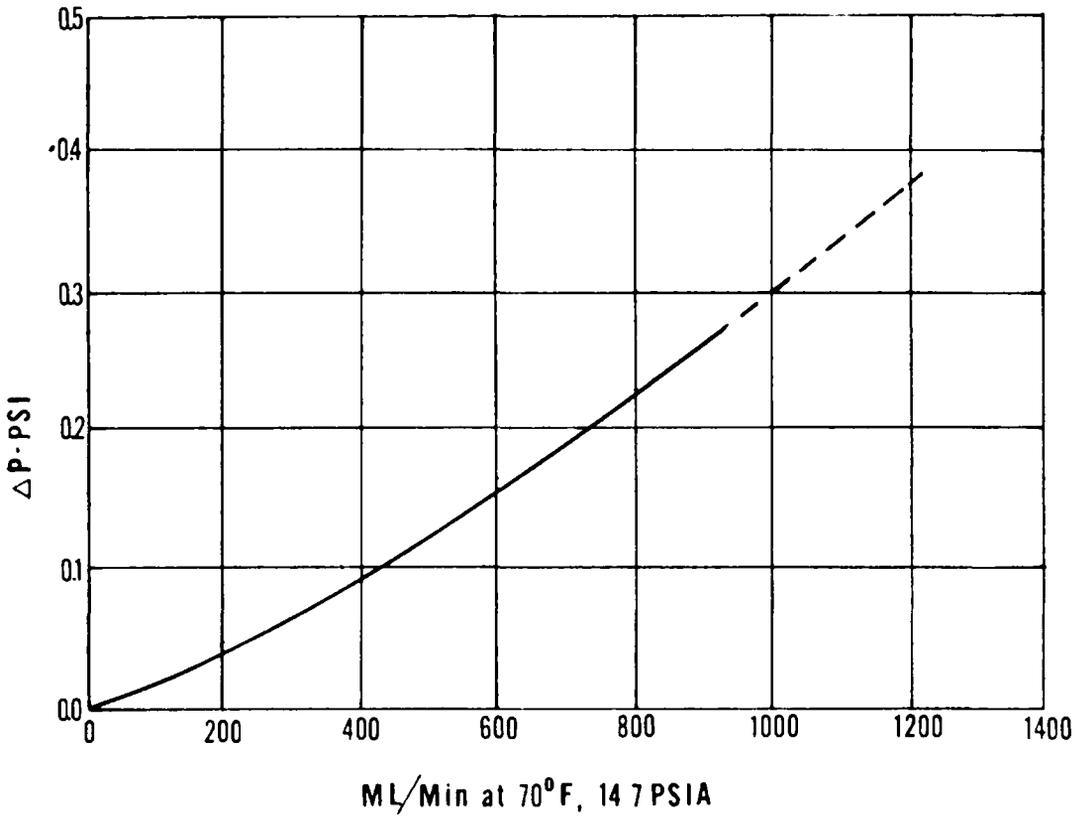


FIGURE 4 EFFECT OF HELIUM FLOW RATE ON PRESSURE DROP THROUGH SAMPLING VALVE PORTS

column was 1/4 in. OD by 16 ft. long. The column packing was granular firebrick coated with DC 200/500 Silicone Oil. It was necessary for this column to be adapted to the chromatograph as the Perkin-Elmer Model 820 is designed for a vertically coiled column and the CEC column was coiled flat.

The detector consisted of four filaments enclosed in a stainless steel block. The filaments were connected in a bridge circuit to measure the difference in thermal conductivity between the reference and sensing chambers. The detector was enclosed in an insulated oven separate from the column oven, and was capable of being heated to 500°C.

For this study, the chromatograph was operated at the following conditions:

Column Temperature-----	30°C
Detector Temperature-----	110°C
Detector Current-----	100 MA
Helium Pressure-----	20 psig

The signal from the detector was recorded on a Leeds & Northrup Company Speedomax G fast acting recorder. This recorder had a range of 0 to 1 millivolts and a response time for full scale pen travel of 1 second.

The recorder was equipped with a Disc Integrator Model 203. The Disc Integrator provided a trace readout

which automatically and continuously recorded on the side of the strip chart. The integrator produced a count which increased linearly with the displacement of the recorder pen; the total count produced being proportional to the area under the peak. An example of the integrator pen trace is shown in Figure 7.

There was virtually no lag between the movement of the recorder pen and the corresponding motion of the integrator pen, except at zero, where a possible 0.2 per cent dead band might have existed, since some motion of the recorder pen was necessary to activate the integrator from zero. These errors are not serious since they are constant and are diminished to some extent by the calibration procedure.

The response of the chromatograph and the linearity of the mechanical integrator were checked by injecting different quantities of liquid 1-hexene into the sample injection block of the chromatograph with a syringe. The results of these checks are shown in Figure 5.

The least squares method was applied to give the best linear fit to the experimental points. At the concentrations shown the integrator counts deviated from the line in a range of 1.2 to 6.77 per cent error.

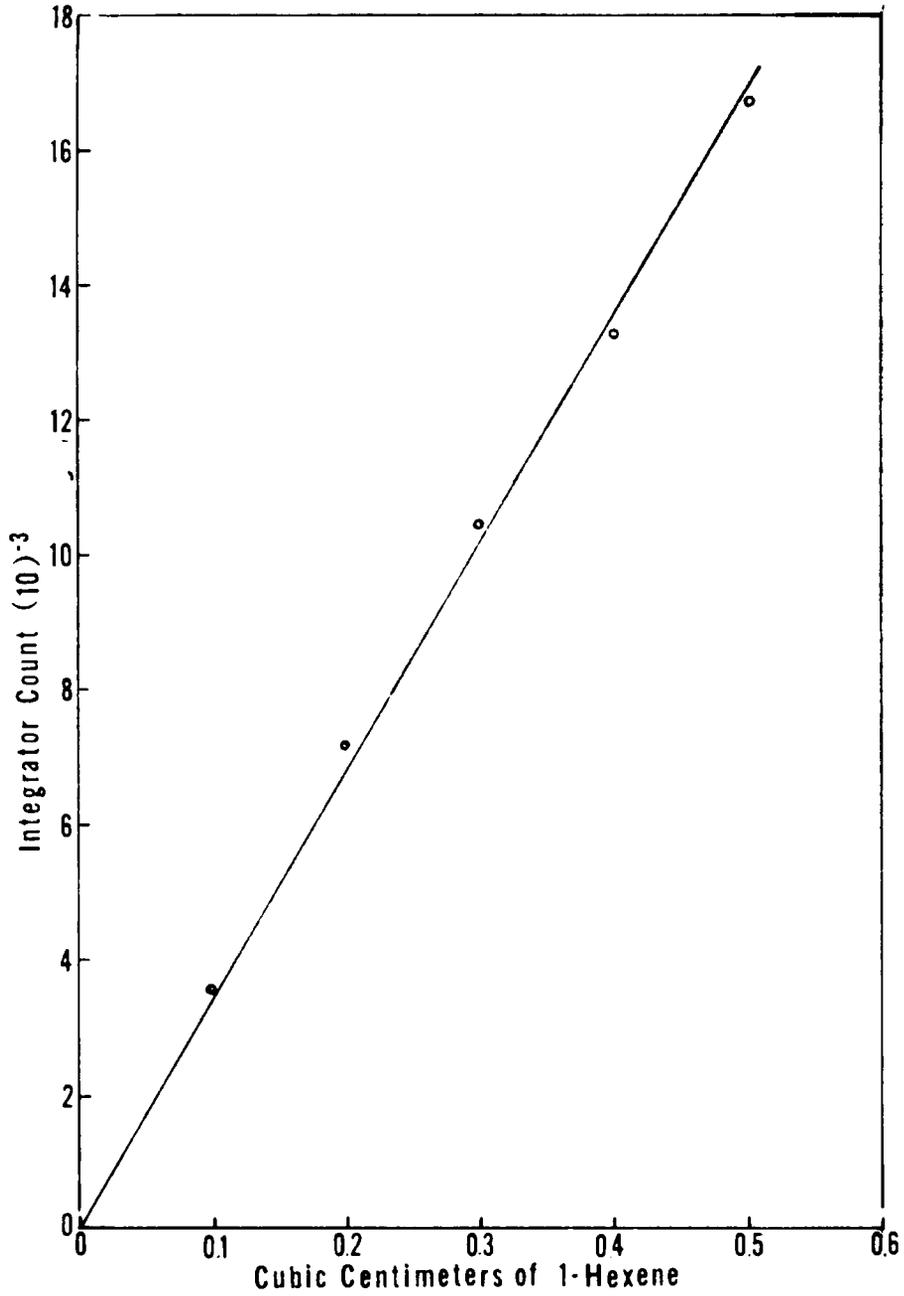


FIGURE 5 RESPONSE OF CHROMATOGRAPH AND LINEARITY OF MECHANICAL INTEGRATOR

MATERIALS

The reaction gas was propylene which was used without further refining from a cylinder provided by Phillips Petroleum Company at Bartlesville, Oklahoma. As it came from the cylinder, the gas was 99.5 mole per cent propylene. For some tests, the propylene was diluted with argon with both gases being metered through separate mass flowmeters and combined before entering the microreactor.

The catalyst was FC-2 Unicat Fluid Cracking Catalyst provided by the Universal Oil Products Company of Des Plaines, Illinois. The catalyst was a silica-alumina catalyst that was 15.7 weight per cent alumina (Al_2O_3). The surface area was 488 sq. meters/gram. The average particle size was 58 microns. The chemical analysis of the catalyst on a per cent dry weight basis is as follows:

Alumina-----	15.7
Iron-----	.03
Sodium-----	.030
Sulfate-----	.16
Silica-----	84.08

The Refrasil cloth used to retain the catalyst was woven quartz made by the H. I. Thompson Fiber Glass Company, 1788 Cordova Street, Los Angeles, California. The cloth was woven tightly enough that the catalyst particles were held, but the feed gas was passed through.

IV. EXPERIMENTAL PROCEDURE

The reaction studied was the polymerization of propylene to 1-hexene over a silica-alumina catalyst. Although the reaction resulted in some 15 products, the precision of the microreactor apparatus and the development of an unusual analysis procedure enabled this investigator to single out the product 1-hexene for study.

In all tests, the ratio of the catalyst weight to the total feed rate, W/F , was kept constant. The sand bath temperature was varied and reaction rates determined at the different temperatures. The results of these tests were used to determine the activation energy and the order of the reaction of propylene to 1-hexene.

MICROREACTOR PROCEDURE

The first step in making a catalytic conversion test was to fill the microreactor with catalyst. The microreactor was first blown free of clinging particles of used catalyst and dust with air, and new Refrasil cloths were installed. In the early stages of experimentation, the importance of the catalytic activity of the stainless steel reactor and fittings was tested. Propylene was passed through the microreactor at 400°C, 350°C, and 300°C.

The conversion to products was almost undetectable and was neglected in further research.

The microreactor bayonet containing the catalyst was placed in the fluidized sand bed which was previously adjusted to 400°C. An absolute pressure of 25 in. of mercury was maintained on the catalyst for 8-10 hours (usually overnight) while the temperature was held at 400°C. This pretreatment procedure always preceded the conversion test and was for the purpose of driving off chemisorbed water. Many of the tests were run at 400°C, but in the cases where the reaction temperature was lower, the catalyst remained under vacuum while the temperature was lowered.

At the end of the pretreatment period, the sand bath was brought to the temperature at which reaction was to be measured. Argon was purged through the microreactor at 100 cc/min. to fluidize the catalyst bed in case it had become partially frozen during the pretreatment.

The argon was turned off and the propylene feed was adjusted to the predetermined feed rate as quickly as possible.

A sample of the effluent was taken 8 minutes after the propylene feed was started. The catalyst increased in activity slightly during the first hour, so the first sample taken generally served only to establish optimum chromatograph attenuation settings for following analyses.

The analysis of a sample required 24 minutes. By the time the second sample had been analyzed and the third sample was taken, the test had usually been going 50-60 minutes. The aging characteristics of the catalyst showed that at this time the catalyst had reached peak activity and had started a very slow decline. The analysis of the third sample was used, in all cases, for reaction rate calculations.

At the completion of a test, the microreactor bayonet was removed and the sand bath returned to 400°C.

ANALYSIS PROCEDURE

Vapor phase chromatography was used to analyze the microreactor effluent. With this apparatus, qualitative analysis is based on the times at which components emerge from the adsorption column. For a particular column and a given set of operating conditions, the retention time for each component is unique to that substance. There were a total of 15 detectable products of the polymerization reaction, each one producing a peak on the recorder chart.

To determine which peak represented 1-hexene, it was necessary to find the exact time at which 1-hexene emerged from the column. A tracer gas, argon, was bubbled through pure 1-hexene at constant conditions. Some of the

1-hexene was picked up by the argon. It was not necessary for the argon to pick up much of the 1-hexene due to the sensitivity of the chromatograph. The argon stream carrying 1-hexene flowed to the sampling valve and samples were injected into the helium carrier gas stream to the chromatograph. The 1-hexene required 15 min.-12 sec. to emerge from the CEC DC 200/500 Silicone Oil column. Of course, this would only hold for the column temperature of 30°C and the helium pressure of 20 psig.

The concentration of any component is directly proportional to the area under the recorder peak caused by the emergence of that component from the column. Since the recorder used with this chromatograph was equipped with a mechanical integrator, the areas under the peaks were used in the calibrations.

For the simplest case, when all components have essentially the same thermal conductivity, the fraction of a component present in a mixture is simply the area under the peak for that component divided by the sum of all the peak areas caused by the mixture. Since the components used in this study vary in thermal conductivity, allowance had to be made for this in calculating the analysis.

In the previous discussion of the chromatograph (Sec. III), it was shown that the response of the

chromatograph to a component is directly proportional to the volume of that component introduced into the column, or

$$V = S A \quad (\text{IV-1})$$

where: V = volume of a component emerging from the column; cc

A = area under the recorder peak produced by that component; in integrator counts

S = a constant, termed a chromatograph response factor (5); cc/counts.

Since the mechanical integrator on the chromatograph recorder produced a count which was directly proportional to the area under the peak, the area could be replaced by the integrator counts.

The relationship between the volume of a component and its recorder area was used to determine the mole fraction of 1-hexene in the microreactor effluent.

Initially, pure argon was sampled by the sampling valve and its recorder trace analyzed. Knowing the volume of the argon sample taken to be equal to the volume of the sample coil, and with the counts under the peak produced by the argon, the chromatograph response factor for argon, S_T , was calculated from

$$S_T = \frac{V_D}{A_T^0} \quad (\text{IV-2})$$

where: V_D = volume of the sample coil; 1.415 cc
 A_T^O = integrator counts under the peak
 produced by the pure argon.

The next step was to bubble argon through a quantity of pure 1-hexene and sample the resulting stream. Two widely separated peaks were produced. The integrator counts under the argon peak were obtained and, utilizing the previously determined chromatograph response factor for the argon, the volume of argon sampled was obtained. The difference between the volume of the sample coil and the calculated volume of argon was taken to be the volume of 1-hexene vapor. This volume divided by the counts produced by the 1-hexene peak gave the chromatograph response factor for the 1-hexene,

$$S_H = \frac{V_H^O}{A_H^O} \quad (\text{IV-3})$$

where: V_H^O = calculated volume of 1-hexene picked up by the argon tracer gas; cc
 A_H^O = the integrator counts produced by the 1-hexene peak.

The chromatograph response factors were re-calculated periodically because of build-up of deposits on the sensing instruments.

As mentioned previously, the fraction of a component in the microreactor effluent could be determined by dividing

its peak area by the areas of all peaks in the mixture if all the chromatograph response factors were equal or known. Rather than define each component and its response factor, the response factor for the 1-hexene was used with the volume of the sample coil to determine the area of the peak that would have been produced had the sample coil been filled with pure 1-hexene vapor,

$$A_H^* = \frac{V_D}{S_H} \quad (\text{IV-4})$$

where: A_H^* = area that would be produced if the sample coil had been filled with 1-hexene vapor only; in integrator counts.

It was assumed that if all the gases in the effluent had the same compressibility, which is reasonable when dealing with only hydrocarbons, the area A_H^* would represent the total area of all the peaks produced by the effluent. Due to the linearity of the chromatographic response, (Sec. III) the amount of 1-hexene in each sample is proportional to the integrator count for the 1-hexene peak. The integrator counts for the 1-hexene peak were calculated as shown in a following section on the integrator count procedure, and divided by the A_H^* . This ratio was the mole fraction of 1-hexene in the microreactor effluent.

The fractional conversion was obtained by dividing the mole fraction of 1-hexene in the effluent by the mole fraction of propylene in the feed.

In the cases where pure feed was being metered to the reactor, the mole fraction of propylene was considered 1.0, although the feed analysis showed 99.5 mole per cent propylene. In the cases where the concentration of the propylene in the feed was varied, argon was simultaneously fed into the reactor and the resulting mole fraction of propylene was used to determine the fractional conversion to 1-hexene.

INTEGRATOR COUNT PROCEDURE

The mechanical integrator count was recorded by an oscillating pen, the rate of oscillation being proportional to the displacement of the recorder pen. The integrator count was taken as 85 for each traverse of the oscillating integrator pen, beginning when the recorder pen first left the zero base line, and stopping when the recorder pen returned to the base line. The integrator pen makes a line straight down the strip chart when the recorder pen is on zero, indicating zero area between the recorder line and the base line.

In the early stages of this study many adsorption columns and varying chromatograph conditions were used in an attempt to completely separate the 1-hexene peak from the preceding and following peaks. The column and chromatograph conditions were chosen to give the best possible

separation of the peaks. However, the 1-hexene peak was never completely separated from its neighbors. A typical chromatographic analysis of the microreactor effluent is shown in Figure 6.

Examination of the reference 1-hexene peaks showed that they were symmetrical. At the half height of the 1-hexene peak, a line drawn across the peak intersected the sides of the peak at points where the tails of the neighboring peaks no longer contributed to the displacement of the recorder pen. The integrator counts between these intersections was used to represent the area under the peak. For consistency, this technique was also applied to the area under the reference 1-hexene peak produced by bubbling the tracer gas, argon, through liquid 1-hexene. The ratio of areas to determine the fraction of 1-hexene in the effluent (discussed in the previous section on analysis procedure) was accurate since the partial areas were proportional to the total areas in all cases.

A typical analysis of a sample of argon tracer gas bubbled through 1-hexene liquid, with integrator record, is illustrated in Figure 7. The zero position for the recorder pen and the integrator pen is indicated at the starting time of the analysis. The component represented by the peak, and the sensitivity of the chromatograph for that component, is labelled at the top of the recorder peak.

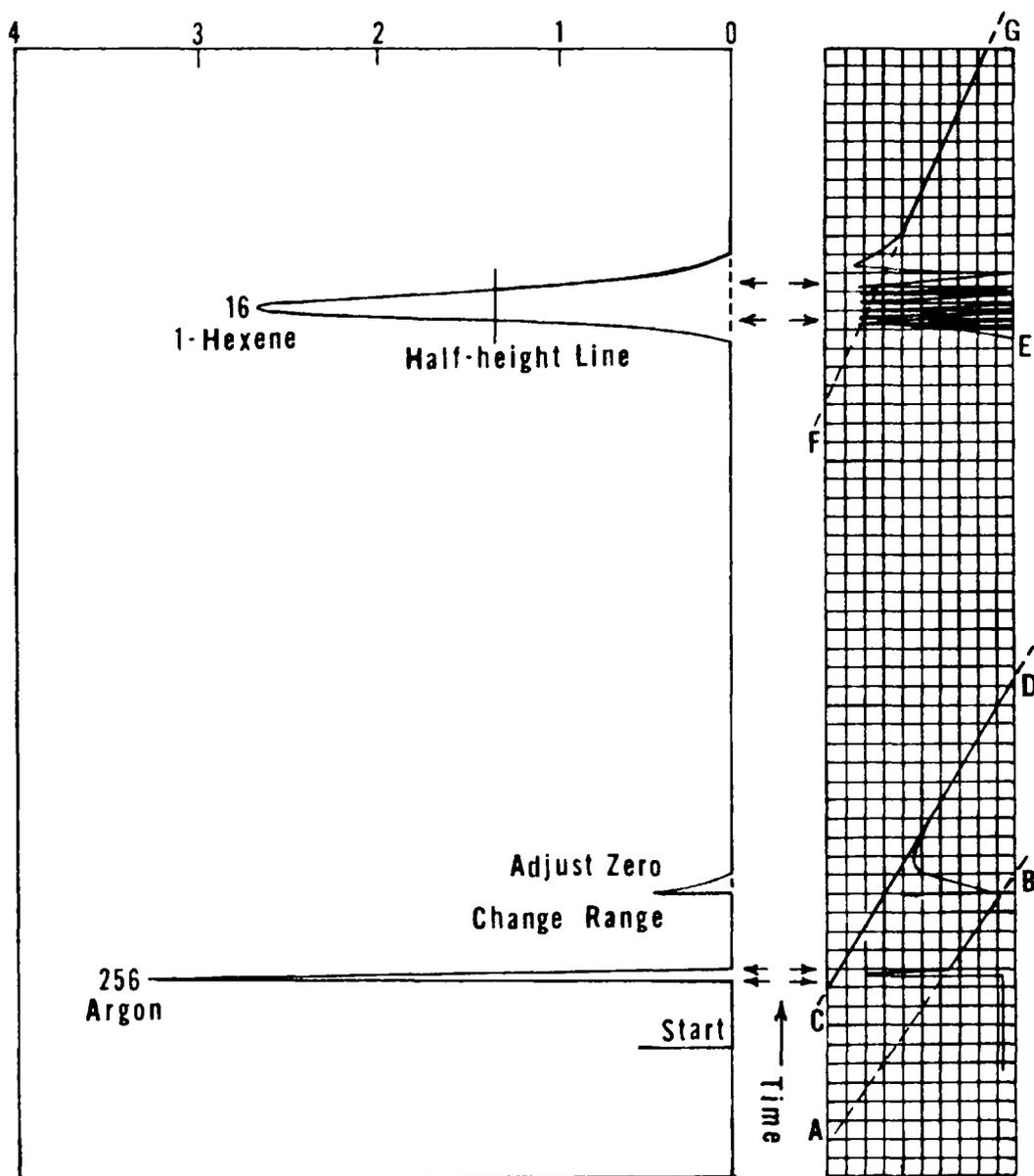


FIGURE 7 COUNT PROCEDURE FOR MECHANICAL INTEGRATOR

The base line for the chromatograph peak does not always start and stop at zero for the recorder, and the integrator pen does not indicate zero at these points. This condition is apparent for the 1-hexene peak in Figure 7. The recorder base line drifts slightly, so that the dashed line E-F represents the displacement of the pen for the base line at the end of the 1-hexene peak. An average of the slopes F-G and D-E (which is zero in this case) represents the average displacement of the recorder base line during the time of the 1-hexene peak. If this average slope is multiplied by the time under the half height mark (represented by the arrows), a very good count correction is obtained for the chromatograph peak count. This correction may then be subtracted from the total counts to obtain the correct count for the peak. The count for the 1-hexene peak in Figure 7 is $1015 - 5 = 1010$.

The correction for the integrator count was kept as small as possible, so that it would be a small per cent of the total count. When the argon peak was completed and the range of the chromatograph was changed from 128 to 16, there was usually a large displacement of the recorder pen, indicating a slight tail on the argon peak. This displacement was decreased manually by adjusting the recorder back toward zero. Perfect alignment was not always possible, but this effect was a minor part of the error in the analysis.

CALCULATION OF REACTION RATE

Once the fractional conversion was obtained, as described in a previous section, the rate of reaction of the propylene feed to the dimer, 1-hexene, was calculated.

A material balance for a differential element of the catalyst charge is

$$r \, dW = F \, dx \quad (\text{IV-5})$$

where: r = rate of reaction; cc. converted per gram of catalyst per hour

dW = weight of the catalyst in the differential element; grams

F = feed rate; cc/per hour

dx = fractional conversion; cc. converted in the differential element per cc. of feed.

In a microreactor such as that used in this study the fractional conversion is small, and the differentials in Eq. (IV-5) can be treated as the actual change. Since this study only required the comparison of reaction rates and activation energies in equivalent units, the units of the quantities were used just as they were measured in the laboratory. The reaction rate was obtained by

$$r = \frac{(F) (\Delta x)}{W} \quad (\text{IV-6})$$

where: W = weight of catalyst charge; grams

Δx = fractional conversion in the microreactor, mole fraction 1-hexene in the effluent divided by the mole fraction propylene in the feed.

QUANTITATIVE EXPERIMENTS

To examine the kinetics of the dimerization of propylene to 1-hexene over silica-alumina cracking catalyst, a series of experiments were set up to correlate the rate of dimerization with temperature and with propylene feed concentration.

The activation energy of the reaction was obtained at three different feed rates: 60 cc/min, 40 cc/min, and 20 cc/min. Corresponding catalyst charge weights were 0.375 grams, 0.250 grams, and 0.125 grams in order to keep the catalyst weight to feed rate ratio, W/F , constant. These tests were each made at 400°C, 350°C, and 300°C. From the reaction rates calculated at the various temperatures, a plot of log rates versus $1/T$ was made for each flow rate from which the slope was taken. This gave the activation energy.

By simultaneously metering argon and propylene into the microreactor, the feed concentration was varied. However, the total feed was adjusted so that W/F was constant as before. A plot of log rate versus propylene concentration in the feed gave a straight line at 400°C and 350°C. The slopes of these lines gave the order of the reaction.

The importance of film diffusion was examined in the effect of feed rate on the conversion at 350°C.

Continuing to hold W/F constant, but varying both catalyst weight and feed rate, samples were taken at increasing feed rate. The conversion to 1-hexene was calculated and plotted against the flow rate. A curve was obtained indicating film diffusion was important below 36 cc/min.

A catalyst aging curve was produced by continuously sampling the microreactor effluent for six hours. This test was made at 350°C with a feed rate of 40 cc/min and a catalyst charge weight of 0.250 grams.

V. RESULTS

The kinetics of a reaction are characterized by the activation energy of the reaction and the reaction order. These were determined, but in addition the magnitude of diffusional effects and the aging characteristics of the catalyst were determined for the reaction of propylene to 1-hexene over silica-alumina cracking catalyst. The accuracy of the information obtained was within an experimental error of ± 2.5 -10 per cent. All calculated values appear in tabular form in the Appendix.

EXPERIMENTAL

The activation energy of the reaction was obtained from a plot of log rate versus $1/T$. A typical plot is shown in Figure 8 for a flow rate of 60 cc/min of propylene and a catalyst weight of 0.375 grams. This ratio of catalyst weight to feed rate, W/F , was kept constant at 6.25×10^{-3} gram/(cc)(min) throughout the tests for activation energy so that the information obtained would also be useful in ascertaining the importance of film diffusion. The temperature at which reaction rates were determined were 400°C , 350°C , and 300°C . Below these temperatures the production of 1-hexene was very small and the inaccuracies were such that the data was not considered meaningful.

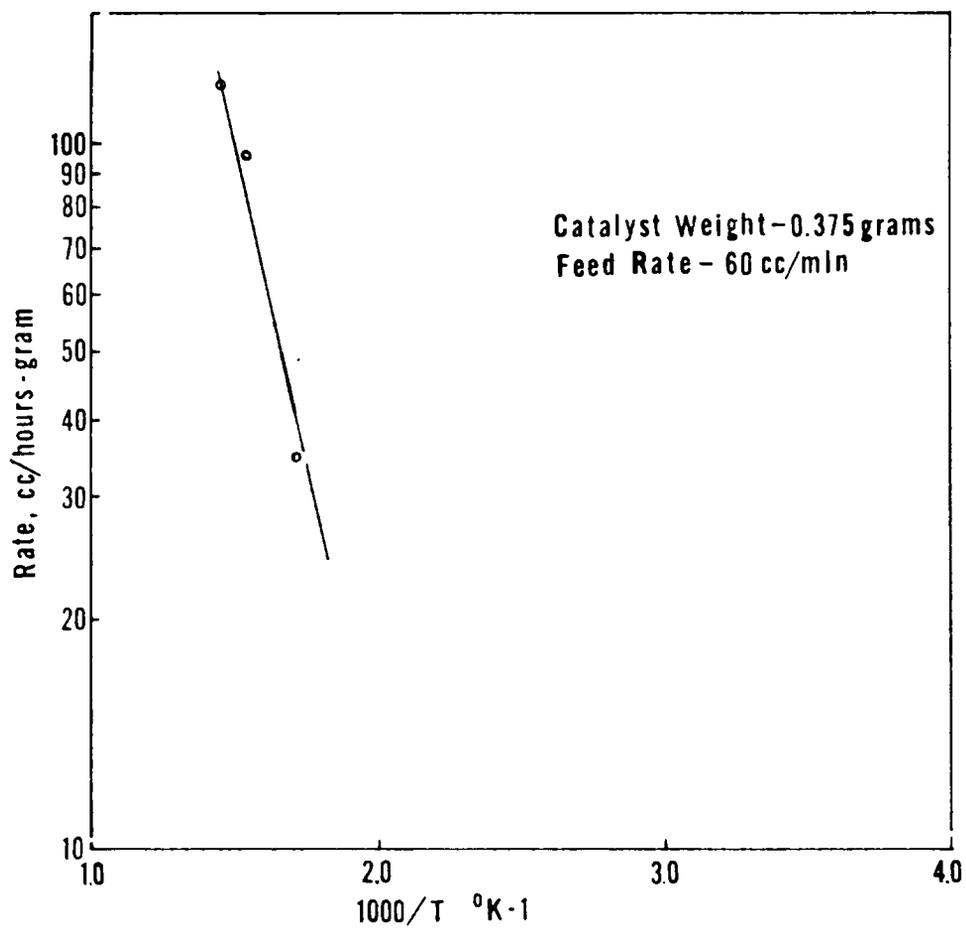


FIGURE 8 EFFECT OF TEMPERATURE ON REACTION RATE
FOR RUN 9-28

The activation energy obtained from Figure 8 was 9.3 kcal/g-mole. This is in the range of activation energies, 8-15 kcal/g-mole, for reaction controlled systems. An activation energy of 2-5 kcal/g-mole indicates a diffusion controlled situation.

Figure 9 is another plot of reaction rate versus $1/T$. The ratio W/F was kept constant with a catalyst weight of 0.250 grams and a feed rate of 40 cc/min. The activation energy calculated from this plot was 9.1 kcal/g-mole.

Figure 10 shows quite reduced reaction rates. This curve was obtained at 20 cc/min feed rate and 0.125 grams of catalyst. The activation energy from this curve was 10.4 kcal/g-mole. The low conversion at this flow rate resulted in such small 1-hexene peaks that their areas probably did not represent the true volumes. Such inaccuracies may have resulted in the higher slope of the curve and, thus, the higher activation energy.

Although the activation energies determined for the reaction indicated that diffusion was not important, information was desired to be certain of this point. Levenspiel (11) has presented a lucid description of a method for determining the importance of diffusion. If film diffusion is important, at constant W/F the conversion will vary with varying flow rate. A number of tests were made at flow

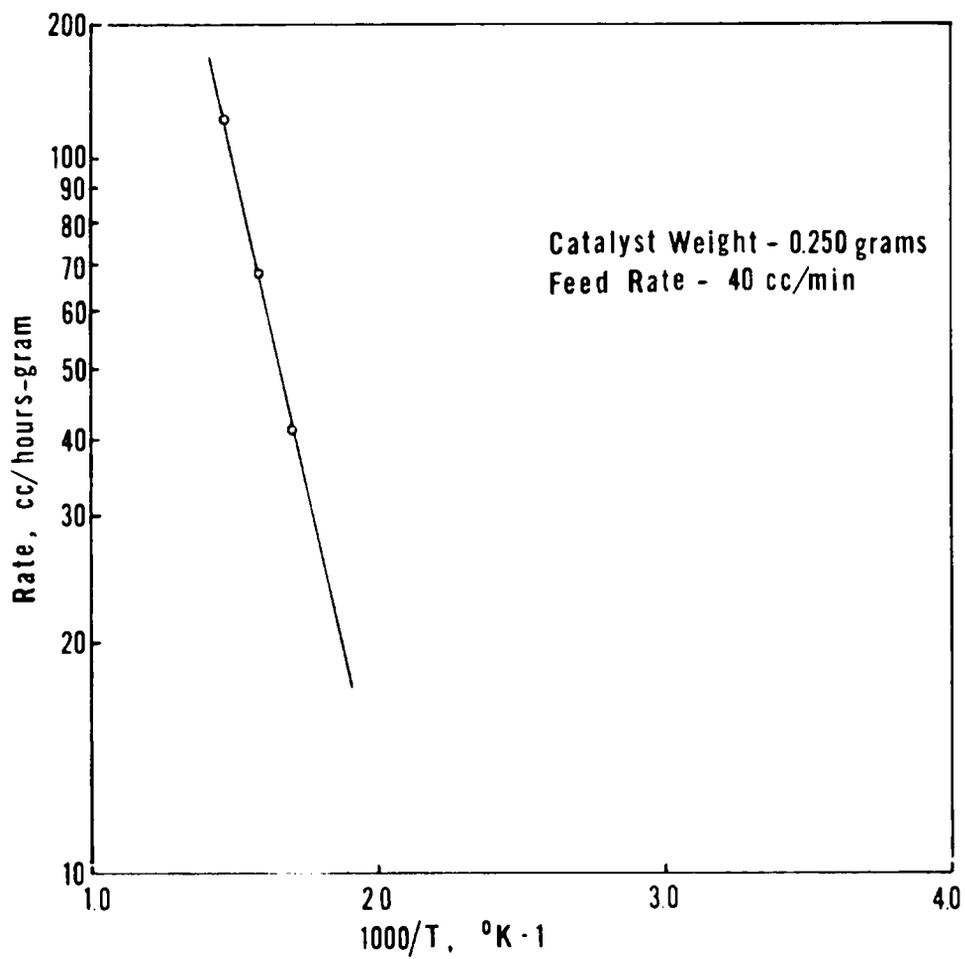


FIGURE 9 EFFECT OF TEMPERATURE ON REACTION RATE FOR RUN 9-27A

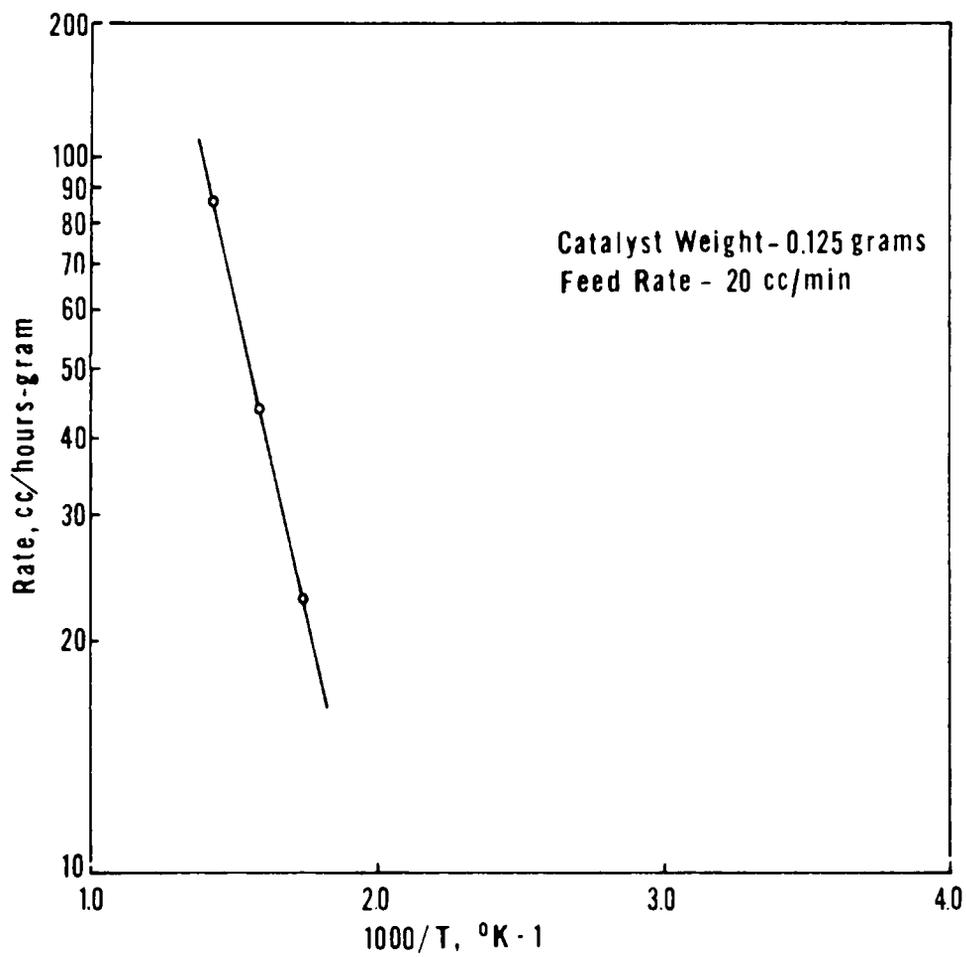


FIGURE 10 EFFECT OF TEMPERATURE ON REACTION RATE FOR RUN 9-27E

rates other than those used to obtain the activation energy, with W/F constant as before. The temperature of 350°C was chosen for this study. Figure 11 shows the results of these tests. Apparently, diffusion was important below 36 cc/min feed rate in this experimental system.

An attempt was made to ascertain the order of the reaction, that is, the value of α in Eq. (II-14). The initial concentration of the propylene was varied by simultaneously feeding argon to the catalyst with the propylene. The ratio of catalyst weight to total feed was kept constant as before, but the mole fraction of propylene was varied from 0.50 to 1.00. Plots of log rate versus log mole fraction propylene were made for 400°C , and 350°C . The resulting curves are shown in Figures 12 and 13. The slope of the plot at 400°C was 2.5 and the slope at 350°C was 2.9. An integral value of 3 was decided upon for the reaction order, α .

The catalyst was also examined for aging characteristics. Samples of the reactor effluent, at 350°C again, were taken and analyzed continuously for six hours. A scatter of points resulted as shown in Figure 14. As mentioned previously (Sec. IV), the third sample, at the end of 55 minutes of reaction, gave the maximum rate of reaction of 109.5 cc/hr-gram. The activity of the catalyst rose quickly to this point and then began a slight declining

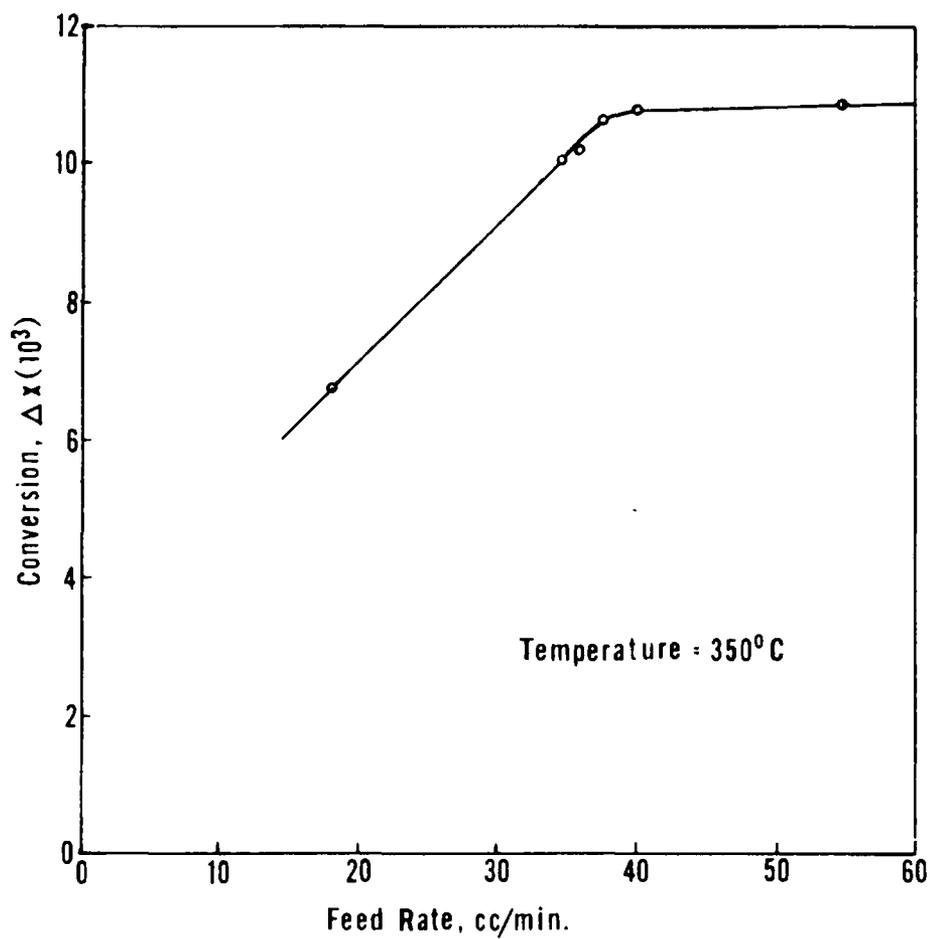


FIGURE 11 EFFECT OF PROPYLENE FEED RATE ON CONVERSION AT CONSTANT W/F

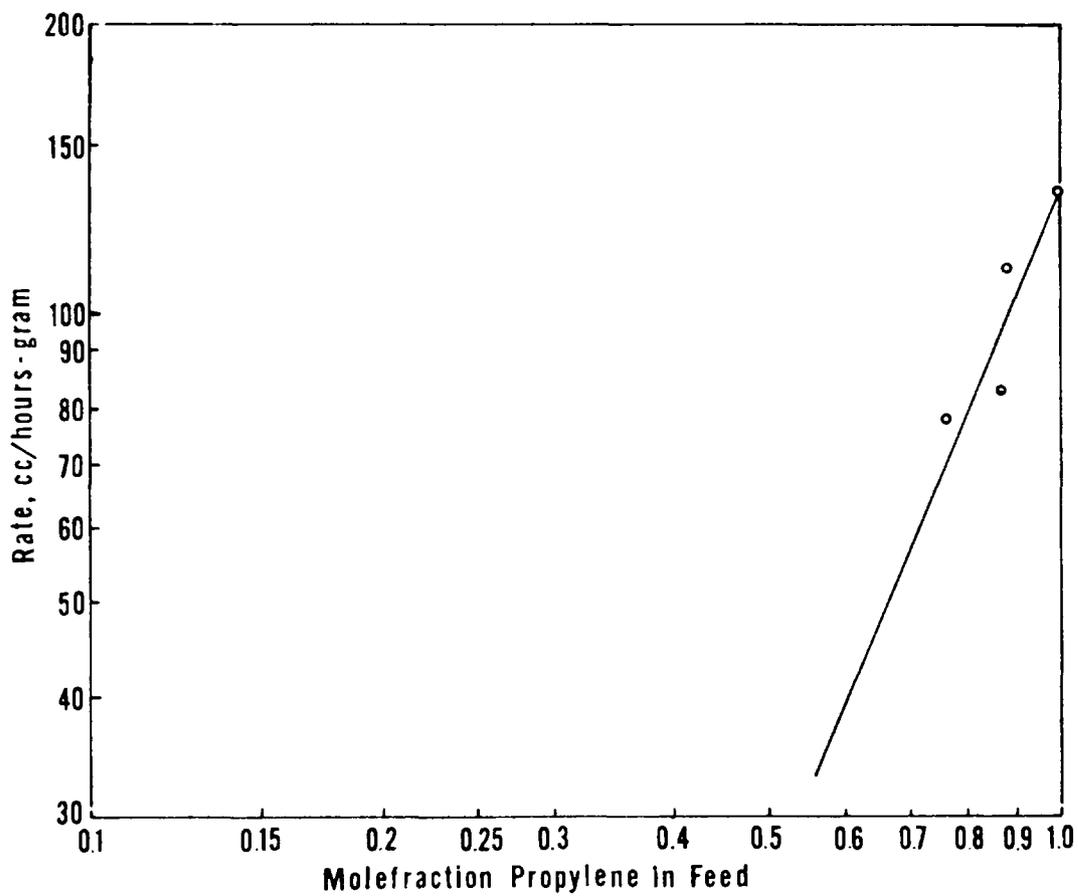


FIGURE 12 EFFECT OF PROPYLENE CONCENTRATION ON THE RATE OF REACTION AT 400°C

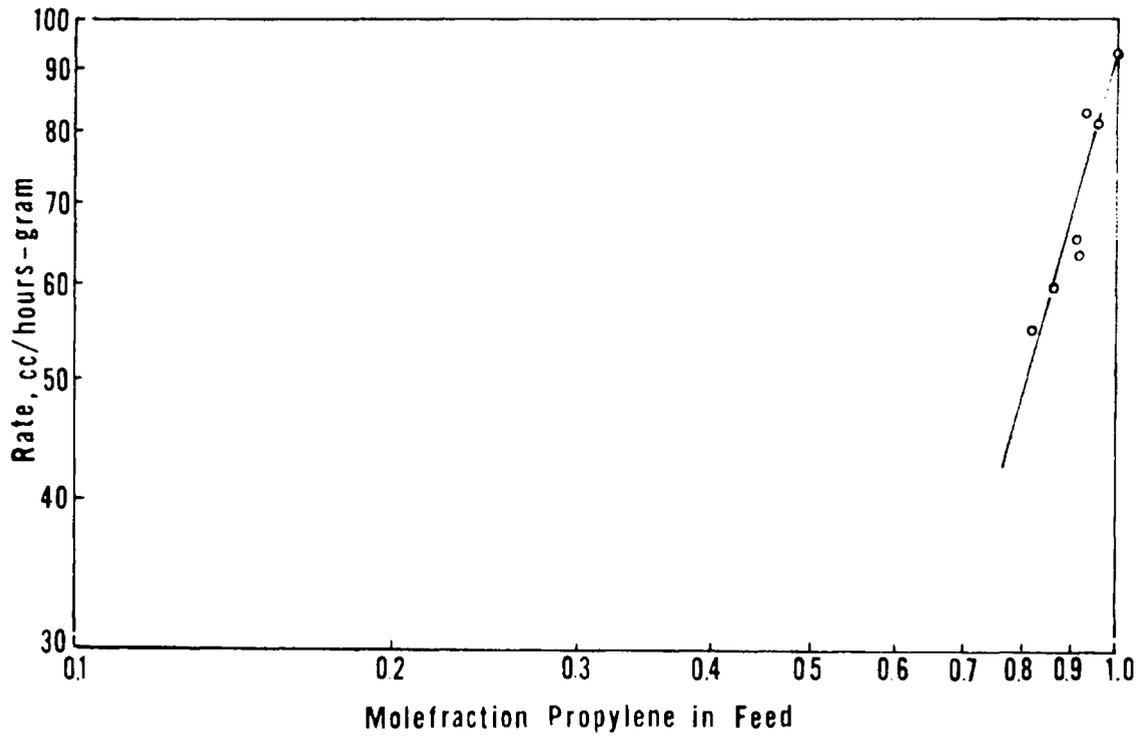


FIGURE 13 EFFECT OF PROPYLENE CONCENTRATION ON THE RATE OF REACTION AT 350°C

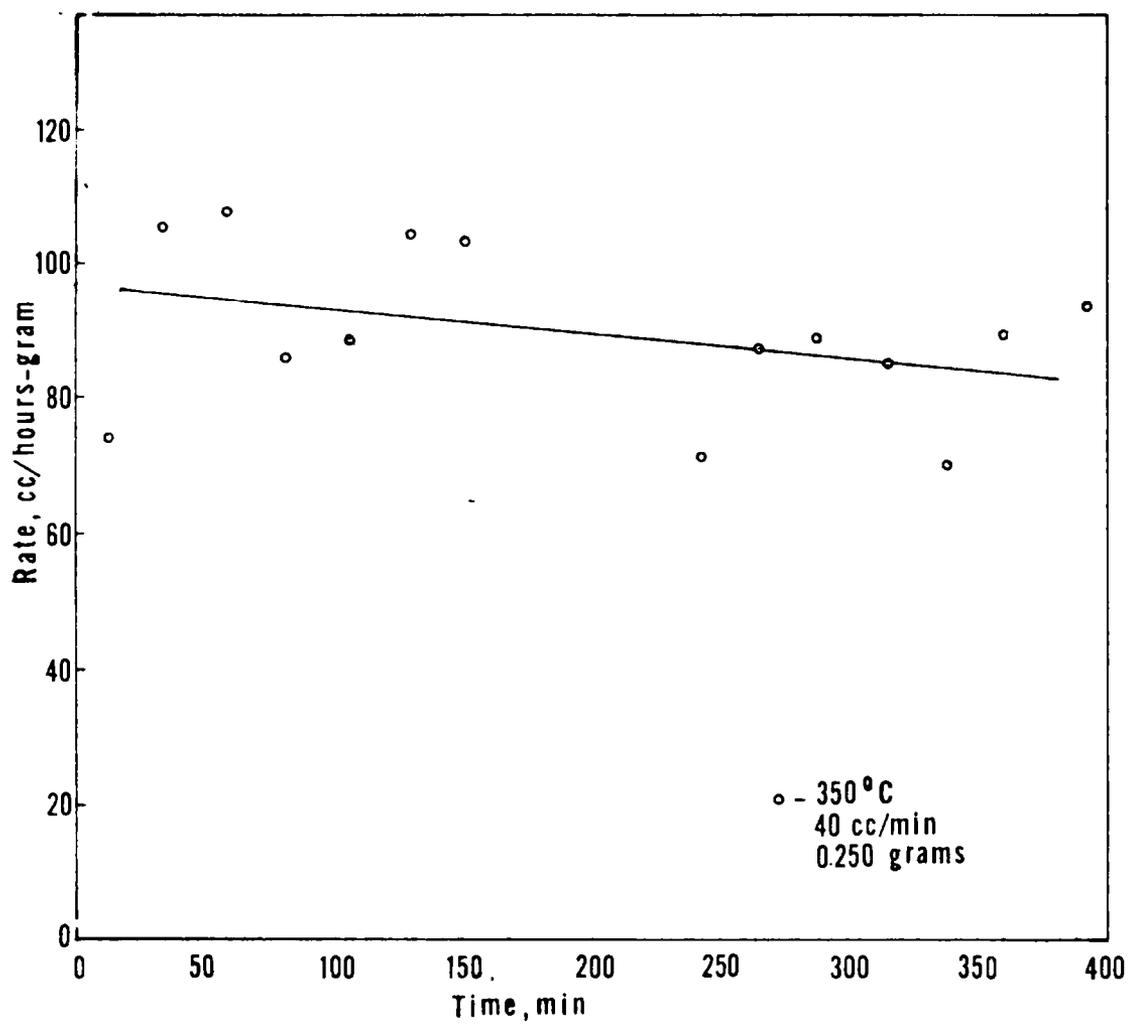


FIGURE 14 DECREASE IN REACTION RATE WITH CATALYST AGE AT 350°C

trend. The points were fed into a digital computer program (4) designed to give the best linear fit of the data. The resulting line had a slope of $-0.03023 \text{ cc/gram-min}^2$ indicating a very slight fall in catalyst activity over the six hour aging period.

DISCUSSION

Examination of Figure 11 shows that diffusion was quite important at feed rates below 36 cc/min. An activation energy of 2-5 kcal/g-mole is normally expected for diffusion phenomena, but low conversion resulting from the diffusion problem caused some increased errors in the analysis. These problems with accuracy explain the activation energy of 10.4 kcal/g-mole obtained at the low flow rate of 20 cc/min. Therefore, the determination of the true activation energy of the reaction was based on an examination of curves at 60 cc/min and 40 cc/min feed rates. An activation energy of 9.2 kcal/g-mole, based on these two curves, was accepted and was calculated to be reproducible, in the feed rate range of 36 cc/min to 60 cc/min, within 2.5 to 10 per cent error. This activation energy does not compare favorably with a value of 2-3 kcal/g-mole for the dimerization of propylene over a 20 per cent alumina catalyst by Borisova, Dizisiko, and Cherednik (2). However, these three investigators admit many difficulties hindered

accurate determination of the activation energy of their reaction. The low activation energy reported was probably due to a diffusion controlled reaction.

The author found no other work that reported the reaction order of the dimerization of propylene. The reaction order of three indicates it was necessary for two propylene molecules to react at an active site. This necessitated that one propylene molecule adsorb to the site from an activated complex and react with another propylene molecule in the fluid stream or on an adjacent site. This mechanism is supported by the fact that the reaction rate increased rapidly with increased concentration of propylene in the feed. Such a result is characteristic of a reaction controlled by the adsorption of the reactant at the catalyst surface. On this basis, it is felt that the value of three for the reaction order is correct.

The catalyst aging curve in Figure 14 was compared with a similar curve reported by Borisova, et al. Their aging curve showed a marked fall in catalyst activity in the first 20 minutes of testing from 4000 cc/hr-gram to 400 cc/hr-gram and levelled out at 200 cc/hr-gram after 80 minutes. The large difference between Figure 14 and the data reported by Borisova is explained by the large initial difference in catalytic activity due to the method of

catalyst preparation. Borisova prepared catalysts by precipitation of a mixture of solutions of aluminum nitrate and silicon ethylate by ammonia. The present study was made with a commercially prepared catalyst that was probably sintered at the temperatures used during spray drying. Borisova subjected some samples of the same catalyst to steam sintering for varying lengths of time. The resulting catalyst aging curves were similar to Figure 14.

CONCLUSIONS

The utility of a microreactor apparatus for measuring the kinetics of the dimerization of propylene has been demonstrated. By precise analysis procedure and unique treatment of data it was possible to single out one of several simultaneous reactions for study.

The kinetics of the reaction were characterized by the determination of the activation energy of the reaction and the reaction order. An average activation energy of 9.2 kcal/g-mole was determined, based on accuracy of data as discussed above. Figures 12 and 13 indicate a third-order reaction. Points at very low conversions were discarded. This was due to the inability of the chromatograph recorder to produce areas which were commensurate with the small volumes of 1-hexene produced.

The reaction order of three and the characteristically (11) large increase in reaction rate due to increasing propylene concentrations, led to the conclusion that the reaction is controlled by the adsorption of propylene on the catalyst.

APPENDIX

TABLE 1

Effect of Temperature on Reaction Rate at Constant W/F

Run	Reaction Rate cc/hr-gram			Catalyst Weight W grams	Propylene Feed Rate, F cc/min.
	400°C	350°C	300°C		
9-27A	122.0	70.5	39.5	0.250	40
9-27E	86.5	41.5	22.6	0.125	20
9-28	135.0	94.0	34.6	0.375	60

TABLE 2

Effect of Propylene Concentration in the Feed on Reaction Rate at 400°C

Run	Propylene Feed cc/min.	Argon Feed cc/min.	Reaction Rate cc/hr-gram
1	40	--	134
2	35	5	111
3	34	6	83
4	31	9	78

Total Feed - 40 cc/min.

Catalyst Weight - 0.250 grams

TABLE 3

Effect of Propylene Concentration in Feed on Reaction Rate at 350°C

Run	Propylene Feed cc/min.	Argon Feed cc/min.	Reaction Rate cc/hr-gram
1	40	--	94.0
2	38	2	82.2
3	37	3	83.4
4	36	4	65.5
5	35	4	62.8
6	34	6	59.2
7	32	18	54.0
8	30	10	24.2
9	20	20	10.3

} Discarded
due to
recorder
inaccuracies

Total Feed - 40 cc/min.

Catalyst Weight - 0.250 grams

TABLE 4

Effect of Propylene Feed Rate on Conversion at 350°C

Propylene Feed Rate cc/min.	Conversion, $\Delta x(10^3)$	Catalyst Weight, grams
18	4.8	0.112
35	10.1	0.220
36	10.2	0.225
37	10.5	0.232
40	10.5	0.250
45	10.8	0.280
55	10.7	0.344

TABLE 5

Effect of Catalyst Age on Reaction Rate

Sample	Time, min.	Reaction Rate, cc/hr-gram
1	10	75.1
2	33	107.0
3	55	109.5
4	79	87.6
5	101	91.5
6	124	107.3
7	146	105.6
8	232	74.0
9	254	89.2
10	276	91.5
11	314	87.0
12	336	71.7
13	358	92.1
14	380	96.0

Catalyst Weight - 0.250 grams

Feed Rate - 40 cc/min.

Furnace Temperature - 350°C

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