The Role of the Liquid Phase in the Performance of a Trickle Bed Reactor

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The effect of the addition of an inert liquid into a gas-phase reaction occurring on a solid catalyst was studied using the isomerization of cyclopropane to propylene on a silica-alumina catalyst as the model reaction and one of three hydrocarbon solvents as the liquid. With a nonadsorbing liquid the intrinsic reaction rate constant is the same in both the gas and the gas-liquid systems but adsorption of impurities from the liquid or adsorption of the liquid itself can have an enormous retarding effect on the reaction rate. Even in the absence of these effects the addition of a liquid phase decreases the percent conversion and increases the likelihood of occurrence of mass transfer limitations.

A trickle bed reactor, as the term is used here, is one in which a liquid phase and a gas phase flow concurrently downward through a fixed bed of catalyst particles. Trickle bed reactors are used extensively in the petroleum industry on a very large scale for such processing as hydrodesulfurization of heavy oil fractions, hydrocracking of high boiling point stocks and hydrotreating and refining of lubricating oils and waxes, and to a lesser extent in the chemical and pharmaceutical industries. However, surprisingly little is known about the variables involved in trickle bed operation and their influence on performance. In many of these cases the reactant may be partly in the gas phase and partly in the liquid phase, much of the liquid phase may be inert, or changes in the nature of the feed stock or processing conditions may involve shifting from all vapor phase operation to mixed phase operation or vice versa. Indeed a reactor may operate as a trickle bed system at the inlet and as an all vapor system at the exit, as molecular weight of the reactant is reduced, for example, in hydrocracking. To advance our understanding of complex systems such as these, this study examined both experimentally and analytically the effects of introducing an inert liquid into a gas-phase catalytic reaction proceeding in a packed bed reactor. In previous related studies we have demonstrated the applicability of analytical methods of predicting the degree of diffusion limitation when the pores of a catalyst are filled with liquid (*10*) as is usually but not always the case in a trickle bed reactor and methods of estimating mass transfer limitations through the liquid film (*11*).

The reaction chosen was the isomerization of cyclopropane to propylene in the presence of nitrogen on a silica-alumina cracking catalyst, carried out either in the gas phase alone or in the presence of one of three different hydrocarbon liquids. The reaction was selected on the basis of its reported first-order kinetics, irreversibility, negligible side products, reasonably constant catalyst activity, and the fact that the rate of reaction at moderate temperatures is comparable to that of many commercial trickle bed reactors.

In the presence of an inert liquid phase a system is obtained with characteristics similar to a hydrogenation reaction that is zero-order with respect to the liquid reactant and first-order in hydrogen. There may also be cases in which it is desirable to introduce an inert liquid as such into a gas-phase catalytic reactor, in order to minimize temperature gradients or to wash off catalyst poisons. Whether the liquid is inert or a reactant, the gas reactant must be absorbed in the liquid, be transported to the catalyst surface through the external liquid film and through the catalyst pores, be adsorbed onto the active catalyst sites, and then the products of the reaction must, in many cases, diffuse back out into the gas phase.

MATHEMATICAL DEVELOPMENT

Gas-Phase Rate Equation

The reaction rate constant for a first-order irreversible reaction under isothermal conditions with no volume change is given by the following familiar expression where F_g is feed rate, V_c is catalyst volume, and η is the catalyst effectiveness factor.

$$k_g\eta = \frac{F_g}{V_c} \ln \frac{y_1}{y_2} \tag{1}$$

The catalyst effectiveness factor η can be readily calculated from measured rate data by the use of the modulus Φ_s

$$\Phi_s = \frac{R^2\,(k_g\eta)}{D_{\text{eff}}} \tag{2}$$

where R = radius of the catalyst particle and $D_{\text{eff}} = D(\theta/\tau)$; θ is the catalyst particle porosity and τ is the "tortuosity" factor. The value of η can then be obtained from the known relationship between η and Φ_s (*9*).

Two-Phase Rate Equations

In a trickle bed reactor it is customary to formulate the rate expression in terms of the liquid-phase concentration since this is the phase in contact with the catalyst surface. However, in the general case considered here with the reactant present in both phases, the rate equation may alternatively be expressed in terms of the equilibrium gas-phase concentration. The following assumptions are made:

1. Isothermal operation. 2. Plug flow. 3. Volume change in either phase throughout the reactor is insignificant. 4. Mass transfer resistance in the gas phase is negligible. 5. Vapor-liquid equilibrium is maintained at every point in the reactor, that is, $y = Kx$ where K is the vapor-liquid equilibrium constant.

The notation k_{ll} is used to designate the rate constant based on the concentration in the liquid phase at the catalyst surface c_s and k_{lg} that based on the equilibrium concentration in the gas phase c^*_g. The latter is the concentration that would be in equilibrium with c_s. Defining γ as the ratio of the concentration at the catalyst outside surface to that at the gas-liquid interface ($\gamma = c_s/c_i = c^*_g/c_g$), the rate equations may be written as

$$\text{rate} = -\,k_{ll}\eta\gamma c_i = -\,k_{lg}\eta\gamma c_s \qquad (3)$$

where c_g is the concentration in the gas, and γ represents the degree to which mass transfer through the liquid film outside the catalyst particles comprises a significant resistance.

From this equality it can be shown that the two forms of the rate constants are related by

$$\frac{k_{ll}}{k_{lg}} = \frac{KV_l}{V_g} \qquad (4)$$

where V_g and V_l are the gas and liquid molar volumes, cu.cm./g.-mole.

The ratio in Equation (4) is a function of temperature and for the experimental systems studied here follows an exponential relationship

$$\frac{KV_l}{V_g} \propto \exp\,(-\,E_K/RT) \qquad (5)$$

where E_K is an activation energy with a value of about 3 kcal./g.-mole. The activation energy E for the rate constant based on the liquid phase concentration k_{ll} is about 3 kcal./g.-mole greater than that based on the gas phase concentration k_{lg}.

Analogous to Equation (1) the first order constant k_{ll} can be evaluated from measured data where reactant is present in two phases by the expression (*13*)

$$k_{ll}\eta\gamma = \frac{1}{V_c}\left[F_l\left(\frac{1+\gamma}{2}\right) + F_g\left(\frac{KV_l}{V_g}\right)\right]\ln\frac{x_1}{x_2} \qquad (6)$$

where x_1 and x_2 are the average mole fractions of reactant in the liquid entering and leaving, respectively. In these studies, mass transfer limitations in the liquid film were small, that is, γ was near unity, so the following simplification of Equation (6) is a close approximation.

$$k_{ll}\eta\gamma = \frac{1}{V_c}\left[F_l + F_g\left(\frac{KV_l}{V_g}\right)\right]\ln\frac{x_1}{x_2} \qquad (7)$$

Under these conditions, k_{ll} becomes a rate coefficient based on the mean or bulk concentration in the flowing liquid.

To evaluate γ, first make a mass balance around a single cylindrical pellet of diameter = length = d

$$(k_{ll}\eta\gamma c_i)\,\frac{\pi d^3}{4} = K_{ls}\left(\frac{\pi d^2}{2} + \pi d^2\right)\,(c_i - c_s) \qquad (8)$$

where K_{ls} is the overall mass transfer coefficient from the gas-liquid interface to the catalyst surface. Simplifying and substituting $c_s = \gamma c_i$

$$1 - \gamma = (k_{ll}\eta\gamma)\,\frac{d}{6K_{ls}} \qquad (9)$$

It is evident from Equation (9) that under isothermal, constant flow conditions, γ will be constant through the reactor, providing the liquid flow and K_{ls} do not change. Combining Equations (6) and (9) gives the desired expression for γ in terms that are obtainable from experimental data:

$$1 - \gamma = \frac{\dfrac{1}{V_c}\left[F_l + F_g\left(\dfrac{KV_l}{V_g}\right)\right]\ln\dfrac{x_1}{x_2}}{\dfrac{6K_{ls}}{d} + \dfrac{F_l}{2V_c}\ln\dfrac{x_1}{x_2}} \qquad (10)$$

In trickle bed reactors liquid flow rates are low compared to those in absorption columns and the stagnant film model can be applied. Assuming uniform wetting of the catalyst particles the mass transfer coefficient can be approximated as

$$K_{ls} = \frac{D}{\Delta} = \frac{Da}{h} \qquad (11)$$

where h is the external liquid holdup, and a is the specific external surface area of the catalyst, sq.cm./cu.cm., both expressed per unit of total bed volume. For spheres and cylinders, $ad = 6(1-\epsilon)$, giving

$$K_{ls} = \frac{6D(1-\epsilon)}{hd} \qquad (12)$$

Substituting Equation (12) into Equation (9) gives

$$1 - \gamma = \frac{(k_{ll}\eta\gamma)\,hd^2}{36D(1-\epsilon)} \qquad (13)$$

and Equation (10) becomes

$$1 - \gamma = \frac{\dfrac{1}{V_c}\left[F_l + F_g\left(\dfrac{KV_l}{V_g}\right)\right]\ln\dfrac{x_1}{x_2}}{\dfrac{36D(1-\epsilon)}{hd^2} + \dfrac{F_l}{2V_c}\ln\dfrac{x_1}{x_2}} \qquad (14)$$

Equations (11) to (14) apply to systems in which the reactant is predominately in the gas phase, as was the case here. If the reactant is distributed mainly in the liquid phase, for example, in hydrodesulfurization reactions, Equation (11) becomes $2D/\Delta$ and the constant 36 in Equations (13) and (14) becomes 72. A linear approximation between these limits can be used for intermediate cases.

With the value of γ obtained from Equation (14), $(k_{ll}\eta\gamma)$ can be calculated with Equation (6). Alternatively, if γ approaches unity, for example, exceeds about 0.9, $(k_{ll}\eta\gamma)$ can be closely approximated by Equation (7), with γ obtained from Equation (13). Finally, the catalyst effectiveness factor η can be obtained from the relationship between η and Φ_s (9), in which k_{ll} replaces k_g in Equation (2).

$$\Phi_s = \frac{R^2\,(k_{ll}\eta)}{D_{\text{eff}}} \qquad (15)$$

Applying Equation (4) to Equations (6) and (7) results in equivalent expressions in terms of k_{lg}. The complete and simplified forms become respectively:

$$k_{lg}\eta\gamma = \frac{1}{V_c}\left[F_l\left(\frac{V_g}{KV_l}\right)\left(\frac{1+\gamma}{2}\right) + F_g\right]\ln\frac{y_1}{y_2} \qquad (16)$$

$$k_{lg}\eta\gamma = \frac{1}{V_c}\left[F_l\left(\frac{V_g}{KV_l}\right) + F_g\right]\ln\frac{y_1}{y_2} \qquad (17)$$

Note that with the assumption of vapor-liquid equilibrium and isothermal conditions $x_1/x_2 = y_1/y_2$ = the ratio of total reactant in both phases at the inlet to the total reactant in both phases at the outlet. As with the k_{ll} form, γ can be calculated from Equation (14) and $k_{lg}\eta\gamma$ from Equation (16) or (17).

Insight into the behavior of a two-phase reactor compared to a gas phase reactor can be gained by comparing the gas-phase rate expression Equation (1) with the two simplified two-phase expressions Equation (7) and Equation (17). The bracketed term in Equations (7) and (17) can be considered the effective feed rate in the two-phase equations, comparable to F_g in Equation (1).

From the experimental results it will be shown that in the absence of adsorption effects of the liquid on the catalyst, the two-phase constant k_{lg} equals the gas-phase constant k_g, so the difference in conversion between all gas-phase operation and two-phase operation can be determined by comparing the terms in Equations (1) and (17). This difference results from possible differences in the gas-phase effectiveness factor η compared to the two-phase overall mass transfer term $(\eta\gamma)$, and from differences in the gas-phase feed term F_g compared to the two-phase effective feed term $[F_l(V_g/KV_l)] + F_g$. With a typical value for (V_g/KV_l) of 12 for the experimental systems used here, even a small liquid feed rate added to a gas-phase operation will appreciably increase the two-phase effective feed term compared to F_g, and thereby significantly reduce the conversion term y_1/y_2. Physically the effect may be visualized as follows:

Consider the introduction into a gas phase, packed bed, differential reactor of a liquid containing reactant at a concentration corresponding to equilibrium with the inlet gas. Assuming that the average residence time of the gas phase remains constant and that mass transfer and adsorption effects are negligible, the rate of reaction expressed as moles per unit time remains the same but the rate of introduction of reactant has increased; hence the percent conversion will drop.

In an integral reactor, the effect of introduction of the liquid phase may be visualized as providing a flowing reservoir of reactant that is fed to the system, providing partial replenishment of reactant. Thus in the specific case above, the actual overall rate of reaction expressed as moles per unit time in the integral reactor would be increased at the same time that the percent conversion dropped. At another extreme one can visualize the addition to a gas-phase integral reactor of a liquid phase containing no reactant, in which case both the percent conversion and overall rate of reaction will decrease. In this case the addition of the liquid phase would distribute the reactant between gas and liquid phases, thereby reducing the chemical potential in both phases and hence the rate of reaction.

In addition to the effect of distribution of reactant between two phases, external and pore diffusion resistances are more likely to be encountered in a two-phase operation, further reducing the conversion; for example, under conditions in which η approaches unity in gas-phase operation, the term $\eta\gamma$ may be substantially less than unity for the two-phase system. The magnitude of this difference is well illustrated in the experimental program.

For a two-phase system in which the volume change in the gas phase is linearly related to the extent of the reaction (typical of many hydrogenation reactions), the following expression applies for first-order kinetics

$$k_{ll}\eta\gamma = \frac{\sigma}{V_c}\left(\frac{KV_l}{V_g}\right)(F_{g,1} - F_{g,2}) \qquad (18)$$

Here σ is the selectivity expressed as a function of the total gas consumption accounted for by the reaction of interest. Again, Equation (13) can be used to evaluate γ, and η is then readily obtained by using Equation (15).

Use of Equation (15) here requires a method of prediction of the diffusivity of cyclopropane in each of the three liquids studied. Values calculated by the Wilke-Chang equation (*15*) were compared to experimental studies by Hu (*4*), Shim (*12*), and Sage (*8*) on the diffusivity of methane in *n*-hexane, *n*-octane and in white oil over the temperature range of 0° to 125°C. On the basis of a detailed analysis, it was concluded that the diffusivity of cyclopropane in light hydrocarbon liquids such as Isopar L and Solvesso 150 could be adequately predicted by the Wilke-Chang equation and that the term T/μ appearing in that equation adequately represents the temperature dependence over the temperature range studied here. However, for higher molecular weight, high viscosity liquids the accuracy falls off appreciably, especially at low temperatures. The best values for diffusivity in Nujol as estimated here were about twice those calculated from the Wilke-Chang equation. Details are given by Way (*13*).

EXPERIMENTAL APPARATUS AND PROCEDURE

The reaction system for all studies was the isomerization of cyclopropane to propylene, using a feed gas consisting of 2% cyclopropane in nitrogen (before equilibration with the liquid). Three "inert" liquids were used in the following two-phase experiments: 1. Isopar L, a highly paraffinic hydrocarbon solvent (92.7% isoparaffins) consisting primarily of C_{11} fractions, with a boiling point range of 373 to 406°F.; 2. Solvesso 150, a highly aromatic hydrocarbon solvent (97% aromatics) with a boiling point range of 370 to 410°F.; and 3. Nujol, a highly refined, high-viscosity paraffinic mineral oil with an average molecular weight of about 400.

Two types of silica-alumina cracking catalyst were used in studying the reaction: a 13% alumina catalyst referred to as Catalyst A, and a 28% alumina catalyst referred to as Catalyst B. Both were in the form of 3.2 mm. extruded cylinders. All the reaction data shown in the figures were obtained with Catalyst A. Catalyst C, consisting of 1.6 mm. cylinders, was used for holdup measurements only.

The reactor was operated at atmospheric pressure, over the temperature range of 40° to 120°C. Although conversions as high as 90% were obtained, the use of a dilute feed gas and complete reactor jacketing limited the reactor temperature rise to about 1°C. The reactor system is shown in Figure 1. Feed liquid from the metering pump, which contained no reactant, was heated by a finned immersion heater to the set reactor temperature and then was joined by the gas feed, the two streams being caused to flow concurrently upward through Raschig ring packing to bring them into equilibrium. The two streams were then separated in the top chamber of the reactor. The gas phase flowed through a center chimney onto the top of the catalyst bed. The liquid distributor plate contained three small diameter tubes to distribute the liquid uniformly. The reactor

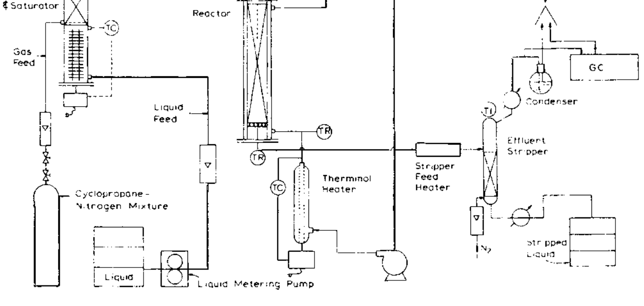

Fig. 1. Flow diagram of experimental reactor system.

consisted of a stainless steel tube 28 mm. in inside diameter with an overall height of 46 cm. The catalyst bed height was about 33 cm. and was supported on a screen grid plate. The tube was fully jacketed and Therminol FR-1 (Monsanto) was circulated as the heat transfer oil.

Leaving the reactor, the mixed effluent stream was heated to about 100°C., flashed above the packing in the effluent stripper; and the resulting liquid was stripped of cyclopropane and propylene by nitrogen which entered the base of the stripper. The gas stream was analyzed by gas chromatography. Temperatures were recorded at various points as indicated by the symbol *TR* on the figure. The two thermocouples in the catalyst bed were located about 51 mm. below the top and 25-mm. above the bottom, respectively. Further details are given by Way (*13*).

Preliminary experiments were carried out to determine the vapor-liquid equilibrium constants ($K = y/x$) of cyclopropane in the three liquids, and the external liquid holdup under widely varying conditions. In both cases the equipment was the same as that used in the reaction experiments.

RESULTS AND DISCUSSION

Liquid Holdup

The liquid present in the reactor consists of that which is held internally in the pores of the catalyst and that which is flowing downward outside the catalyst particles, the latter being termed the external holdup. When liquid flow into the reactor is stopped, some liquid is retained on the surface of the catalyst particles and in lenses between particles. The difference between this residual holdup and the external holdup is termed the free-draining holdup. Values of the external holdup h are needed for use in calculating the external mass transfer resistance from the observed two-phase reaction rate data. Studies were made with Isopar L at 22° and 50°C. on 3.2 × 3.2 mm. cylinders (Catalyst A), on 1.6 × 8 mm. cylinders (Catalyst C), and on 3-mm. glass spheres (nonporous), and with Nujol over a temperature range of 50° to 110°C. on Catalyst A. The viscosity range covered was thus 1.07 to 40 cp. The liquid flow rate was varied from 12.2 to 100 cu.cm./min. and the gas (nitrogen) rate from 0 to 840 cu.cm./min.

The data were well represented by the equation

$$h = AU_l^{1/3}\mu^{1/4} + B \qquad (19)$$

where U_l is the superficial liquid velocity in cm./sec., μ is the liquid viscosity in centipoises, and A and B are constants characteristic of the particle size and shape. The exponent of 1/3 was determined by plotting log h versus log U_l at constant values of μ. The 1/4-power dependency on viscosity was then determined by cross-plotting log h versus log μ. The values of the constants are as follows:

	A	B
1.6-mm. cylinders	0.218	0.025
3.2-mm. cylinders	0.188	0.02
3-mm. glass spheres	0.102	0.01

The final correlation is presented in Figure 2.

The effect of gas flow rate on holdup was very slight. The constant B can be visualized as an apparent residual holdup, although there was some evidence that the true residual holdup was slightly higher.

A good check on the above correlation is provided by the holdup data of Ross (*7*) for 51- and 102-mm. diam. reactors packed with 4.8-mm. pellets. Adding a typical residual holdup of 0.03 to his values of free-draining holdup, Ross' data are in close agreement with Equation (19) [using the constants for 3.2-mm. pellets], including his results at liquid flow rates up to seven times the maximum studied here.

Single-Phase Gaseous Reaction

The intrinsic kinetics of the cyclopropane isomerization reaction are needed as a base for analyzing the two-phase results. First it was established that the catalyst activity reached a constant value after about 40 hours operation, and that the reaction is first-order by operating at various flow rates resulting in a wide range of conversion. Finally, runs were made over the temperature range of 50° to 110°C. to determine the temperature dependence of the reaction rate constants. The results of studies with Catalyst A are shown as the top line in Figure 3; the percent conversion varied from 7.8% at the lowest temperature to

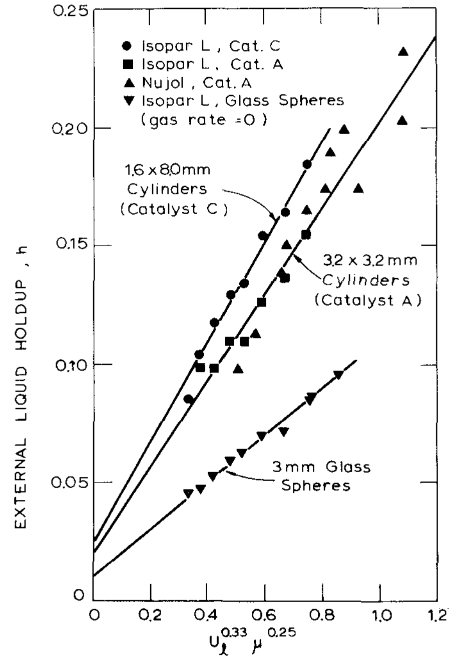

Fig. 2. External liquid hold-up. Superficial gas linear velocity = 1.38 cm/s at 50°C.

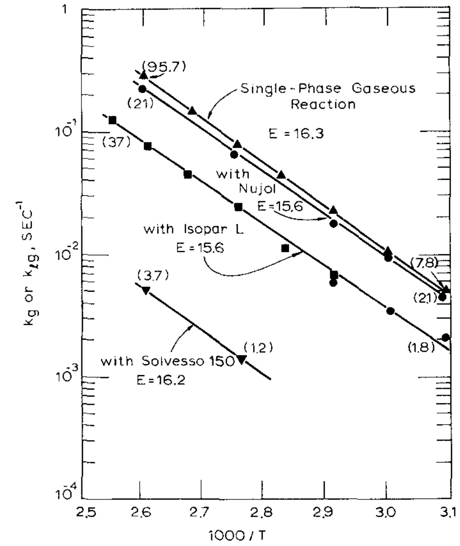

Fig. 3. Rate constants for single-phase and two-phase systems. Catalyst A. Numbers in parentheses are the % conversion.

95.7% at the highest. Similar results, not shown, were obtained with Catalyst B. After a series of runs at progressively higher temperatures, a final run at the lowest temperature yielded the same results, illustrating the good reproducibility of the data and the constant activity of the catalyst. From the slope of the straight line, the activation energy was found to be 16.3 kcal./g.-mole; for Catalyst B a value of 15.8 was obtained. These compare well with the value of 16.0 reported by Ishii and Osberg (5) who studied the same reaction on silica-alumina catalyst over the range 150° to 250°C.

Pore diffusion effects were negligible at the lower temperatures but the effectiveness factor η decreased to a value of about 0.80 at the highest temperature 110°C. based on studies with ground catalyst and calculations (*13*), assuming Knudsen diffusion and a tortuosity factor of about 3.

TRICKLE BED STUDIES

Time for Catalyst Equilibration

With Catalyst A and Isopar L at 50°C., a constant rate of reaction was reached after about 17 hours, which is appreciably less than the time required for steady state to be achieved in single-phase operation. The rate constant at 17 hours was slightly less than ½ that at 4 hours. With Solvesso 150 which is highly aromatic and Catalyst A, steady state at 50°C. was reached in the first several hours of operation. With Nujol the rate of reaction at 50°C. was essentially constant from the beginning of the operation; after 6 hours of operation, the rate was only slightly less than that at 0.5 hours.

The variation in catalyst equilibration time is believed to be caused by differences in the nature and concentration of the adsorbate causing the catalyst deactivation. In completely gas-phase operation, it is probably an impurity in the cyclopropane itself or a polymer of propylene that was being adsorbed on some of the active sites of the catalyst. The long time to reach steady state in the all gaseous reaction suggests that the adsorbed material was present in low concentration. Isopar L consists of about 97% paraffinic hydrocarbons, the balance being primarily aromatics, so probably adsorption of the aromatic fraction caused the gradual deactivation. In contrast, the essentially aromatic Solvesso 150 is strongly adsorbed by the catalyst and the time required for equilibration is short. The Nujol system is at the other extreme. Being a highly refined, high molecular weight paraffin, it is apparently only slightly adsorbed and showed a low level of deactivation, comparable to that encountered in single-phase operation. The fact that steady state was reached at the outset indicates that it was the paraffinic material itself that was adsorbed, and not a low concentration impurity.

During a catalyst life run with Isopar L at 50°C., the gas rate was varied from 100 to 880 cu.cm./min. and the liquid rate from 25 to 50 cu.cm./min. There was no significant effect on the calculated rate constant, as would be caused by deviation from first-order kinetics, or by an improper form of the two-phase rate equation.

Steady State Measurements

The performance of the trickle bed reactor with Catalyst A was studied with each of the three solvents over the temperature range of 50° to 120°C. In each case the catalyst was allowed to reach steady state activity before measurements were made. The results, presenting the reaction rate constant in the k_{lg} form, are shown in Figure 3. Figure 4 presents the results with Isopar L with the reaction rate constant expressed in the k_{ll} form and Figure 5 the results with Nujol in the same form. In Figures 4 and 5 the difference between the curve for $k_{ll}\eta\gamma$ and the line for k_{ll} represents the magnitude of the mass transfer resistance. At the lowest temperature (50°C.), γ and η were calculated by Equations (13) and (15) to be 0.997 and 0.95, respectively, while at the highest temperature (120°C.) they are 0.95 and 0.39. The activation energy for k_{ll} is 18.2 kcal./g.-mole. For k_{lg} (Figure 3) it is 15.6, which compares well with the gas-phase value.

In calculating the reaction rate constants, the Isopar L was treated as a nonvolatile liquid. The effect of the Isopar L vapor pressure on the two-phase effective feed term at temperatures up to 100°C. was negligible. At 120°C., correcting for vapor pressure would increase the effective feed term (and $k_{ll}\eta\gamma$) by 8.5%.

In calculating η, D_{eff} was expressed as $D_{1m}\theta/\tau$, the value of θ/τ taken as 0.2, corresponding to a value of τ of about 3. The calculations were also repeated for values of τ of 4 or 5. The deviations from a straight line were not greatly different, but the calculated activation energies

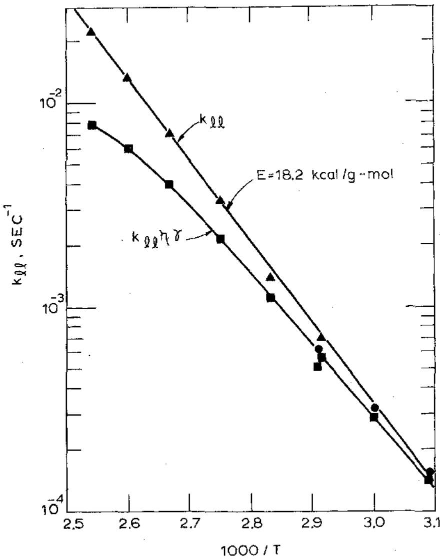

Fig. 4. Two-phase reaction rate constants k_{ll}. Catalyst A and Isopar L.

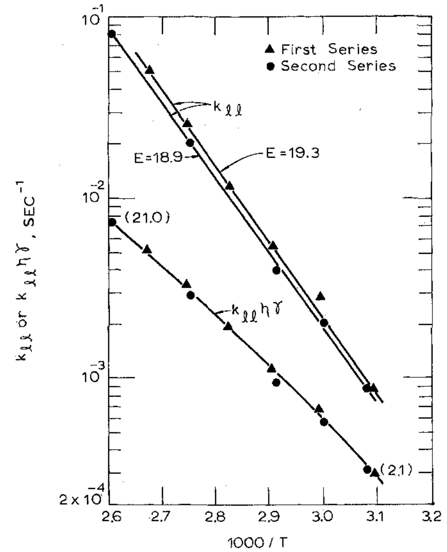

Fig. 5. Two-phase reaction rate constants. Catalyst A and Nujol. Numbers in parentheses are the % conversion.

were 16.3 and 16.9 kcal./g.-mole respectively. If the value of 16.0 is taken as being the most reliable, the correct value of τ lies between 3 and 4.

Two series of runs with Nujol and Catalyst A were made; these are especially interesting because of the severe mass transfer resistance encountered throughout the entire temperature range. The results of the two series are closely comparable as shown by the two upper curves in Figure 5. At the lowest temperature η and γ were calculated by Equations (14) and (15) to be 0.88 and 0.39, respectively, and at the highest temperature (111°C.), 0.75 and 0.12. In spite of these large mass transfer resistances, the plots of the true rate constants determined from the observed rates and the calculated η and γ values show excellent straightline representation. The activation energy for k_{ll} is 18.9 kcal./g.-mole and for k_{lg}, 15.6 to 16. The latter is again in excellent agreement with the completely gas-phase reaction. Using a value of the tortuosity factor of 4 or 5 increases the calculated value of the activation energy by only 1.2% or 2.2% respectively. The liquid-phase diffusivities for Nujol are approximate, having been adjusted from the Wilke-Chang values by a factor of about two, based on a comparison of data for similar systems, so any fine adjustment to calculate τ is unjustified. As with the Isopar L data, however, a value of 3 to 4 appears reasonable.

A significant result of the study with Nujol is that the plot of k_{lg} is almost identical with the plot of k_g for the single-phase gaseous reaction (Figure 3). (Only one series of data points are shown in Figure 3. The other series virtually overlapped the results from the single-phase gas studies.) In the absence of blocking of catalyst sites by adsorption, thermodynamic reasoning leads to the conclusion that the two-phase k_{lg} constant should equal the gas-phase k_g constant. It is plausible that this occurs with a relatively pure paraffinic liquid which should be relatively nonadsorbed. The good straight line representation of the Nujol data, and the close agreement with the gas-phase results, is excellent verification of the mathematical development, the applicability of vapor-liquid equilibrium K data and holdup data as well as of the experimental procedure. Although straight-line Arrhenius plots do not verify any of these individually, they support the overall approach and methods.

With Solvesso 150 only the results at 90° and 110°C. were usable. However, the calculated activation energy from k_{lg} data was 16.2 kcal./g.-mole, in agreement with other results.

A comparison of the results of the three liquids studied with the gas-phase results as shown in Figure 3 yields the following values for the ratio of the rate constant under two-phase conditions to that in gas-phase reaction alone: Nujol, 0.85-1.0; Isopar L, 0.31; Solvesso 150, 0.019.

It seems clear from these studies that the cyclopropane and the inert liquid compete for sites on the catalyst surface and that aromatic liquids, which are more strongly adsorbed than paraffinic substances, can cause a major reduction in the rate of reaction. As a further test of this hypothesis, a run was made with diethylene glycol, which is more highly polar than aromatic hydrocarbons. At 50°C., reaction was imperceptible, that is, glycol was so strongly adsorbed that the isomerization reaction was essentially stopped.

The degree of adsorption is presumably a function of both temperature and time. It is hypothesized that as temperature is increased, desorption of these adsorbed components will gradually take place, and if sufficient time is allowed, steady state at a higher level of catalyst activity will be reached. In the steady state studies described above, the interval at each temperature was usually less than 1 hr., sufficient for the system to reach steady state as determined by consistent analytical results, but perhaps not the catalyst from the standpoint of adsorption. This might be particularly important with respect to minor but highly adsorbed impurities.

Some evidence for this is revealed by comparison of runs with Isopar L and Catalyst A, each at 50°C. but following slow cooling overnight after a series of studies at temperatures up to 120°C., or following a period of four days at room temperature in which the reactor was idle but the catalyst was in contact with Isopar L. The calculated rate constant in the second case was about two-thirds that in the first case.

The solvent effect on homogeneous reaction rates has been given extensive treatment in the literature, for example, by Amis (*1*), Eckert (*2*), Wells (*14*), and Wong and Eckert (*16*). It has been demonstrated that the kinetic solvent effect can be enormous, with a variation in rate constant caused by different solvents of the order of 100 to 1,000 being common, and in some cases as high as 10^9 (*2*). In the area of heterogeneous reactions, the single work by Eckert appears to give the only theoretical treatment, which, however, is restricted to nonpolar liquids, and implicitly assumes that differences in the adsorption characteristics of the solvent on the catalyst surface do not affect the reaction rate. For many systems this assumption must be questioned. Differences in competitive adsorption between the reactant and the "inert" solvent on the active catalyst sites can cause large differences in the rate of reaction, as found in this work. The factors involved in competitive adsorption are discussed by Kipling (*6*). A simple generalization is that polar compounds are more strongly adsorbed than are nonpolar compounds by polar solids and that the reverse is true of nonpolar solids. The π-electrons of aromatic hydrocarbons are responsible for the strong preferential adsorption of aromatic compounds from mixtures with aliphatic compounds by polar solids, such as silica gel or silica-alumina catalyst.

The solvent effect in heterogeneous reactions is a complex problem. Considering its importance to all liquid-phase catalyst systems, particularly in chemical synthesis, and noting the scarcity of experimental data, further research along these lines should yield significant results. Wider recognition of these effects may also be important in understanding the processing characteristics of various petroleum fractions. For example, Frye and Mosby (*3*) reported studies of the hydrodesulfurization of light cycle oil (40% aromatic hydrocarbons) in which the rate of reaction was inhibited not only by the H_2S formed, but also by the aromatic species in the feed.

SUMMARY

The overall effect of temperature on two-phase reactor performance with an essentially nonvolatile "inert liquid" is a combination of four individual factors:

1. The intrinsic rate constant increases with temperature. For the hydrocarbon systems used here, the activation energy for the reaction rate constant in the form of k_{ll} is greater than that in the form of k_{lg} by about 3.0 kcal./g.-mole. This is primarily caused by the fact that as temperature is increased, the concentration of the reactant in the liquid phase (the driving force for k_{ll}) is decreased, while the gas phase concentration (driving force for k_{lg}) is increased. This effect is expressed by the term (V_g/KV_l) in the rate equations.
2. The diffusivity of the reactant in the liquid phase, which affects both the external mass transfer and pore diffusion resistances, increases with temperature, but the reac-

tion rate constant increases even more rapidly, so mass transfer resistance is the most significant at the highest temperatures.

3. Increasing temperature decreases liquid viscosity and hence the liquid holdup h, and this acts to reduce the external mass transfer resistance.

4. Temperature affects the adsorption of those materials which block the reaction by occupying active catalyst sites. In addition, if the liquid phase has a significant vapor pressure, then phase change at higher temperatures will in most cases ($K > 1$) increase the effective feed term and thereby reduce conversion.

The introduction of an "inert" liquid phase to a gas-phase reaction occurring on a solid catalyst in a packed bed can cause the conversion to decrease by one or more of three effects.

1. The effective feed term will increase, which decreases the percent conversion.

2. An increase in the pore diffusion resistance (a lower value of η), and the added resistance of external mass transfer (the term γ) may occur.

3. Adsorption of some constituent in the liquid phase, either major or minor, onto catalyst sites, can cause a reduction in the intrinsic rate constant. Solvent effects on the reaction species may similarly modify the reaction rate.

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NOTATION

a = superficial surface area of catalyst packing, sq.cm. of outside surface per cu.cm. of total bed volume
c = concentration, g.-mole/cu.cm.; c_g, concentration of reactant in the gas phase, g.-mole/cu.cm. of gas; c_g^*, in the gas that would be in equilibrium with the concentration in the liquid at the catalyst surface, g.-mole/cu.cm. of gas; c_i, in the liquid at the gas-liquid interface, g.-mole reactant/cu.cm. of liquid; c_s, reactant concentration at the catalyst surface, g.-mole/cu.cm. of liquid.
d = diameter and length of cylindrical catalyst pellet, cm.
d_p = equivalent spherical particle diameter; $d_p = 6(1 - \epsilon)/a$
D = diffusion coefficient, sq.cm./sec.
D_{eff} = effective diffusion coefficient for a porous solid, sq.cm./sec.; $D_{\text{eff}} = D\theta/\tau$
E = activation energy, kcal./g.-mole
E_K = activation energy for the group (KV_l/V_g)
F = feed rate at reactor temperature and pressure, cu.cm./sec.; F_l for liquid, F_g for gas
h = external liquid holdup as fraction of total bed volume, the latter consisting of gas plus catalyst pellets plus liquid external to catalyst pellets, cu.cm. liquid/cu.cm. catalyst bed volume
k = intrinsic first-order reaction rate constant per unit volume of catalyst pellet, sec.$^{-1}$; k_g refers to gas-phase reaction, (cu.cm. gas)/(cu.cm. catalyst particle volume) (sec.); k_{lg} refers to two-phase reaction using gas-phase concentration, same units as k_g; k_{ll} refers to two-phase reaction using liquid-phase concentration at the catalyst surface, (cu. cm. liquid)/(cu.cm. catalyst particle vol.) (sec.)
K = vapor-liquid equilibrium constant, $K = y/x$
K_{ls} = overall mass transfer coefficient in the liquid, based on the average of the outside catalyst surface and the liquid surface
R = gas constant, kcal./(g.-mole) (°K.)
R = radius of sphere, cm.
T = temperature, °K. or °C.
U_l = superficial liquid velocity, cm./sec.
V_c = volume of catalyst particles, cu.cm.
V_g = molar volume of gas phase at reactor conditions, cu.cm. of gas/g.-mole of gas mixture
V_l = molar volume of liquid at reactor conditions, cu.cm. of liquid/g.-mole of liquid
x = mole fraction in liquid, bulk average
y = mole fraction in gas

Greek Letters

γ = external mass transfer resistance factor, $\gamma = c_s/c_i$
Δ = liquid film thickness, cm.
ϵ = void fraction of packed catalyst bed external to catalyst particles
η = catalyst effectiveness factor; the ratio of actual rate of reaction in a porous catalyst to that which would occur if the interior surface were entirely exposed to the reactants at the same concentration and temperature as that existing at the outer surface of the pellet
θ = void fraction (porosity) of the catalyst particle
μ = viscosity, centipoises
τ = empirical factor to correct for "tortuosity" and for nonuniformity of catalyst pore cross section
Φ_s = dimensionless modulus defined by Equation (2)
σ = fraction of gas consumption attributable to the reaction represented by k_{ll}; if no side reactions occur, $\sigma = 1$

Subscripts

1 = inlet conditions
2 = exit conditions

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