Catalyzed Gas-liquid Reactions in Trickling-bed Reactors

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Kinetic studies were made in a differential flow reactor of the hydrogenation of α-methylstyrene with the liquid trickling over a bed of catalyst pellets countercurrent to a stream of hydrogen. The catalysts consisted of palladium, platinum, rhodium, ruthenium, and nickel supported on the external surfaces of alumina pellets.

With palladium at pressures above 3 atm. the apparent rate-controlling step was a surface reaction between dissociated hydrogen and α-methylstyrene both adsorbed on different types of active sites. Below 3 atm. pressure the reactants competed for similar active sites. With platinum the apparent rate-controlling step was a surface reaction between dissociated hydrogen and α-methylstyrene on similar active sites. Rhodium and nickel catalyzed the polymerization α-methylstyrene together with slow hydrogenation. Ruthenium had negligible activity for catalyzing the hydrogenation under the moderate conditions used in this work.

In all cases mass transfer resistances were negligible.

Part I. Hydrogenation of α-Methylstyrene Catalyzed by Palladium

This study was undertaken to demonstrate the utility of applying established concepts of mass transfer and chemical kinetics to the correlation of reaction-rate data obtained on a three-phase system in a flow reactor. The particular system chosen for study was a liquid-gas reaction catalyzed by a bed of solid particles, that is, a trickling-bed reactor. The chemical reaction studied in this investigation was the hydrogenation of liquid α-methylstyrene to form liquid cumene. The reaction was carried out in a fixed bed of catalyst pellets consisting of palladium deposited on the external surfaces of alumina pellets. A flow system in a differential bed was selected with the liquid trickling over the pellets and with hydrogen flowing countercurrently. The accuracy of the analysis permitted the use of a thin-bed reactor, which resulted in small changes in temperature, pressure, and composition across the bed. Such conditions allowed the use of arithmetic mean values of these properties calculated from the terminal conditions of the bed for correlation with reaction rates.

SELECTION OF THE SYSTEM

A gas-liquid reaction was desired which would proceed rapidly to completion at moderate temperatures and pressures in the presence of a solid catalyst and which would proceed at a negligible rate in the absence of a solid catalyst. Alpha-methylstyrene was selected as the liquid reactant for its low volatility, ease of hydrogenation, ease of accurate analysis of reaction products, and completeness of reaction at moderate temperatures. It proved to be an ideal compound for kinetic studies of a gas-liquid reaction although the reaction itself is of no commercial importance.

Palladium supported on alumina pellets was chosen as the catalyst for its ability to hydrogenate liquid α-methylstyrene rapidly to a single product, cumene, at moderate temperatures and pressures. In the manufacture of this catalyst the palladium was deposited on the exterior surfaces of $\frac{1}{8}$- by $\frac{1}{8}$-in. cylinders as a thin layer making up 0.5 weight % of the pellets.

PREVIOUS WORK

Trickling Reactors

Previous experiments on the kinetics of trickling-bed reactors were reported by Miller (*6*) and Klassen (*5*). Miller used an integral reactor for the hydrogenation of cottonseed oil over a pelletted nickel catalyst. Mass transfer resistances were reported to be negligible. Klassen used a differential reactor for the air

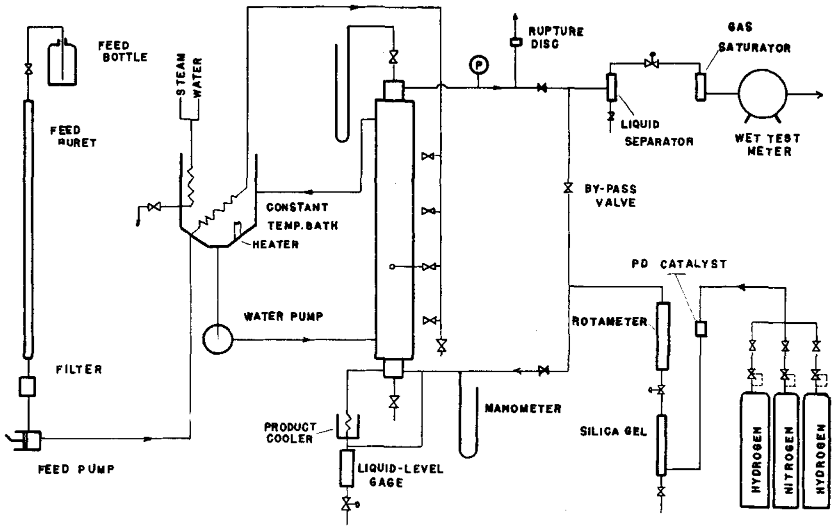

Fig. 1. Flow diagram.

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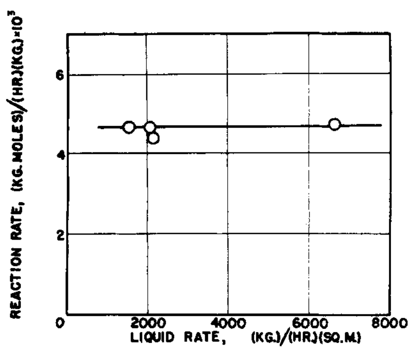

Fig. 2. Dependence of reaction rate on liquid rate; $G = 16.6$ kg./(hr.)(sq. meter), $T = 39.5°$C., and $\pi = 1.93$ atm.

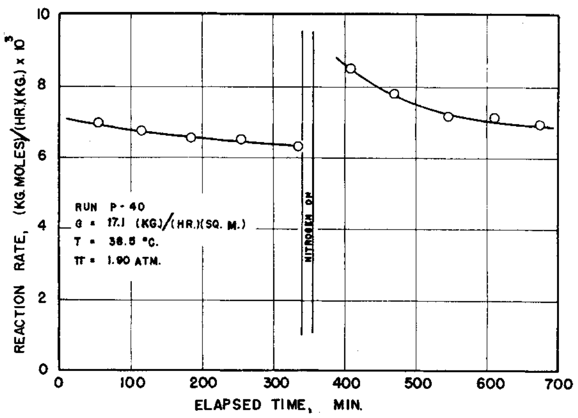

Fig. 4. Variation of catalyst activity with time at the beginning of a run.

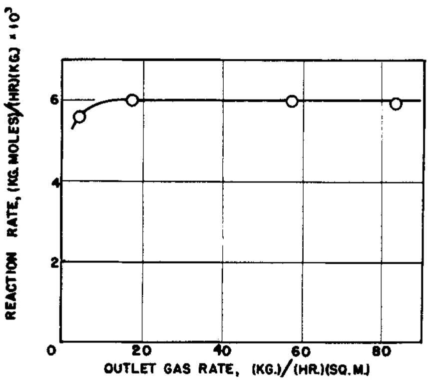

Fig. 3. Dependence of reaction rate on gas rate; $T = 39.5°$C. and $\pi = 1.93$ atm.

oxidation of ethanol to acetic acid in the presence of a palladium catalyst. He found that the apparent rate-controlling chemical step was the reaction between adsorbed molecular ethanol and adsorbed molecular oxygen. Mass transfer coefficients were calculated for the transfer of oxygen through the gas and liquid phases to the catalyst surface.

Palladium-hydrogen System

Palladium has an unusual capacity for dissolving and transmitting hydrogen. Below 300°C. two palladium-hydrogen phases exist, the α phase, low in hydrogen, and the β phase, rich in hydrogen (*7*). Palladium has a face-centered cubic structure with a lattice constant which is increased by the adsorption of hydrogen as follows:

Palladium	3.883 Å.
α-Pd-H	3.894 Å.
β-Pd-H	4.018 Å.
Excess hydrogen in Pd-H	> 4.018 Å.

The adsorption and occlusion of hydrogen by palladium occurs as atomic hydrogen, as is demonstrated by the observation that the amount adsorbed or occluded is proportional to the square root of the pressure.

In the vapor-phase hydrogenation of benzene on palladium Alchudzhan (*1*) found that the α-phase palladium-hydrogen crystal was an active catalyst whereas the β phase was relatively inactive. The β phase was formed by prolonged exposure of palladium to hydrogen at room temperature. The α phase was restored by subsequent displacement of hydrogen by contact with either nitrogen or oxygen.

EXPERIMENTAL EQUIPMENT

A flow diagram of the experimental equipment is shown in Figure 1. The reactor consisted of a stainless steel pipe 49 in. long by 1½ in. I.D. jacketed with a 3-in. steel pipe. A flow of water through the annulus maintained the desired temperature in the reactor, which was packed with an 8-in. depth of inert alumina pellets both immediately above and below the catalyst bed to distribute the liquid feed and to mix the reaction products thoroughly. Thirty grams of catalyst were used throughout this work. Surface-area measurements of the catalyst pellets were not attempted, as only the exterior areas of the pellets were covered with active catalyst.

Liquid feed was pumped into the reactor by a Hills-McCanna duplex pump with a delivery rate variable from 0 to 11 liters/hr. Pulsation in the flow of the liquid over the catalyst was minimized by the superimposed inert packing.

Commercial α-methylstyrene was used in these studies without further purification. The feed and product of the various runs were tested for polymers by the method of Boundy and Boyer (*2*), and in no case was any polymer detected.

The hydrogen was purified to remove traces of oxygen by passing the gas over a palladium catalyst to convert the oxygen to water and then through a silica gel bed to remove the water. Only a small fraction of the hydrogen stream fed to the reactor was consumed; therefore calculation of the hydrogen consumption by difference was not attempted.

Temperature measurements were made with bare thermocouples extending into the reactor both above and below the catalyst. The wires were sealed in steel tubes with an epoxy resin, and the resin exposed to the process was coated with Sauercisen cement to prevent contamination of the catalyst. Despite attempts to maintain isothermal operation, some temperature rise through the catalyst bed was unavoidable. For adiabatic operation this temperature rise is about 5.8°C. for each 1% conversion. The actual rise through the bed averaged 3°C. for each per cent of conversion, an indication that the operation was between adiabatic and isothermal. An arithmetic average value of temperature across the bed was used in correlating rate data. Since the reaction rate was nearly linear with temperature over the small ranges of temperature rise which occurred in the reactor, no significant errors are introduced through use of the arithmetic mean valves.

Pressures were measured both above and below the bed with mercury manometers and Bourdon gauges. The pressure drop through the reactor did not exceed 5 mm. Hg in any of the runs.

Pure cumene, which was needed for preparation of the various feed compositions between 10 and 90% α-methylstyrene, was prepared by complete hydrogenation of α-methylstyrene and was purified by simple distillation.

The extent of conversion in the reactor was determined by the difference in refractive indexes between feed and product samples as measured with a dipping refractometer. The refractive indexes of the three related hydrocarbons at 30°C. are as follows:

		n_D
α-methylstyrene	(*2*)	1.5331
Cumene	(*3*)	1.4865
Isopropylcyclohexane	(*3*)	1.4364

Complete hydrogenation of the α-methylstyrene yielded a product with the refractive index of cumene thus demonstrating that the benzene ring is not hydrogenated under the conditions used in this work.

Reaction rates were calculated as

$$r = -\frac{F\Delta x}{W} \tag{1}$$

For the thin catalyst bed Δx ranged between 0.01 and 0.03 and could be determined with a precision of ±0.0005.

PRELIMINARY EXPERIMENTS

To establish the limitations of experimental procedures several preliminary experiments were performed. With nickel as a catalyst extensive polymerization of the α-methylstyrene took place, whereas with palladium only hydrogenation of the side chain occurred.

The homogeneous reaction rate was found to be negligible in the temperature and pressure ranges under study. Further tests showed that the reaction was not catalyzed by the catalyst support, alumina, or by the walls of the reactor.

Feed Flow Rates

Preliminary tests to determine the effects of gas and liquid flow rates showed that reaction rates were independent of the flow rates of either the gas or the liquid provided that these rates exceeded 1,500 kg./(hr.)(sq. meter) for the liquid and 15 kg./(hr.)(sq. meter) for the gas (Figures 2 and 3). These results are partial proof that under these conditions mass transfer resistances are of negligible importance in controlling the reaction rate.

Catalyst Activity

Several months of experimentation was carried out before techniques for securing reproducible catalyst activity were acquired. Poisoning of the palladium catalyst, caused by the epoxy resin used to seal the thermocouples, was prevented by covering the exposed resin with Sauereisen cement.

The activity of fresh catalyst was initially high but decreased to a constant value after several hours. Exposure of the catalyst to nitrogen, oxygen, or argon caused a temporary increase in the activity of the catalyst, as shown in Figure 4. This effect was due to the displacement of hydrogen from the palladium structure with a resulting change of phase to a more active catalytic form. The catalyst was therefore kept wetted with feed stock and in contact with hydrogen at atmospheric pressure when the unit was not in operation.

Fresh feed or feed stock that had been stored for some time gave unusually high reaction rates when first passed through the reactor, probably owing to the presence of dissolved oxygen or oxidation products. After the feed had been circulated through the reactor for several hours the reaction rate returned to normal.

Following this preliminary work it was possible to make a complete study of the effects of pressure, temperature, and feed composition on reaction rates at a constant level of catalyst activity.

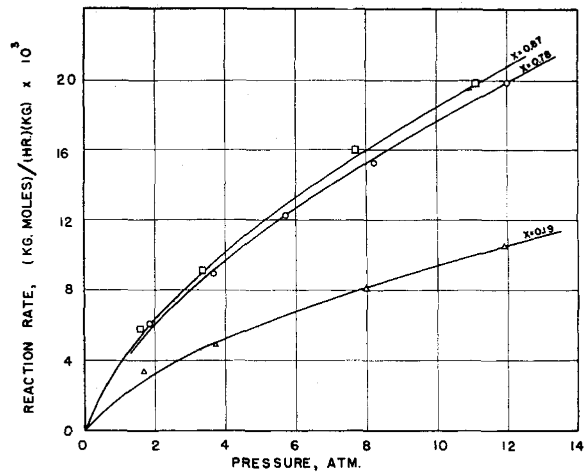

Fig. 5. Reaction rate as a function of pressure at 38.2°C.

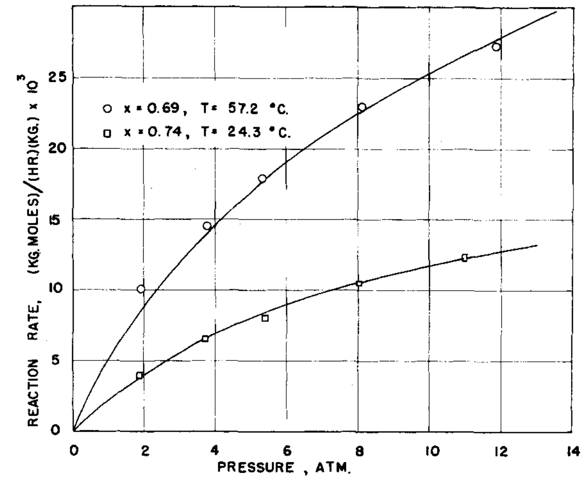

Fig. 6. Reaction rate as a function of pressure at 57.2° and 24.3°C.

CORRELATION OF EXPERIMENTAL DATA

The following conclusions were drawn from the experimentally determined reaction rates, plotted as functions of concentration, temperature, and pressure in Figures 5 to 8.*

1. Mass transfer resistance in the gas phase is nonexistent, as the phase is pure hydrogen.
2. Mass transfer resistance in the liquid surrounding the pellets is negligible as evidenced by the independence of reaction rates of liquid and gas flow rates. Furthermore at low pressures a maximum is observed in the reaction rate plotted as a function of mole fraction of α-methylstyrene (Figure 7), an impossible condition if mass transfer were rate controlling.
3. Mass transfer resistance inside the catalyst pellets is small, as the reaction is restricted to the exterior surface where the catalyst resides. A rough calculation by the Thiele method gave an effectiveness factor of 80% if it was assumed that hydrogen must diffuse through liquid α-methylstyrene and of 99% if it is assumed that the diffusion of α-methylstyrene is limiting. It is likely that hydrogen enters the catalyst by diffusion through the palladium structure as well as through portions of the catalyst surface which are not wetted by liquid. The actual effectiveness factor is therefore between 80 and 99%.
4. Adsorption rates of the reactants or desorption rates of the product cannot be rate controlling because if (*a*) adsorption of hydrogen were rate controlling, the reaction rate would be proportional to hydrogen pressure; (*b*) adsorption of α-methylstyrene were rate controlling, the reaction rate would be proportional to the first or higher power of the concentration of α-methylstyrene, depending on the adsorption equilibrium constant for cumene; and (*c*) desorption of cumene were rate controlling, the reaction rate would be nearly independent of the concentration of α-methylstyrene and of hydrogen pressure.

It was concluded therefore that the surface reaction is rate controlling. A consideration of possible surface-reaction steps showed that previously formulated rate equations were not satisfactory over the entire range of pressure. None of the mechanisms postulated by Hougen and Watson (*4*) explained the difference in the effects of liquid feed composition on reaction rate at 1.9 and 3 atm. pressure, as shown in Figure 7. At a hydrogen pressure of 1.9 atm. the maximum rate occurred at a mole fraction of α-methylstyrene of 0.5. At increased pressures the maximum rate occurred at increasingly higher mole fractions of α-methylstyrene.

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*These data in tabular form have been deposited as document 5307 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

The most satisfactory interpretation of the experimental results for pressures above 3 atm. postulates that the reaction rate is controlled by a surface reaction between adsorbed α-methylstyrene and two adsorbed hydrogen atoms where the two reactants are adsorbed on different types of active sites. The rate equation corresponding to this rate-controlling step, with Langmuir type of adsorption isotherms assumed, is

$$r = k_s K_H K_\alpha \pi x \left[\frac{1}{1 + \sqrt{K_H \pi}}\right]^2 \cdot \left[\frac{1}{1 + K_\alpha x + K_c(1 - x)}\right] \qquad (2)$$

This equation was rearranged into the form

$$r = A\pi x \left[\frac{1}{1 + B\sqrt{\pi}}\right]^2 \left[\frac{1}{1 + Cx}\right] \qquad (3)$$

for convenience in evaluating the constants. The three constants, which are functions of temperature only, were calculated at the three temperatures by the method of least squares. It was next assumed that K_c, the adsorption constant for cumene, is much less than K_α, the adsorption constant for α-methylstyrene. With this assumption the logarithms of the three constants should be linear functions of the reciprocal absolute temperatures. This relationship is shown in Figure 9. Again the best straight line was determined by the method of least squares. The solid lines shown in Figures 5 to 8 are the values of the reaction rates calculated from Equation (3) by use of the calculated constants. The final form of the rate equation is then

$$r = k_s K_H K_\alpha \pi x \left[\frac{1}{1 + \sqrt{K_H \pi}}\right]^2 \cdot \left[\frac{1}{1 + K_\alpha x}\right] \qquad (4)$$

$$\ln k_s = -\frac{1225}{RT} + 0.17$$

$$\ln K_H = -\frac{5780}{RT} + 6.16$$

$$\ln K = \frac{1325}{RT} - 0.98$$

A comparison of the experimental and calculated results is shown in Table 1.

TABLE 1

Temperature, °C.	Average deviation of a single measurement, %	Maximum deviation, %	Number of experimental points
24.3	3.0	5.6	8
38.2	2.3	5.3	18
57.2	2.7	5.3	9

DISCUSSION OF RESULTS

Selection of Rate-controlling Step

The proposed rate equation fits the experimental data with an average deviation of a single measurement of less than 3% for pressures above 3 atm. Below 3-atm. pressure the proposed equation is not so accurate. The data indicate that below 3-atm. pressure the α-methylstyrene and hydrogen compete for the same active sites. Such an assumption results in a rate equation of the form

$$r = \frac{A\pi x}{(1 + B\sqrt{\pi} + Cx)^3} \qquad (5)$$

Sufficient data were not taken to evaluate the constants of this equation because the available catalyst volume in the reactor was too low to permit sufficient conversion for accurate analysis.

The change in the apparent rate-controlling step as pressure is increased is consistent with the observations of Alchudzhan (*1*) concerning the activity of the two palladium-hydrogen phases. At higher pressures the β phase would be present which could have markedly different adsorption characteristics from the α phase.

Heats of Reaction and Adsorption

The energy of formation of the activated complex was found to be 1,225 cal./g.-mole. This is consistent with the endothermic nature of the formation of an activated complex.

The observed heat of adsorption of α-methylstyrene, $-1{,}325$ cal./g.-mole, is consistent with the exothermic nature of molecular adsorption. The relatively small value suggests that physical adsorption may be involved rather than chemisorption.

The observed heat of adsorption of hydrogen, $+5{,}780$ cal./g.-mole, does not agree with the exothermic behavior reported by Smith (*7*). However, the nature of the adsorption on the restricted areas of the surface of the catalyst cannot be expected to be directly comparable with adsorption in the bulk of the metal. The endothermic nature of the adsorption observed in this work is in agreement with the observation that the heat of dissociation of the hydrogen molecule is greater than the heat of adsorption of molecular hydrogen.

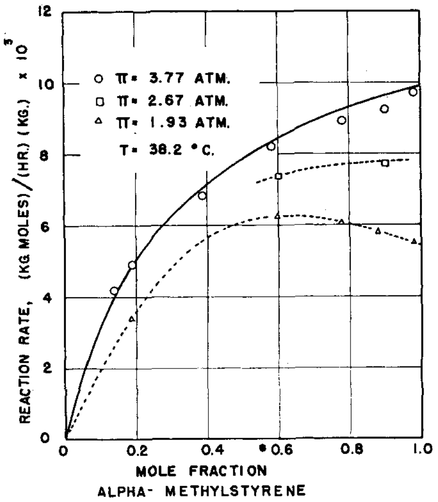

Fig. 7. Reaction rate as a function of conversion at 38.2°C.

Errors

Errors in measuring the various experimental quantities are estimated as follows:

	Estimated error
Liquid flow rate	±2%
Gas flow rate	±2%
Temperature	±0.2°C.
Pressure	± 15 mm. Hg (1 to 3 atm.) ± 0.07 atm. (3 to 12 atm.)
Conversion	±0.03%
Reaction rate	±5%

SUMMARY

1. The catalytic activity of palladium for hydrogenation is increased by pretreatment with air or nitrogen. Subsequent exposure to hydrogen reduces the activity.

2. All mass transfer resistances were negligible under the conditions of operation.

3. Above 3-atm. pressure the apparent rate-controlling step is a surface reaction between adsorbed α-methylstyrene and adsorbed atomic hydrogen on different types of active sites. A rate equation is presented which fits the experimental data with an average deviation of 3%. The maximum deviation of a single measurement is 5.6%.

4. Below 3-atm. pressure the mechanism of the reaction changes, owing to a phase change in the palladium-hydrogen catalyst system. Insufficient experimental data were obtained to formulate a rate equation in this region.

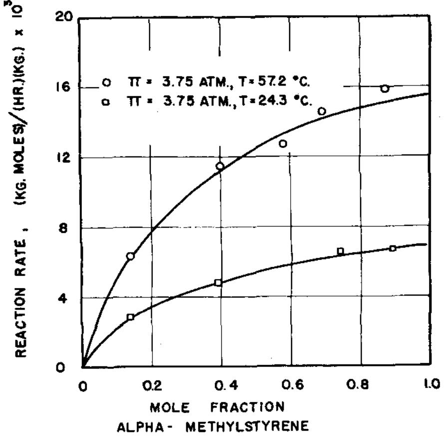

Fig. 8. Reaction rate as a function of conversion at 57.2° and 24.3°C.

Part II. Hydrogenation of α-Methylstyrene Catalyzed by Platinum

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This second investigation on the kinetics of catalyzed gas-liquid reactions in trickling-bed reactors is similar to that described in Part I except that platinum was used as the catalyst instead of palladium. A few exploratory experiments were also made with ruthenium, rhodium, and nickel.

CATALYST

A platinum catalyst supported on 1/8- by 1/8-in. cylindrical pellets of alumina was used. The platinum appeared as a fine-grain deposit on the exterior surfaces of the pellets, which had the following properties:

Bulk density	0.91 ± 0.01 g./cc.
Pellet density	1.39 ± 0.01 g./cc.
Platinum content	2%

Interior surface areas of the pellets were not measured, as only the external surfaces of the pellets were covered with the active catalyst and hence involved in the reaction.

To obtain sufficient conversion for reliable determinations of reaction rates 100 g. of catalyst was used for runs Pt-12 to Pt-15 and 350 g. for the remaining runs. The catalyst bed was replaced after runs Pt-15 and Pt-20. Between runs the catalyst was kept wetted with the liquid feed and in contact with hydrogen at 1 atm.

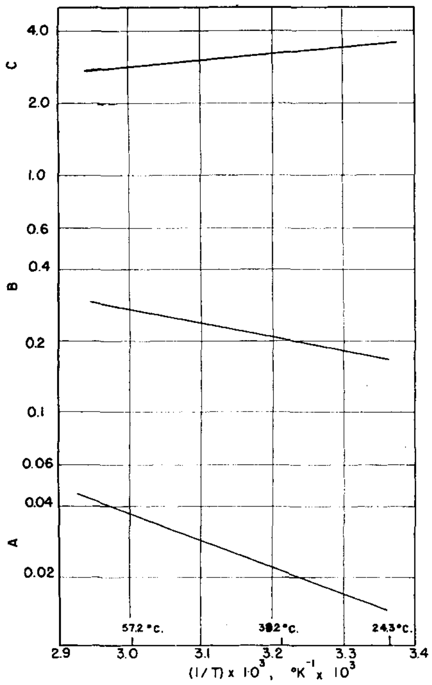

Fig. 9. Temperature dependence of constants of Equation (3).

EXPERIMENTAL OBSERVATIONS

Compared with the palladium catalyst the activity of the platinum was much more difficult to reproduce and did not reach a constant value within 100 hr. of operation.

The observed behavior of the platinum catalyst is summarized as follows:

1. The catalyst activity showed an irreversible decline with time of operation and did not attain a constant value as was the case with palladium. After an initial rapid rate of decline the catalyst activity continued to decline indefinitely at a slow rate.
2. In contrast to the behavior of palladium, the reduced activity of platinum after storage under hydrogen was not restored by exposure to air or nitrogen.
3. The activity of a fresh supply of catalyst decreased rapidly during the first 16 hr. of operation, dropping to less than 10% of its initial value during operation at constant pressure and feed composition. With a fresh supply of catalyst, experimental runs were continued for at least 20 hr. before samples and data were taken for correlation.
4. An increase in the pressure of hydrogenation produced a considerable decrease in catalyst activity. Further variations in pressure did not alter this activity unless the former highest pressure was subsequently exceeded. Any increase in pressure above this former highest pressure caused a further decrease in activity. These results are shown in Figure 10. In any given series of pressure runs the experiments were, therefore, started with the highest pressure of the planned series in order that runs at subsequent pressures would be made at nearly the same activity.

Standard Run

In the course of making experimental runs at variable conditions of pressure and composition, the extreme sensitivity of the catalyst activity made it necessary to make intermediate runs at frequent intervals under some arbitrary standard conditions of operation. From the decline in activity between two succeeding standard runs the catalyst activities of intermediate runs at variable pressure and composition were estimated. This standard run was chosen at the arbitrary conditions of 40°C., 3.7 atm., and a liquid feed composition of 60 mole % α-methylstyrene.

To secure several data at nearly constant activity the experimental operation was continued for 30 to 80 hr. in each series without interruption.

CORRELATION OF DATA

All experimental data on significant runs are tabulated in Table 1.* The reaction rates, adjusted to a standard activity are plotted in Figures 11 and 12 as functions of liquid composition at different pressures. From these data the following conclusions were drawn:

1. Mass transfer resistances were negligible, as the reaction rates were independent of the flow rates of either gas or liquid. This conclusion is supported by the results of the first investigation using palladium catalyst, where although the reaction rate was ten times faster than with platinum the mass transfer resistances were negligible. In this investigation the resistance to the mass transfer of hydrogen was much less than 1% of the resistance imposed by the chemical reaction.
2. The adsorption rate of hydrogen is not rate controlling. If it were, the reaction rate would be directly proportional to the pressure of hydrogen, whereas the observed rate varied with a fractional power of pressure much less than unity.
3. The adsorption of α-methylstyrene is not rate controlling, as this would require a rate proportional to the concentration to a first or higher power depending upon the adsorption constant of cumene. The reaction rate was a complex function of liquid composition, reaching a maximum rate at compositions below unit mole fraction of α-methylstyrene.
4. The desorption of cumene is not rate controlling, as this would require a rate nearly independent of pressure and concentration, contrary to observations.
5. The rate-controlling step does not involve the impact of one unadsorbed reactant with the other adsorbed. This would give a reaction rate proportional to the concentration of the unadsorbed reactant, contrary to observations.

Development of Equations of Rate-controlling Step

The experimental data combined with the observations above indicate that the rate-controlling step is a surface

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*See footnote on page 368.

reaction between the adsorbed α-methylstyrene and adsorbed atomic hydrogen on adjacent sites. By the methods outlined by Hougen and Watson (*4*), extended to gas-liquid reactions, this postulation results in the following rate equations:

$$r=\frac{k_s(L-c_p)^3K_\alpha K_H x\pi}{(1+K_\alpha x+K_c(1-x)+\sqrt{K_H\pi})^3} \quad (1)$$

Equation (1) may be written in the following form:

$$r = \frac{A\pi x}{(1 + B\sqrt{\pi} + Cx)^3} \quad (2)$$

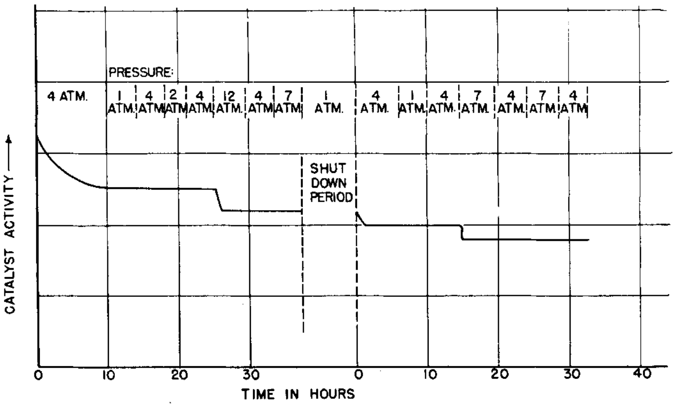

Fig. 10. Typical behavior of platinum catalyst.

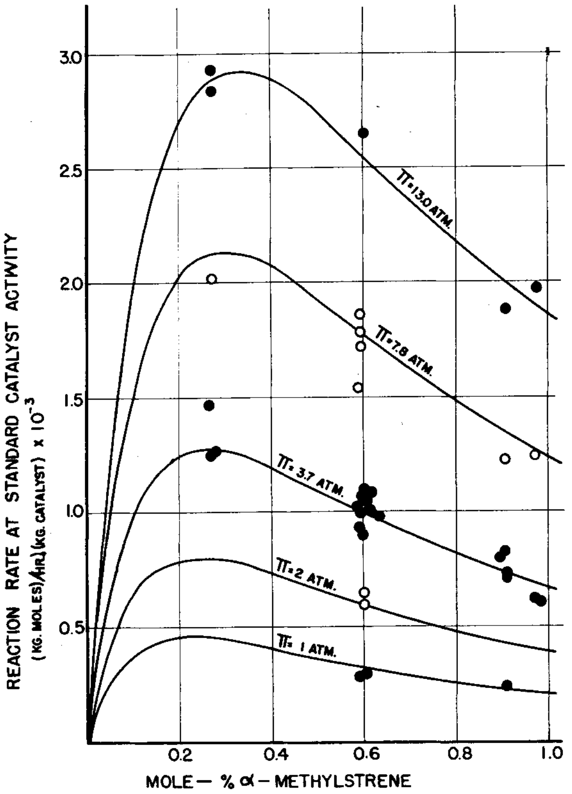

Fig. 11. Reaction rate as a function of liquid composition at standard catalyst activity.

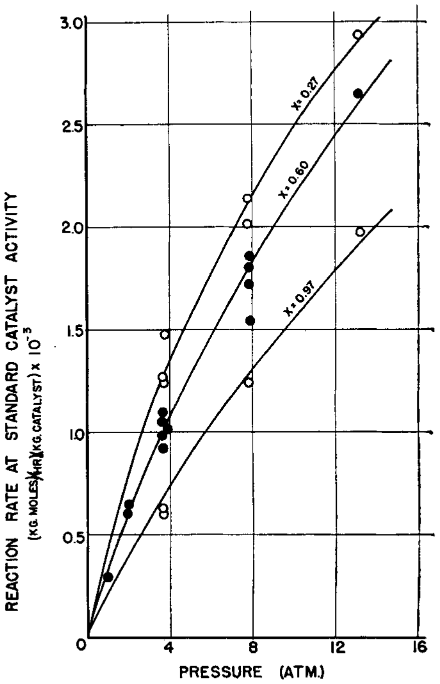

Fig. 12. Reaction rate as a function of hydrogen pressure at standard catalyst activity.

where

$$A = \frac{k_sK_HK_\alpha(L - c_p)^3}{(1 + K_c)^3} \quad (3)$$

$$B = \frac{\sqrt{K_H}}{1 + K_c} \quad (4)$$

$$C = \frac{K_\alpha - K_c}{1 + K_c} \quad (5)$$

The values of B and C are constant for all experimental runs at constant temperature, whereas A is a function of the catalyst activity.

Standard Activity

If A_s is the value of A for a "standard activity," arbitrarily defined as the catalyst activity having a reaction rate of 1×10^{-3} (kg-moles)/(hr.)(kg. catalyst) under standard conditions, namely, 40°C., 60 mole % α-methylstyrene, and a hydrogen pressure of 3.7 atm., from this definition and Equation (2),

$$A_s = \frac{1(10^{-3})}{(3.7)(0.6)} \cdot(1 + B\sqrt{3.7} + 0.6C)^3 \quad (6)$$

The value of A at any other catalyst activity will then be given as

$$A = A_s\alpha \quad (7)$$

where

$$\alpha = \frac{A}{A_s} = \left(\frac{L - c_p}{L - c_{p_s}}\right)^3 = r_s \times 10^3 \quad (8)$$

Introducing the activity factor in Equation (2) gives

$$r = \frac{\alpha A_s\pi x}{(1 + B\sqrt{\pi} + Cx)^3} \quad (9)$$

Evaluation of Constants in Rate Equation (1)

Rearrangement of Equation (2) gives

$$\sqrt[3]{\frac{\pi x}{r}} \quad \frac{1}{\sqrt[3]{A}} + \frac{B\sqrt{\pi}}{\sqrt[3]{A}} + \frac{Cx}{\sqrt[3]{A}} \quad (10)$$

The constants A, B, and C were determined from Equation (10) by the method of least squares, and the value of A_s was calculated from Equation (6). At a temperature of 40°C.

$A_s = 1.155 \times 10^{-2}$, $B = 0.195$,

and $C = 2.623$.

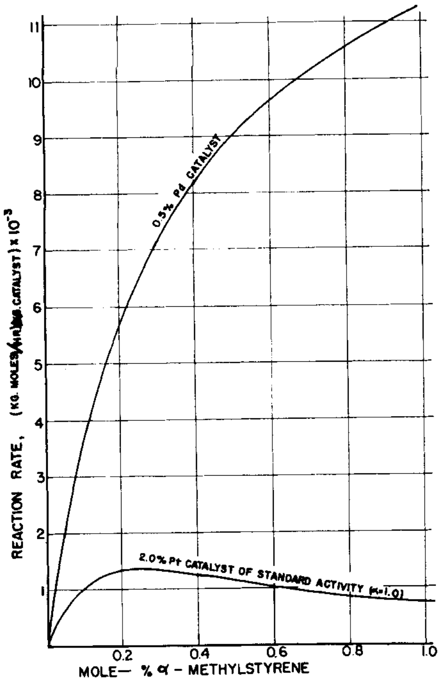

Fig. 13. Comparison of reaction rates with 0.5% palladium and 2% platinum catalysts at 40°C. and $\pi = 4$ atm.

Inserting these values in Equation (9) gives

$$r = \frac{\alpha 0.01155 \pi x}{(1 + 0.195\sqrt{\pi} + 2.623x)^3} \qquad (11)$$

The catalyst activity factor defined by Equation (8) is a function of the history of the catalyst. The values of α used in these correlations are given in Table 1.*

In Figure 12 the reaction rates at standard activity are plotted against hydrogen pressure π at three values of liquid composition, namely, at $x = 0.27$, 0.6, and 0.97. In Figure 11 the reaction rates at standard activity are plotted against liquid composition at five pressures: 1, 2, 3.7, 7.8 and 13.0 atm. The unusual and unexpected effect of liquid concentration is shown in Figure 11, where for any given pressure the maximum rate does not occur at a mole fraction of unity, but at a mole fraction ranging from 0.2 to 0.35. The constants k_s, k_α, k_H, and K_c in Equation (1) are exponential functions of temperature. The constants A_s, B, and C in Equation (2) were evaluated only at 40°C. Evaluation of A_s, B, and C at other temperatures did not seem warranted unless the variables influencing the activity factor L-c_p were also formulated in terms of the past history of the catalyst and operating variables.

Comparison of Catalysts

In this investigation on the catalytic hydrogenation of α-methylstyrene five catalysts were used. A comparison of the reaction rates obtained at 40°C. and 3-atm. pressure as a function of liquid feed composition is shown in Figure 13. These results are based upon unit mass of catalyst. It will be observed that palladium is fully ten times as effective as platinum. With palladium a constant activity is obtainable; with platinum, the results are based upon a standard activity. Actually the activity of platinum steadily declined without reaching a constant value.

At pressures below 3 atm. both platinum and palladium exhibited similar behavior where the rate-controlling chemical step was the surface reaction between adsorbed α-methylstyrene and adsorbed atomic hydrogen. The effect of composition was remarkable in exhibiting a maximum rate at mole fractions of α-methylstyrene less than unity. With platinum, pressures were increased to 12 atm. without reaching a maximum rate at a concentration of unity. With palladium the rate-controlling step changed at pressures above 3 atm., corresponding to a phase change in the palladium-hydrogen alloy. The initial reaction rate with rhodium as a catalyst was of the same order of magnitude as that of palladium. However, the catalyst activity decreased so rapidly that the reaction rate was almost negligible after 10 hr. of operation. The reaction rates with rhodium and ruthenium were too slow for study, and nickel caused a polymerization of the α-methylstyrene. Because of polymerization or low rates no data were correlated for these three catalysts.

SUMMARY

1. With platinum as a catalyst the apparent rate-controlling chemical step in the hydrogenation of α-methylstyrene consisted of a surface reaction between adsorbed α-methylstyrene and adsorbed atomic hydrogen.

2. At a given temperature and pressure the maximum rate occurred at a mole fraction below unity. With palladium similar concentration effects were observed; however, the maximum rate occurred at a mole fraction of unity at about 3 atm. and above.

3. Platinum showed extreme variation in activity, depending upon pressure, temperature, time, and past history. A condition of constant activity was not obtained within running times of 100 hr. Rate equations were, therefore, expressed in terms of a standard activity or activity factor.

4. For the same condition of temperature, pressure, and concentration the reaction rates were at least ten times faster with palladium than with platinum.

5. Rhodium and ruthenium reaction rates were too slow for study in the available apparatus.

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NOTATION

A = constant in rate equation
A_s = value of constant in rate equation at standard catalyst activity
B = constant in rate equation
C = constant in rate equation
c_p = diminished number of active sites due to deactivation of catalyst or to gradual and irreversible accumulation of adsorbed poisons
F = liquid feed rate, kg.-moles/hr.
G = gas flow rate, kg./(hr.)(sq. meter)
K_c = adsorption constant for cumene
K_H = Adsorption constant for hydrogen
K_α = adsorption constant for α-methylstyrene
k_s = surface reaction velocity constant, kg.-moles/(hr.)(kg. of catalyst)
L = total number of active sites/g. of catalyst
L = liquid flow rate kg./(hr.)(sq. meter)
R = gas constant = 1.987 cal./(°K.)(g.-mole)
r = reaction rate, kg.-moles/(hr.)(kg. of catalyst)
r_s = reaction rate under standard conditions
T = temperature, °K.
W = mass of catalyst pellets, kg.
x = mole fraction α-methylstyrene in an α-methylstyrene–cumene mixture
α = catalyst activity factor
π = hydrogen pressure, atm.

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*See footnote on page 368.