# Reaction Mechanism of 1-Hexanol and di-*n*-Hexyl Ether over Alumina in a Flow System

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EVERAL years ago one of the authors (9) reported the results of a study of the vapor-phase dehydration of dodecanol over alumina in a flow system. The results of that study indicated that the reactions of aliphatic alcohols over alumina in flow systems might be particularly interesting for kinetic studies since the catalyst is readily available, easily activated, and relatively constant in activity, and since reactions other than those involving alcohol, ether, and olefin occur only to a minor extent. A kinetic study should include experiments on the reactions of aliphatic ethers over alumina since the ether formed in alcohol dehydration obviously reacted further. The present study was therefore undertaken in order to explore the mechanism of the consecutive and simultaneous reactions involved when the vapors of aliphatic alcohols and ethers are passed over alumina. 1-Hexanol and di-n-hexyl ether were chosen as the feed materials since the boiling points of the reactants and products are such that a system designed for operation at atmospheric pressure is not complicated by the requirement of excessively high temperatures for vaporization (as with higher homologs) or excessively low temperatures for condensation (as with lower homologs).

The reactions occurring when the vapor of an aliphatic alcohol is passed over alumina at suitable temperatures have been considered by various workers to be

$$2RCH_2CH_2OH \rightarrow RCH_2CH_2OCH_2CH_2R + H_2O$$
(1)

$$RCH_2CH_2OH \rightarrow RCH=CH_2 + H_2O$$
 (2)

$$\mathrm{RCH}_{2}\mathrm{CH}_{2}\mathrm{OCH}_{2}\mathrm{CH}_{2}\mathrm{R} \rightarrow 2\mathrm{RCH}=\mathrm{CH}_{2} + \mathrm{H}_{2}\mathrm{O}$$
(3)

In the present study, the products of reaction of di-*n*-hexyl ether over alumina included appreciable amounts of hexyl alcohol. The presence of the alcohol in the products could be explained by either a reaction involving the splitting of ether to olefin and alcohol or a reaction involving the hydration of the olefin. The former was considered to be more likely from chemical equilibrium considerations since the conditions used in this work were such that the equilibrium concentrations of alcohol and ether would be expected to be very small. Hence the following reaction was included in the interpretation of results:

$$RCH_2CH_2OCH_2CH_2R \rightarrow RCH_2CH_2OH + RCH = CH_2 \quad (4)$$

The reaction scheme includes both simultaneous and consecutive reactions. Furthermore, all of the reactions would be expected to occur with either alcohol or ether as the feed, since ether is a product of the reaction of alcohol, and alcohol is a product of the reaction of ether. The material flowing through the reactor would therefore be a mixture of alcohol, ether, olefin, and water in the case of either alcohol or ether as the feed.

The conversion over a solid catalyst in a flow system of reactants in the bulk vapor phase to products in the bulk vapor phase is considered (3, 4) to involve at least the following steps: transfer by gaseous diffusion of reactants and products between the bulk vapor phase and the exterior catalyst surface; adsorp-

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tion of reactants and desorption of products on the catalyst surface; and chemical reaction on the catalyst surface. The conversion may also involve transfer of reactants and products between the exterior catalyst surface and the pores of the catalyst. The objective of a kinetic study is to determine which step is of greatest importance in the over-all rate of chemical reaction.

Experimental data for a kinetic study of chemical reactions occurring in a constant-pressure isothermal flow system may be obtained by the use of either a differential or integral reactor. The differential reactor contains a catalyst bed so small that relatively small changes in composition are obtained by passing a reactant through the bed. This reactor may offer some simplification in interpretation in that the differential rate equations for various assumed rate-controlling steps may be applied to the data without resorting to formal or graphical integration since simple average values of concentrations may be used without appreciable error. However, very accurate methods of analysis are necessary and these are not available for the system alcoholether-olefin. It was therefore necessary to use an integral reactor in which relatively high conversion of the reactants is obtained. The catalyst used was a commercial grade of alumina selected for its availability and for the reproducibility and constancy of its catalytic activity.

For the purposes of a kinetic study the independent variables must be chosen carefully to provide the most satisfactory data for purposes of interpretation. Some of the independent variables that might be considered are catalyst mass, feed composition, flow rate, temperature, pressure, and reactor diameter. A study of conversions as a function of catalyst mass represents an attractive possibility since it is usually desired to obtain a relationship between these particular variables for design purposes. The experimental task is difficult, because the range of catalyst masses that must be used is rather wide. One method of overcoming this difficulty is the recycle scheme proposed and used by Dohse (1), but this method is effective only when a method of continuously analyzing the product stream is available. A study of conversions as a function of feed composition again provides interesting possibilities. In this case both the reactants and the products of reaction should be included in the feed stream, a difficult experimental task if the products of reaction include more than one phase at the feed conditions. This study was based on only two feed compositions, either pure alcohol or pure ether was used as the feed. A study of conversions as a function of flow rate with catalyst mass fixed is simpler experimentally than the use of a variable catalyst mass and provides adequate information except in those cases where the diffusion rates of reactants and products in the vapor phase are low. However, interpretation of data is possible since the dependence of mass transfer coefficients on flow rates in packed beds has been established by the work of Hougen and others (2, 8). This method of experimentation was chosen for the present work. Studies of conversion as functions of temperature, pressure, and reactor diameter are important, because they may provide useful clues in determining the rate-controlling step; such studies were included in the present work.

The equipment is similar to the apparatus employed by Walker  $(\mathcal{G})$  in his study of dodecanol dehydration. It consists of a small cylindrical glass vaporizer, superheater, reactor immersed in a molten salt bath, and the equipment necessary to feed the reactant to the vaporizer and to condense the products from the reactor (Figure 1).



The feed (1-hexanol or di-*n*-hexyl ether) in the runs at 1 atmosphere was delivered to the vaporizer-reactor assembly by means of two Zenith Type B pumps. In runs at reduced pressure it was not possible to use these pumps because of slippage past the gears. In these runs the feed was introduced by flow from the reservoir to the weir overflow, A, the rate being adjusted by changing the length of travel through a series of capillary tubes. The net discharge from the pump system or from the capillary tubing was fed through glass tubing to the weir overflow, whence it dropped into borosilicate glass U-tubes B and C. The U-tubes were immersed in a molten salt bath, K, contained in an insulated stainless steel tank, L, heated by a 1000-watt immersion heater, M. The U-tubes were and pproximately 12 inches in height on each leg. The first U-tube, B, was filled with small pieces of borosilicate glass tubing and functioned as a vaporizer and superheater for the feed. The second U-tube, C, contained the catalyst, supported on a drilled glass plate, in one leg. A 7-mm. outside diameter glass tube extending down the center of the leg of tube C containing the catalyst served as a thermocouple well.

The product stream passed from the second U-tube, C, out of the salt bath to the water-cooled finger condenser, E. In order to prevent condensation in the short length of tubing between the exit from the salt bath and the condenser, a Nichrome wire was wound around the section, D, and covered with insulation. A thermocouple was placed next to the tube wall. The electrical input to the Nichrome wire was adjusted so that the wall temperature was maintained at  $340^{\circ}$  C.

The liquid product from the finger condenser passed into the collector, F. Uncondensed vapors passed to the low-temperature traps, G, which were cooled in a bath of dry ice in acetone. These traps were arranged in parallel to permit switching when one of these became plugged with ice. The ice traps were vented to the atmosphere for those runs made at atmospheric pressure or to a surge tank, H, for those runs made at reduced pressure. The control of pressure in these latter runs was accomplished by the solenoid valve, J, which was actuated by a mercury manostat.

The temperatures of the salt bath and of the reactor were measured by copper-constantan thermocouples. Both temperatures were recorded periodically during operation. The temperature in the center of the reactor was found to be  $0.5^{\circ}$ to  $6^{\circ}$  C. below that in the salt bath, the greater differences occurring at the higher flow rates. The temperatures reported here were measured in the center of the reactor and these were maintained constant within 0.5° C. by manual control of the electrical input to the heater M. Variations in temperature along the length of the reactor were not measured; Walker ( $\vartheta$ ) showed experimentally that these were small, because the heat capacities of the materials involved are large compared with the heats of reaction, and because the catalyst is distributed in a relatively thin layer.

#### PROCEDURES

The data were obtained by intermittent operation of the equipment in a number of periods, each of 5 to 9 hours' duration. Walker (9) found this procedure satisfactory if the feed flowed over the catalyst at all times while the reactor was immersed in the salt bath. Extended periods without flow resulted in decomposition on the catalyst of organic materials adsorbed in previous runs. Hence in this work the feed was started as soon as the salt bath was raised into its operating position and stopped just as the salt bath was lowered. This procedure was satisfactory as is shown by the consistency and reproducibility of the data reported here.

Three batches of catalyst (8 to 14 mesh activated alumina, grade F-1 purchased from Aluminum Co. of America) were used in this work. Each batch was activated in place by heating in the presence of air, raising the temperature of the salt bath from 150° C. to 300° C. in about 7 hours and from 300° C. to 330° C. in about  $\frac{1}{2}$  hour, followed by a 1-hour period at 330° C. After a new batch of catalyst was placed in the reactor it was used for at least 8 hours before any of the data

reported here were recorded in order to permit the relatively high initial catalyst activity to fall off to a steady state activity. When data were being taken at a single temperature and at variable flow rates, it was found that 1 hour after a flow rate change was made the steady state had been achieved—i.e., there was no further change in product composition after this time. When a temperature change was made, however, an operation period of about 6 hours was necessary before reproducible analyses of the products were obtained. Again the consistency and reproducibility of the data reported are adequate proof that the method of activation of the catalyst, the practice of waiting 1 hour after flow rate changes before taking data, and the practice of waiting 6 hours after temperature changes before taking data constituted satisfactory procedures.

The gear pumps did not function as positive displacement pumps in this study, because the fluids involved were much less viscous than those for which the pumps were designed. Although the pumps delivered the feed at constant flow rate, it was not possible to calculate the flow rate from the pump data because of slippage past the gears. The flow rate was determined by a timed collection and weighing of the condensed products. At least 99% of the product condensed in the finger condenser. The very small portion of the product that condensed in the cold traps was neglected in the flow rate calculations and in the analyses.

The products of reaction were analyzed by the following procedures:

1. The iodine number of the sample was calculated from results of the bromination method of Rowe, Furnas, and Bliss (5). The method was modified by reducing the exposure time of the sample to the brominating agent (pyridine sulfate dibromide) from the recommended 16 hours to 1 hour. This modification minimized the reaction between the brominating agent and alcohol or ether. In calculating the olefin content of a sample from the iodine number, a value of 3.7 was used to represent the iodine number of the alcohol and of the ether. This value was established by analyses of synthetic mixtures of

alcohol, olefin, and ether. The accuracy of the iodine number determination is estimated to be  $\pm 3\%$ .

2. The alcohol content of the sample was determined by the acetylation procedure of Smith and Bryant (6). The accuracy of the alcohol content determination is estimated to be  $\pm 1\%$ .



Figure 2. Conversion of Ether to Olefin-Run A

3. Samples that showed high alcohol contents were further analyzed for water, since water is appreciably soluble in *n*-hexyl alcohol. The Karl Fischer method was employed, following the procedure described by Smith, Bryant, and Mitchell (7). 4. The ether content of the sample was determined by difference.

The commercial grade of 1-hexanol supplied by Eastman Kodak Co. was fractionated in a 30-plate Oldershaw column at high reflux ratio, and the middle cut was used as reactor feed. This material was found by analysis to contain 98.1% *n*-hexyl alcohol. The di-*n*-hexyl ether was the c.p. grade supplied by Eastman Kodak Co.

### RESULTS

A summary of the experimental conditions under which the runs of this work were performed is given in Table I. This table is intended only to indicate the scope of the work and the sequence in which the work was done. Graphical presentations of the experimental data (Figures 2–13, inclusive) are considered adequate for the purposes of this discussion.

 TABLE I.
 SUMMARY OF EXPERIMENTAL CONDITIONS

 Pressure:
 1 atm. except runs C, D, and J, 0.5 atm.

 Reactor:
 2.3 cm. diam. except runs G, H, J, 1.25 cm.

 Catalyst weight:
 10 grams except runs E and F, 50 grams

Catalyst I	Period	° C.	No. Samples
Run A, ROR	$     \frac{1}{2}   $	$340 \\ 360 \\ 320$	10
	45	350 360 370	
	7 8 9	360 320 360	1 2 1
Catalyst II Run A, ROR Bun B, ROH	10	360 360	4
	2 3 4	350 340 300	7 7 7
Run C. ROH Run D, ROR Catalyst III	5 6 1	320 360 360	752
	$\overline{1}$	360 360	1 2
Run E, ROR Run F, ROH Bun G, BOH	1 1	360 360 360	4 4 4
Run H, ROR Run J, ROR	1 1	360 360	43

The bases for choosing the independent variables of this study were outlined above, where it was noted that conversions were to be obtained as a function of flow rate with all other conditions fixed. The data obtained with a 10-gram catalyst bed, showing the effects of both flow rate and temperature on conversions, are presented in Figures 2 and 3 for ether feed and in Figures 4 and 5 for alcohol feed. These are the basic data used for the kinetic studies. Data were also obtained for a larger catalyst mass (50 grams) at a single temperature and are presented in Figure 6 for ether feed and in Figure 7 for alcohol feed.

The reproducibility of catalyst activity was investigated briefly as indicated by the results shown in Figure 8. The two batches of catalyst used to obtain these data were activated by the procedure previously outlined. The two batches yielded almost identical results with the exception of the olefin content of one sample. Since this particular sample was the first one taken after Catalyst II had been activated and conditioned, it probably was taken before the catalyst activity had reached a constant value.

The constancy of catalyst activity was also investigated briefly, and the results in Figure 9 compare the activity of Catalyst II shortly after it had been put into use with the activity of this catalyst about 3 weeks later. During this 3-week period that elapsed between the taking of these two sets of data, the equipment was in use for about 10 operating days of 8 hours each at temperatures of 300 to  $340^{\circ}$  C. and various feed rates. The catalyst activity obviously changed only slightly during this period.



Figure 3. Conversion of Ether to Alcohol-Run A

The effect of operating pressure on the reaction rate of din-hexyl ether is presented in Figure 10. Figure 11 presents similar data for the rate of reaction of 1-hexanol. In both cases the rate of reaction at a given temperature, molal feed rate, and catalyst mass is not changed by a twofold decrease in pressure. Walker  $(\mathcal{P})$  investigated this variable in dodecanol dehydration and showed that there was no effect of pressure in the range of 40 to 320 mm. mercury absolute pressure.

The effect of a change in the reactor diameter on the rate of reaction of di-*n*-hexyl ether is presented in Figure 12 and similar data for 1-hexanol are presented in Figure 13. The comparison in this case is not direct, since two separate batches of catalyst were used in obtaining the two sets of data for each figure. The change in reactor diameter is 1.8-fold and the change in reactor cross-sectional area 3.2-fold. If the rate of diffusion in the vapor phase of either the reactants or the products were of importance in determining the over-all rate of reaction, the effect of reactor diameter would be expected to be much greater than the very small effects shown in Figures 12 and 13.

## INTERPRETATION OF RESULTS

Hougen and Watson  $(\mathcal{Z}, 4)$  outlined the basic differential rate equations for reactions taking place on a solid catalyst in a flow system. The general method involves assuming that one particular process—adsorption, desorption, surface reaction, or diffusion—is so much slower than all other processes that it becomes controlling in the over-all rate of reaction. Before con-



Figure 4. Conversion of Alcohol to Olefin-Run B

sidering the particular reactions involved in this work note the general forms of such equations for the general type reaction  $A \rightarrow B + C$ . The assumptions made in arriving at the equations are:

1. All processes other than the assumed rate-controlling step occur so rapidly that equilibrium in these processes may be assumed.

2. The activity of any component is equal to the molefraction of that component multiplied by the total pressure.

3. The chemical reaction is irreversible.



Figure 5. Conversion of Alcohol to Ether-Run B

The following differential rate equations may thus be developed:

Rate of adsorption of reactant controlling

$$-\frac{dN_A}{dV_R} = \frac{k'_A L N_A P}{N_T \left(1 + \frac{N_B K_B P}{N_T} + \frac{N_C K_C P}{N_T}\right)}$$
(5)

Rate of desorption of product controlling

$$\frac{dN_A}{dV_R} = \frac{k_B'L}{K_B} \tag{6}$$

Rate of surface reaction controlling:

Adsorbed molecule reacting with adjacent active center

$$\frac{dN_A}{dV_R} = \frac{k'' s L K_A N_A P}{N_T \left(1 + \frac{N_A P K_A}{N_T} + \frac{N_B P K_B}{N_T} + \frac{N_C P K_C}{N_T}\right)^2}$$
(7)

Adsorbed molecule reacting on a single active center

$$-\frac{dN_A}{dV_R} = \frac{k'' L K_A N_A P}{N_T \left(1 + \frac{N_A P K_A}{N_T} + \frac{N_B P K_B}{N_T} + \frac{N_C P K_C}{N_T}\right)} \tag{8}$$

The differential equation for diffusion rate controlling is not included here since the study of the reactor diameter effect in this work indicated that diffusion in the vapor phase could not be controlling. Equations 5, 7, and 8 may be written in the general form

$$-\frac{dN_A}{dV_R} = kP \frac{N_A}{N_T \phi} \tag{9}$$

Furthermore, if one assumes simply that the reaction follows an effective first-order mechanism, the differential rate equation may be written

$$-\frac{dN_A}{dV_R} = \frac{kP}{RT} \frac{N_A}{N_T}$$
(10)



Figure 6. Conversions of Ether to Olefin and Alcohol—Run E

which also has the general form of Equation 9.

F

In the following development of reaction rate equations for this study it is assumed that the differential rate equation has the form of Equation 9. Considering separately each of the four reactions involved the following equations may be written

Reaction 1. 
$$-\frac{1}{2} \left( \frac{dN_A}{dV_R} \right) = \frac{dN_B}{dV_R} = \frac{dN_C}{dV_R} = \frac{k_1 P N_A}{N_T \phi}$$
(11)

Reaction 2. 
$$-\frac{dN_A}{dV_R} = \frac{dN_D}{dV_R} = \frac{dN_C}{dV_R} = \frac{k_2 P N_A}{N_T \phi}$$
(12)

Reaction 3. 
$$-\frac{dN_B}{dV_R} = \frac{1}{2} \left( \frac{dN_D}{dV_R} \right) = \frac{dN_C}{dV_R} = \frac{k_2 P N_B}{N_T \phi}$$
(13)

Reaction 4. 
$$-\frac{dN_B}{dV_R} = \frac{dN_D}{dV_R} = \frac{dN_A}{dV_R} = \frac{k_4 P N_B}{N_T \phi}$$
(14)

Since it is assumed that all these reactions are occurring simultaneously it is necessary to derive equations for the net rates of reactions. Consideration of the stoichiometry of the systems indicates that two independent equations for the reaction rates may be written. Thus the net reaction rates are

$$\frac{dN_B}{dV_R} = \frac{P}{N_T \phi} \left[ k_1 N_A - (k_3 + k_4) N_B \right]$$
(15)

$$\frac{dN_A}{dV_R} = \frac{P}{N_T \phi} \left[ k_4 N_B - (2k_1 + k_2) N_A \right]$$
(16)







Figure 8. Reproducibility of Catalyst Activity O Run A = Catalyst I
 ● Run A = Catalyst II đ



PEED RATE OF ALCOHOL, G. MOLES / HR. Figure 9. Constancy of Catalyst Activity 0 Run B = First points Run B = Final points

Equations representing the rates of formation of water and olefin may also be written, but these are dependent equations.

The complete solution to Equations 15 and 16 for alcohol dehydration would involve the use of the stoichiometric relations

$$N_{A_{b}} = N_{A} + 2N_{B} + N_{D} \tag{17}$$

$$N_{T} = 2N_{A_{2}} - N_{A} - 2N_{B} \tag{18}$$

$$N_C = N_B + N_D \tag{19}$$

By means of these equations  $\phi$  and  $N_T$  may be expressed in terms of  $N_{A_0}$  (the feed rate),  $N_A$  and  $N_B$ , together with such constants as may be involved in the  $\phi$  term. This results in two differential equations with three variables.

In solving Equations 15 and 16 it is convenient to divide Equation 16 by Equation 15

$$\frac{dN_A}{dN_B} = \frac{-(2k_1 + k_2)N_A + k_4N_B}{k_1N_A - (k_3 + k_4)N_B}$$
(20)

Integrating this equation between limits of  $\frac{N_A}{N_B}$  and zero  $\left(=\frac{N_{A_0}}{N_{B_0}}\right)$  and limits of  $N_B$  and  $N_{B_0}$  yields



where

CONVERTED

FEED

×

30

$$a = k_4/k_1$$

$$b = -2 - k_2/k_1 + k_3/k_1 + k_4/k_1$$

$$c = -2 - k_2/k_1 - k_3/k_1 - k_4/k_1$$



Figure 14. Product Distribution Data for Ether Feed

$$\begin{aligned} d &= \left[ 4 + \left(\frac{k_2}{k_1}\right)^2 + \left(\frac{k_3}{k_1}\right)^2 + \left(\frac{k_4}{k_1}\right)^2 + 4\frac{k_2}{k_1} - 4\frac{k_3}{k_1} - 2\frac{k_2k_3}{k_1k_1} - 2\frac{k_2k_4}{k_1k_1} + 2\frac{k_3k_4}{k_1k_1} \right]^{\frac{1}{2}} \\ v &= N_A/N_B \end{aligned}$$

In the case of alcohol feed, it is convenient to divide Equation 15 by Equation 16. Integrating this equation between limits of  $\frac{N_B}{N_A}$  and zero  $\left(=\frac{N_{B_0}}{N_{A_0}}\right)$  and limits of  $N_A$  and  $N_{A_0}$  yields  $\log \frac{1}{-ax^2 - bx + 1} +$ 

$$\frac{c}{d}\log\frac{-2ax-b-d}{-2ax-b+d}\cdot\frac{-b+d}{-b-d} = 2\log\frac{N_A}{N_{A_2}}$$
(22)

where  $x = N_B/N_A$ 

The data obtained with ether as the feed material are plotted in Figure 14 as suggested by the form of Equation 21. This plot indicates that the product distribution for a given percentage conversion of feed is independent of temperature, catalyst volume, feed rate, pressure, and reactor diameter. The same observation may be made of the data obtained with alcohol as the feed material when they are plotted in Figure 15 as suggested by the form of Equation 22. These results indicate that the ratios of the reaction velocity constants are essentially independent of temperature.

Since the results of Figures 14 and 15 agree with the behavior that might be predicted from Equations 21 and 22, these equations were investigated further. A complete test of Equations 21 and 22 against the data requires that the values of three constants  $(k_2/k_1, k_3/k_1, \text{ and } k_4/k_1)$  be obtained from the experimental data. While the grouping of these constants appears formidable, Equation 20 may be of some assistance. Plots of  $N_A$  vs.  $N_B$  must be prepared first. The slope of the ether feed plot in the region of low conversions of ether (and consequently low concentrations of alcohol) gives an order-of-magnitude estimate of the value of  $k_3/k_4$ . A similar interpretation of the alcohol feed plot gives an order-of-magnitude estimate of the value of  $k_2/k_1$ . With these figures as starting points for estimates a set of values of the constants found by trial and error agree with the experimental data and Equations 21 and 22. The curves drawn in Figures 14 and 15 are based on the following values of the constants:

$$\begin{array}{rcl} k_2/k_1 &= & 0.70 \\ k_3/k_1 &= & 0.50 \\ k_4/k_1 &= & 1.04 \end{array}$$

To this point it has been shown that Equation 20 may be applied to data obtained with either alcohol or ether as the feed material over relatively wide ranges of temperature, feed rate, catalyst volume, pressure, and reactor diameter. Equations 15 and 16 are of the proper form. A complete solution to this problem would involve substituting Equation 21 in Equation 15 or 16 and integrating to obtain a relationship between  $N_B$  and  $V_R$ , or between  $N_A$ and  $V_R$ . The relationship between  $N_B$  and  $V_R$ would be preferred for ether as the feed material, and that between  $N_A$  and  $V_R$  would be preferred for alcohol as the feed material. The algebraic complexity of this attack and the lack of a method for evaluating the  $\phi$  terms make it impossible to carry this attack further. The over-all reaction rates are apparently controlled either by the rate of adsorption of the reactants or by the surface reaction rates.

Although the question of reactor design is not involved in this particular problem since the system studied is not of appreciable commercial interest, it is worth noting that all of the data indicate that the space velocity concept could be used for design purposes.

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## NOMENCLATURE

- = adsorption equilibrium constant K
- = active centers, moles per unit volume of catalyst = gram-moles per hour passing any given point in reactor
- $L \\ N \\ P$ = total pressure

- $\begin{array}{l} P &= \text{total pressure} \\ V_R &= \text{reactor volume} \\ a &= k_4/k_1 \\ b &= -2 k_2/k_1 + k_3/k_1 + k_4/k_1 \\ c &= -2 k_2/k_1 k_3/k_1 k_4/k_1 \\ d &= \left[ 4 + \left(\frac{k_2}{k_1}\right)^2 + \left(\frac{k_3}{k_1}\right)^2 + \left(\frac{k_4}{k_1}\right)^2 + 4\frac{k_2}{k_1} 4\frac{k_3}{k_1} 2\frac{k_2k_3}{k_1k_1} 2\frac{k_2k_3}{k_1k_1} 2\frac{k_2k_3}{k_1k_1} 2\frac{k_2k_3}{k_1k_1} 2\frac{k_2k_3}{k_1k_1} 2\frac{k_2k_3}{k_1k_1} + 2\frac{k_3k_4}{k_1k_1} \right]^{1/2} \\ k &= \text{reaction velocity constant for first-order mechanism} \\ k' &= \text{velocity constant for rate of adsorption or desorption} \end{array}$
- $\tilde{k}'$ = velocity constant for rate of adsorption of decorption = reaction velocity constant for surface chemical reactions velocity constant for rate of adsorption or desorption
- k"

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Figure 15. Product Distribution Data for Alcohol Feed

- = number of equidistant centers surrounding each active center
- v = ratio, moles alcohol to moles ether
- x = ratio, moles ether to moles alcohol

## Subscripts

8

- A = alcohol C = water
- $A_0$  = alcohol at reactor inlet D = olefin B = other T = total mol
- B = ether T = total moles $B_0 = \text{ether at reactor inlet}$  1, 2, 3, 4 = reactions
- $D_0 = \text{emer at reactor met} = 1, 2, 5, 4 = \text{reaction}$

#### LITERATURE CITED

- Dohse, H., Z. physik. Chem., B5, 131 (1929); B6, 343 (1930).
- (2) Gamson, B. W., Thodos, G., and Hougen, O. A., *Trans. Am. Inst. Chem. Engrs.*, 39, 1 (1943).
- (3) Hougen, O. A., and Watson, K. M., "Chemical Process Principles," Pt. III, New York, John Wiley & Sons, Inc., 1947.
- (4) Hougen, O. A., and Watson, K. M., IND. ENG. CHEM., 35, 529 (1943).
- (5) Rowe, R. G., Furnas, C. C., and Bliss, H., IND. ENG. CHEM., ANAL. ED., 16, 371 (1944).
- (6) Smith, D. M., and Bryant, W. M. D., J. Am. Chem. Soc., 57, 61 (1935).
- (7) Smith, D. M., Bryant, W. M. D., and Mitchell, J., Ibid., 61, 2407 (1939).
- (8) Taecker, R. G., and Hougen, O. A., Chem. Eng. Progr., 45, 188 (1949).
- (9) Walker, C. A., IND. ENG. CHEM., 41, 2640 (1949).

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## Abrasive Characteristics of Alumina Particles

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USED alumina is marketed widely, under such names as Alundum and Aloxite, as a fast-cutting abrasive. Fluidizable alumina catalysts are extremely mild abrasives, and it seemed that alumina could be produced in many intermediate degrees of abrasive action. The object of this work was to test this hypothesis by a survey of some abrasive characteristics for commercial and experimental aluminas.

Tests were required which would focus attention on the individual abrasive particles. Accordingly, the abrasive action of aluminas has been measured by equipment patterned after the "impact abrasion hardness tester" of Ridgway, Ballard, and Bailey (8) and by the grinding of glass. The impact method is well suited to supplement the meager information on abrasion resistance of various materials, and data on this subject are also presented. The desirability of more data on the factors influencing wear is illustrated by the comment at a recent international symposium (1), that metal technologists at Delft, well aware of the dubious value of abrasion "figures," are rather reluctant to adopt any test at all.

Using a rotating rubber disk that caused abrasives to scour a test specimen, Haworth (4) found that silicon carbide cut tungsten carbide readily, whereas alumina caused only about one twentieth as much wear. On the other hand, the wear rate with alumina on high-carbon high-chromium steel was five times that with silicon carbide. Rollason *et al.* (9) reported that the plate-shaped alumina particles obtained by the calcination of alum had a good metallographic polishing action; the alpha phase formed by heating for 1 hour at  $1250^{\circ}$  C. was superior to the gamma type formed by heating for 1 hour at  $1100^{\circ}$  C. H. W. Wagner (11) in considering the mechanism of abrasive action concluded that