Rate Studies in Tubular Reactors

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The tubular reactor, as the term is used in the present paper, is a cylindrical tube on the inner surface of which a catalyst is deposited. The reacting mixture flows through this tube, the reaction components diffuse to the wall, where reaction takes place, and the products diffuse back into the main gas stream.

Damkohler (*6*) first analyzed this type of system and presented the basic differential equations describing the process. Baron, Manning, and Johnstone (*1*), utilizing this analysis in their studies of the oxidation rates of sulfur dioxide in a tubular reactor, solved the diffusion equation by assuming a first-order kinetic mechanism at the tube wall as a boundary condition. The experimental work was limited to low flow rates. The catalytic oxidation of ammonia in tubular reactors was studied by Johnstone, Houvouras, and Schowalter (*10*), who used the same type of analysis. The maximum Reynolds number was 150.

Rossberg and Wicke (*14*) measured the rate of combustion of graphite tubes when nitrogen-oxygen mixtures were passed through them. The flow rates were in the laminar region and temperatures between 500° and 1,400°C. were used. The mechanism which controlled the process was found to depend on the operating temperature.

Satterfield and coworkers (*15*), studied the decomposition of hydrogen peroxide in a tubular reactor by means of the classical diffusion techniques, using *j* factors and the Chilton-Colburn equation (*2, 3*).

The present study was undertaken in order to extend the theory and technique necessary for the use of tubular reactors in kinetic investigations. The reaction between hydrogen and the olefin-1 hydrocarbons has been investigated extensively, and a review of these studies has been presented by Hoelscher, Poynter, and Weger (*8*). Because of the availability of these kinetic data, the aforementioned reaction was chosen to be studied. The catalyst used was palladium black on carbon.

EXPERIMENTAL WORK

Reaction Apparatus

The experimental apparatus used in this study was quite standard and is shown schematically in Figure 1. Complete details regarding the apparatus and its design are available elsewhere (*9, 16*). Electrolytic hydrogen and olefin of c.p. grade were fed from two commercial high-pressure cylinders through a series of pressure-regulating and flow-stabilizing devices into the gas-purification system. After passing through the purifiers, the gases were metered and mixed intimately prior to entering the heat exchanger section of the constant-temperature bath. Insulated Pyrex manifolds permitted the selection of any one of four reactor-tube assemblies for a particular trial. Temperatures of the catalyst tube during the reaction were measured by means of thermocouples embedded in the tube wall at various points along the tube length. The exit gas stream from the reactor was passed through a flow divider where a small portion of the gas was taken for analysis by a thermal conductivity unit. The remainder was vented to the atmosphere. A blank reactor-tube assembly permitted analysis of the gas entering the catalyst tubes. All outlet streams from the system were sealed from the atmosphere by means of dioctyl-phthalate bubblers.

From the mixing chamber the feed stream passed through a preheater tube and then into an insulated inlet manifold which exhausted through stopcocks into four individual reactor sections. The preheater and the reactor sections were maintained in a constant-temperature bath through which water from a thermostatically controlled supply was pumped continuously. The reactor sections were connected to an exit manifold to which was attached a manometer for measuring pressures in the catalyst tubes.

Each reactor section consisted of a catalyst tube (of different lengths, as explained later) preceded by a calming section at least 100 diameters in length and followed by a tail section. These two sections consisted of tubes identical in diameter (0.44 cm.) with the catalyst tube but not impregnated with catalyst. The purpose of the calming section was to produce a well-developed velocity profile in the feed stream before it entered the catalyst tube. The purpose of the tail section was to prevent any downstream disturbances which might regress into the catalyst tube.

The palladium black catalyst was deposited in the carbon tubes by drawing a 5% palladous chloride solution into them. The tubes absorbed the solution, were dried, and then fired at 500°C. with a stream of nitrogen passing through them. This method gave a very uniform deposit of palladium black. Spectrophotometric analysis of six different catalyst-tube sections yielded a palladium-to-carbon weight ratio of 0.0090 with an average deviation of +0.3%.

The problem of sealing the catalyst tubes was solved by the use of brass tubing with an inside diameter almost identical to the outside diameter of the graphite tubes. It was found that by turning the tubes down a few thousandths of an inch on a lathe they could be made to fit snugly inside the brass tubing (Figure 2). The calming section, catalyst tube, and tail section were butted together inside the brass tubing, which in turn was fastened to the glass-ball joints on either end with Cerroseal, a special indium solder that adheres to both glass and metal. The glass-ball joints provided the connections to the manifolds.

Analytical Apparatus

The apparatus used for gas analysis was a Leeds and Northrup Thermal Conductivity Unit especially constructed so that an accuracy of at least one part in ten thousand might be obtained. Complete details including the circuit diagram for this apparatus are available elsewhere (*9, 16*).

The conductivity unit was calibrated for the hydrogen-olefin mixtures used in this study by running a large number of samples of known composition through the unit and measuring the resulting bridge unbalance. In a study of the characteristics of Leeds and Northrup thermal-conductivity cells Collier (*4*), using the system hydrogen, ethylene, ethane, found that ethane was not differentiated from ethylene as long as the hydrogen concentration was kept above 35%. Since the lowest hydrogen concentration used in the present study was 58%, it was felt that the result cited above could safely be applied in this case and generalized to other olefin-alkane combinations.

The logarithm of the mole percentage of hydrogen in the gas stream was found to be directly proportional to the bridge unbalance.

Experimental Conditions

The main factors which influence the rate of reaction in a tubular reactor are flow rate, temperature, and composition of the reacting system (other factors, such as catalyst activity, being constant).

These primary variables covered as wide a range as possible while still retaining the differential characteristics of the tubular reactor. Thus, since the palladium black is a highly active hydrogenation catalyst, it was possible to run the reaction at relatively low temperatures. The experimental temperature range finally chosen was 30° to 45°C. The range of Reynolds numbers for which experimental data was obtained was 125 to 2,300. At the lower Reynolds number limit and at the higher temperature limit the percentage conversions of the reactants were as high as they could be permitted to become in a differential reactor. At those extreme limits the molal flow rate was decreased by 7% over the reactor length, owing to reaction. At the upper Reynolds number limit and the lower temperature limit the conversions were just high enough to permit accurate measurement.

The composition range used in the experimental work was 58 to 95 mole % hydrogen in the inlet gases. The factor which fixed the lower limit was the possibility of olefin polymerization at high olefin concentrations. The operating range of temperatures was low enough to prevent any polymerization, but the high exothermicity of the reaction could have produced local thermal effects which might have caused polymerization unless an excess of hydrogen had been present.

The length of the reactor tube was varied over a twofold range in order to determine the effect of variation of contact time. The three tube lengths which were

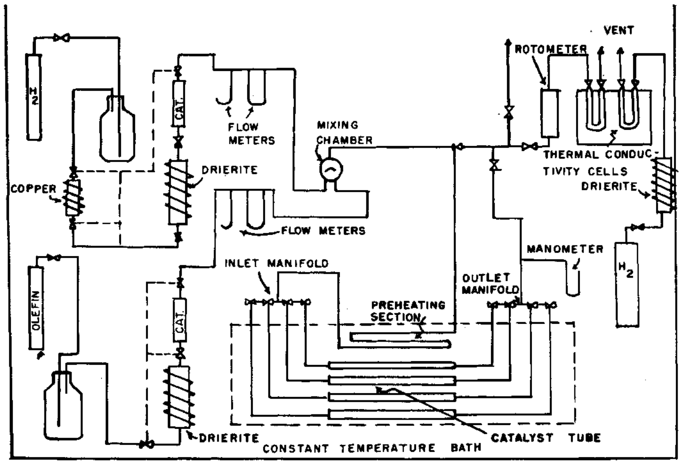

Fig. 1. Schematic flow diagram.

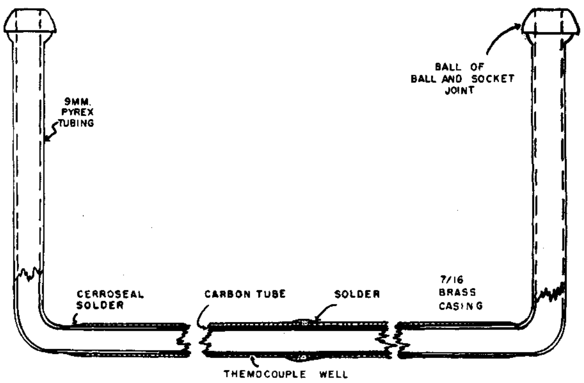

Fig. 2. Catalyst-tube-assembly detail.

used to obtain all the final data were 22.9, 34.3, and 45.7 cm.

As was mentioned previously, temperature measurements were made at various points along the catalyst tube by means of thermocouples, so that it was possible to determine how closely the reaction adhered to the desired isothermal conditions. Owing to the highly exothermal character of the reaction being studied, a small temperature rise at the catalyst surface was to be expected, but this rise was generally observed to be constant—ranging from 2° to 3°C. above the bath temperature.

The complete experimental data are available in a detailed report to the Office of Ordnance Research by the present authors (*9*).

ANALYSIS OF DATA

The physical system used in this work, the range of parameters investigated, and the extensive information available on the highly active nature of the catalyst used combined to suggest initially that the process should be diffusion controlled. On this assumption, a model involving the existence of a boundary layer of product along the tube wall was set up and used as the basis for an analytical description of the process (*9, 16*).

More thorough study of the data has indicated that this model is not correct. The conversion was noted to be affected markedly by slight changes in temperature; an "over-all" energy of activation was computed by plotting the logarithm of the conversion vs. the reciprocal of the absolute temperature for any one set of conditions and was found always to be in the range of 6,000 to 7,000 cal./mole. Such a value is much too high to indicate diffusion control. In addition, the rate of the hydrogenation reaction was observed to be of the same order of magnitude for all the olefins used. Yet the diffusivity of ethylene in a hydrogen-ethylene mixture is more than ten times as great as the diffusivity of butene in a hydrogen-butene mixture. Had diffusion been the controlling factor, one would have expected a sharp decrease in measured rate with increasing chain length of the olefin. Thus a chemical-reaction mechanism was assumed to be controlling the process.

Available evidence seems to indicate that the Langmuir-Hinshelwood mechanism best describes the hydrogenation of olefins (*11, 12*). This mechanism postulates a reaction between an adsorbed olefin molecule and hydrogen adsorbed in either the molecular or atomic form. The olefin is strongly adsorbed and the hydrogen is weakly adsorbed. The differential rate equation for this model is developed by Laidler (*11*), who assumes that the Langmuir form of the adsorption isotherm holds:

$$r = \frac{k'b'by_Ay_B}{(1 + by_A)^2} \qquad (1)$$

The constant b' was assumed to be the same for the hydrogenation of the three olefins used in the present work. The kinetic constant which was therefore determined was $k'b'$. Equation (1) then takes the form

$$r = \frac{kby_Ay_B}{(1 + by_A)^2} \qquad (2)$$

The form of Equation (2) indicates that the rate will pass through a maximum at some intermediate olefin concentration. The results of Constable (*5*) and Pease (*13*) confirm this for the hydrogenation of ethylene on copper. The data of Constable, for example, show that for a reaction temperature of 0°C. the rate passes through a maximum at 0.18 mole fraction ethylene and drops to 90% of this maximum rate at 0.09 and 0.33 mole fraction ethylene. This represents only a 10% change in the rate over a mole fraction of ethylene change of 0.24. Similar conclusions can be drawn from the data of Farkas and Farkas (*7*) on platinum. In the present work the ethylene concentration was varied only over a mole fraction range of 0.17.

As a consequence, hydrogenation data obtained in the region of this maximum can usually be correlated satisfactorily on the basis of an assumed zero-order reaction. The assumption made in this work, that the same mechanism applies to the hydrogenation of propylene and butene-1 as to the hydrogenation of ethylene, is probably justified because of the close structural similarity of the three molecules.

DERIVATION OF RATE EQUATIONS

n_A and n_B represent the number of moles of olefin and the number of moles of hydrogen per unit time, respectively. Then by a material balance over a differential section of the tubular reactor one obtains

$$dn_A = -\pi Dr\,dL \qquad (3)$$

Since the rate is proportional to the mole fractions of the materials present, the problem is to express dn_A in terms of mole fractions.

In the reaction $A + B \rightarrow R$ the following stoichiometric relations will be valid reaction when there is no product in the feed stream:

$$n_A = \frac{y_An_{B_0}}{(1 - y_A)} \qquad (4)$$

and

$$y_B = \frac{y_{B_0} - y_{A_0}(1 - y_A)}{y_{B_0}} \qquad (5)$$

(The subscript $_0$ indicates inlet quantities)

Then $$dn_A = \frac{Fy_{B_0}\,dy_A}{(1 - y_A)^2} \qquad (6)$$

Combining Equations (2), (3), (5), and (6) yields

$$\frac{y_{B_0}^2(1 + by_A)^2\,dy_A}{y_A(1 - y_A)^2(\gamma + y_{A_0}y_A)} = -kb\,\frac{\pi D\,dL}{F} \qquad (7)$$

This equation is integrated over the length of the reactor tube to yield the following result:

$$2.303\left[\frac{y_{B_0}^{\ 2}}{\gamma}\log\frac{\left(\dfrac{\gamma}{y_A} + y_{A_0}\right)}{\left(\dfrac{\gamma}{y_{A_0}} + \gamma_{A_0}\right)}\right.$$

$$+ (b + 1)(b\gamma - 1)\log\frac{(1 - y_A)}{y_{B_0}}$$

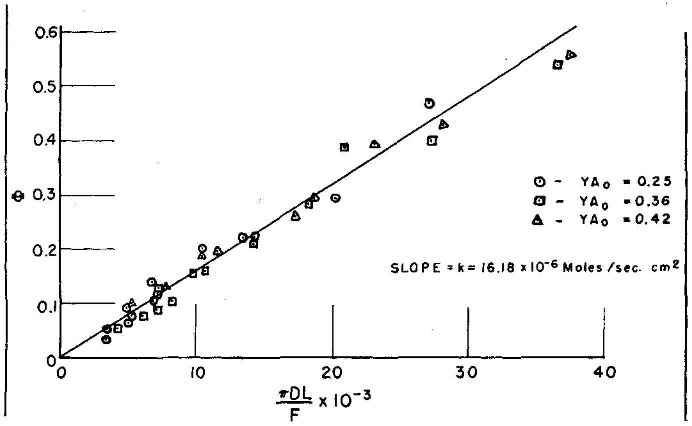

Fig. 3. Typical plot of ϕ vs. π_{DL}/F data for $C_2H_4 + H_2$ at 45°C. [*See* Equation (9).]

TABLE 1. RATE CONSTANTS

Hydrogenation of	$k \times 10^6$, moles/(sec.)(sq. cm.) 30°C.	40°C.	45°C.
Ethylene	9.23	13.37	16.18
Propylene	4.33	6.04	8.13
Butene-1	2.21	3.57	4.67

TABLE 2. FREQUENCY FACTORS AND ACTIVATION ENERGIES

Hydrogenation of	A, moles/ (sec.)(sq. cm.)	E, cal./ g. mole
Ethylene	1.62	7,140
Propylene	2.76	8,130
Butene-1	10.6	9,330

$$\left.\cdot\frac{\left(\frac{\gamma}{y_{A_0}} + y_{A_0}\right)}{\left(\frac{\gamma}{y_{A_0}} + y_A\right)}\right]$$

$$+ (b+1)^2 \frac{(y_{A_0} - y_A)}{(1 - y_A)}$$

$$= kb\,\frac{\pi DL}{F} \qquad (8)$$

[y_A in Equation (8) is the exit mole fraction of olefin]

or

$$\phi = kb\,\frac{\pi DL}{F} \qquad (9)$$

where ϕ = the left-hand side of Equation (8). Since no independent adsorption data were available, the adsorption constant b had to be evaluated before use could be made of Equation (9).

The ethylene hydrogenation runs were made with three values for the inlet ethylene mole fraction (0.25, 0.36, 0.42). As a first approximation it was assumed that the ethylene mole fractions were near the value corresponding to the maximum rate mentioned before. To check this assumption the ethylene data were correlated by use of a zero-order kinetic equation. The data correlated well on this basis, and kinetic constants derived from it checked closely with those derived later from the more elaborate analysis.

Since the reaction at the ethylene mole-fraction values used was determined to be approximately zero order, the initial rates at the extremes of the inlet compositions were now equated and the adsorption constant was evaluated, as follows:

$$r_0 = \frac{kby_{A_0}y_{B_0}}{(1 + by_{A_0})^2}$$

where

r_0 = initial rate

and

$$r_0(y_{A_0} = .25) = \frac{kb(0.75)(0.25)}{(1 + 0.25b)^2}$$

$$r_0(y_{A_0} = 0.42) = \frac{kb(0.58)(0.42)}{(1 + 0.42b)^2}$$

Then

$$\frac{(0.75)(0.25)}{(1 + 0.25b)^2} = \frac{(0.58)(0.42)}{(1 + 0.42b)^2}$$

and

$$b \cong 1.0$$

To check the validity of this procedure, the value of r_0/k was calculated for all three of the compositions used in the ethylene hydrogenation studies. The following values were obtained.

$$\frac{r_0}{k}(y_{A_0} = 0.25) = 0.1200$$

$$\frac{r_0}{k}(y_{A_0} = 0.36) = 0.1240$$

$$\frac{r_0}{k}(y_{A_0} = 0.42) = 0.1210$$

As was to be expected, r_0/k is practically a constant at the compositions under discussion. It should be noted also that the rate constant evaluated independently by means of the zero-order rate equation is approximately 0.12 of the rate constant which was evaluated by means of the equation making use of the Langmuir-Hinshelwood expression. This is also supported by the preceding values.

Since hydrogenation data for propylene and butene were not obtained in the region of a rate maximum (and the available data could not be correlated by a zero-order equation), the same methods could not be applied to the determination of b for these cases. Hydrogenation runs were made with butene at two initial compositions. The constant b was evaluated by a trial-and-error method. Values of ϕ were calculated by use of various assumed values for b, and the ϕ's were then plotted vs. their respective $(\pi DL)/F$ groups. The value of b which gave the best correlation independent of initial composition was chosen as the applicable one. For butene-1 this was found to be $b = 14$.

Since propylene hydrogenation runs were made at only one composition, a value of $b = 10$ was chosen arbitrarily for this case. It was found that the rate constant was not too sensitive to the exact value of b; for instance, $b = 10 \pm 2$ for the case of propylene would not have altered k appreciably.

RESULTS

The rate constants for the hydrogenation of ethylene, propylene, and butene-1 were evaluated by plotting ϕ vs. $(\pi DL)/F$. A typical plot is presented in Figure 3, and activation energies and frequency factors were obtained by means of the conventional Arrhenius plots shown in Figure 4, the results being presented in Tables 1 and 2.

The derived rate equation is based on mixed mean mole fractions at inlet and outlet of the tubes. The composition of the gas at the catalytic surface is obviously somewhat different owing to the gradients existing across the tube radius. A fully rigorous derivation would involve the solution of the diffusion equation with the Langmuir-Hinshelwood equation as a boundary condition.

The values obtained for the rate constant could not be compared directly with other published data as they depend on many factors unique to the particular system and apparatus used in the investigation. It will be observed that the rate constants are of the same order of magnitude for the hydrogenation of all three olefins. This lends support to the previous arguments in favor of a reaction-controlled process.

The activation energies show an interesting trend in that they increase regularly as the number of carbon atoms in the hydrocarbon increases, probably owing to steric effects. The energies reported are within the range of values commonly found for catalysis by the higher molecular weight transition-state metals. Since values shown in Table 2 include the hydrogen adsorption equilibrium constant, comparison with other data is impossible. However, the trend is expected. It may be shown that the frequency factor for a heterogeneous catalytic reaction of this type is inversely proportional to the product of the partition functions and directly proportional to the concentration of available active sites. An estimate of these terms for this problem indicates that the frequency factor should increase with increasing molecular weight and, moreover, that the ratio of the values found is of the right order of magnitude.

It had been expected that the geometry of the tubular reactor, i.e., a high volume-to-surface ratio, would permit the rate of diffusion of reactants to the catalyst surface to become the controlling step in the reaction—at least at low Reynolds numbers. This is a reasonable expectation, since lateral transport occurs only by the mechanism of molecular diffusion in the laminar flow range. It seems likely therefore that a certain amount of turbulence occurred in the tubes, even at low Reynolds numbers, which would greatly increase the lateral diffusion rate, as the mechanism of eddy diffusivity would then be available for reactant and product transport. That such turbulence existed seems probable.

In recent work which required the preparation of a palladium black catalyst on the outer surface of carbon tubes identical to those used in this study, visual observation of the surface was possible, and it was evident that despite care in providing a carbon surface which is initially smooth, the process of impregnation and firing to the amorphous metal results in a highly roughened surface. Furthermore, the process is known to be exothermic; wall temperatures along the reactor tube were measured and found to be as much as 2° to 3° above the bath temperature, and the radial temperature gradient through the gas stream, although not measured because of the small tube diameter, could easily have been appreciable. Such a gradient would cause a convective process at the wall which would, in turn, contribute to gas-phase mixing and a radial-diffusion resistance lower than expected from pure molecular diffusion.

In retrospect it therefore seems likely that considerable turbulence, or lateral mixing, was introduced into the gas stream by surface roughness and convective (thermal) mixing. This accounted for the rapid lateral diffusion rates which caused the over-all process to be rate controlled.

The use of a tubular reactor in kinetic research, however ideal it may seem at first consideration, has several severe drawbacks.

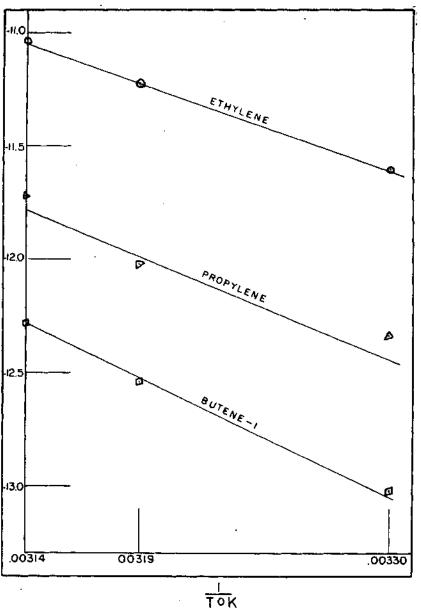

Fig. 4. Arrhenius plots. (*See* **Table 2 for values of** ***A*** **and** ***E*****.)**

One of the seemingly attractive features of using a hollow tube is the possibility of maintaining easily describable velocity and concentration gradients in the laminar region; however, two conditions peculiar to a chemical reactor of this type nullify these advantages. First, an active catalyst surface is by its very nature a rough surface. This roughness tends to destroy the usual streamline character of flow at low Reynolds numbers. Second, since the catalyst must be highly active owing to the high volume-to-surface ratio of a tubular reactor, there is a pronounced temperature rise at the wall for exothermic reactions. This temperature rise can cause additional turbulence in the fluid and is hard to control.

Even were it possible to control these factors so as to obtain truly laminar flow, the possible development of concentration boundary layers at the tube wall would cause difficulties in any attempt at rigorous mathematical analysis of the system.

An experimental difficulty inherent in tubular reactors is that the large free volume makes it necessary for economical reasons to restrict the tube diameter to rather small values. This makes it almost impossible to obtain velocity or concentration gradients experimentally.

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NOTATION

A = Arrhenius frequency factor, moles/(sq. cm.)(sec.)
b = adsorption equilibrium constant for olefin, dimensionless
b' = adsorption equilibrium constant for hydrogen, dimensionless
D = inside diameter of reactor, cm.
E = energy of activation, cal./g.-mole
F = inlet total molal flow rate, moles/sec.
k = $k'b'$, modified rate constant, moles/(sq. cm.)(sec.)
k' = rate constant, moles/(sq. cm.)(sec.)
L = length of reactor, cm.
n_A = molal flow rate of olefin, moles/sec.
n_{A_0} = inlet molal flow rate of olefin, moles/sec.
n_B = molal flow rate of hydrogen, moles/sec.
n_{B_0} = inlet molal flow rate of hydrogen, moles/sec.
r = rate of reaction, moles/(sq. cm.)(sec.)
r_0 = initial rate, moles/(sq. cm.)(sec.)
y_A = mole fraction of olefin
y_{A_0} = inlet mole fraction of olefin
y_B = mole fraction of hydrogen
y_{B_0} = inlet mole fraction of hydrogen
γ = $y_{B_0} - y_{A_0}$
ϕ = left-hand side of Equation (8)

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