Rates of Reaction in a Recycling System—Dehydration of Ethanol and Diethyl Ether Over Alumina

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A new method for measuring isothermal rates of heterogeneously catalyzed gas reactions is described. The method involves a differential reactor incorporated in a recycling system and affords ease of control, accuracy, and many rate measurements in one run.

The results for the reaction system investigated show that four reactions are important: the dehydration of ethanol to ethylene, the reaction of ethanol to form diethyl ether, the dehydration of diethyl ether to ethylene, and the reaction of diethyl ether to form ethanol.

It is also shown that the rate controlling steps are the monomolecular surface reactions for the two dehydrations and for the formation of ethanol from diethyl ether, and the bimolecular surface reaction for the formation of diethyl ether from ethanol.

The values and the temperature dependence of all pertinent rate and adsorption constants are determined and reported, and they are shown to correlate very well the data up to 80% conversion.

The measurement of the isothermal rates of heterogeneously catalyzed gas reactions is ordinarily accomplished directly in differential reactors or indirectly in integral ones. The former is a powerful method but difficulties are met in analyzing small differences in concentration across the short bed. The use of integral conversion data is limited by the necessity to hypothesize a rate equation before interpretation is possible and by the experimental problem of maintaining isothermal conditions in the reactor.

A recycling differential reactor, first proposed by Dohse (*5*), affords ease of temperature control, accuracy of analysis, and direct measurement of rates. A new reactor based on Dohse's original idea but extensively improved and modernized has been developed and used in this research. Reactants and products are continuously circulated through the catalyst, and samples of the reaction mixture are withdrawn frequently for analysis. The extent of reaction per pass through the catalyst bed is very small; consequently maintenance of isothermal conditions is not difficult. Conversion data, and thus rate data, are determined at many points in a run from the sample analyses, so increased accuracy of the rate data is assured. A run may be continued until very high conversions are attained; hence it is possible to measure the rates over an unusually wide range of conversion in one run.

A somewhat similar device was used by Smith, et al. (*13*), with considerable success for ion exchange systems. Perkins and Rase (*10*) and Polotniuk and Dobrovol'skii (*11*) have reported the use of reactor systems involving recycling operations. These devices however involve recycling the reactants and products in a steady state measurement of rates at a given conversion and are not similar to the system described here.

The dehydration of ethyl alcohol over alumina catalyst was selected for study because such rates have not been well-defined and because a moderately complicated array of simultaneous and consecutive reactions is involved. Diethyl ether is an intermediate, and the rates of its reactions over the same catalyst were also measured.

RANGE OF VARIABLES

The variables investigated in this research were as follows:

Temperature: 274°, 294°, and 314°C.

Reactant material:

1. Pure ethanol
2. Pure diethyl ether
3. 84 mole % ethanol—16 mole % ethylene
4. 84 mole % ethanol—16 mole % water

Initial pressure:

1. 250, 520, and 740 mm. Hg (ethanol reactant)
2. 65, 150, and 250 mm. Hg (diethyl ether reactant)
3. 620 mm. Hg (ethanol-water and ethanol-ethylene reactants)

Range of conversion: 0 to 90%

Vapor flow rate: 0.24 to 1.1 cu. ft. (standard conditions)/min.

The catalyst used in all experimental work was Harshaw Type AL-1404 high purity alumina.

EXPERMENTAL

Apparatus

Figure 1 is a schematic diagram of the recycling reactor system. The major portion of the system was constructed of 35-mm. glass tubing, with 3-mm. capillary tubing used for inlet-outlet lines A and M and manometer C. The recycling pump D was a Vanton Flex-i-liner pump with a silicone rubber liner and 316 stainless steel body block. The glass system was connected to the pump with gum rubber tubing protected with high temperature insulating tape. Catalyst bed J consisted of 11.64 g. of high purity alumina in the form of ⅛ × ⅛ in. cylindrical pellets. A 1/16 in. shielded iron-constantan thermocouple G was used to measure catalyst bed temperature. This thermocouple was mounted such that it could be moved over the 3/4 in. bed depth, allowing the measurement of the catalyst bed temperature profile. Temperature of the bath K and of the reaction mixture entering the recycling pump were also measured with iron-constantan thermocouples. Bath K contained molten 312 tempering salt heated by means of a 1,000- and a 500-w. resistance heater. Temperature was controlled to within 0.1°C. with a bimetallic thermometer and relay system connected to the 500-w. heater.

Flow of the reaction mixture was counterclockwise through the system, such that in the U-tube reactor section the down flowing gas was preheated to the reaction temperature before flowing up through the catalyst bed. Feed to the system was introduced, and samples of reaction mixture were withdrawn for analysis through sample ports E or F, fitted with serum stoppers, by means of a hypodermic syringe. The inlet-outlet lines A and M served as vacuum and inert gas systems, respectively. These were isolated from the main reactor system by a valve system (B, O, and N) and included a trap L for the removal of condensible material from the vacuum system. To prevent possible condensation or adsorption of the reaction mixture in the system all exposed surfaces were heated with flexible heating tapes wrapped around the glass tubing and the pump.

Procedure

Operation of the recycling reactor system involved the recirculation of a known amount of reactant through the catalyst bed at conditions of temperature and pressure such that a very small conversion of reactants to products was obtained per pass through the bed. The reactor system was operated in a batch fashion by introducing the reactant and following the reaction by means of concentration, time of reaction information for the constant volume process. Owing to the small conversion occurring per pass in the catalyst bed it was easy to maintain isothermal conditions in the bed while making a run.

To make a run at a given temperature level the experimental apparatus was evacuated to 0 to 1 mm. Hg. absolute and the recirculating section isolated from the remainder of the apparatus. The recycling pump was started, and liquid ethanol or diethyl ether reactant of weighed amount was injected into the system with a hypodermic syringe. On complete vaporization of the reactant in the system the initial conditions of pressure and catalyst bed temperature were noted. After this initial period of operation small samples of the reaction mixture were removed from the system at specified time intervals for analysis, and the system pressure and catalyst bed temperature were recorded for each sample. Samples were withdrawn simultaneously from E and F (Figure 1) in several runs. No difference was ever found, so only E was used thereafter. When the desired conversion range had been studied, the recycling pump was stopped and the reaction mixture evacuated from the apparatus. The system was then purged with nitrogen in preparation of the next run. These methods of experimental operation were used for all conditions of temperature, pressure, and feed material investigated in this research.

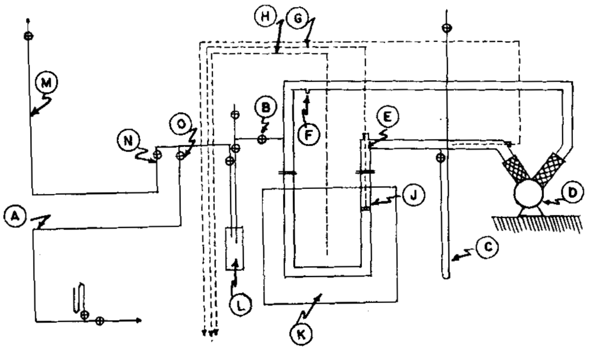

Fig. 1. Recycling reactor system.

It has been pointed out by Brey and Krieger (*1*) and other workers that different conditions for the activation of alumina will result in different levels of activity. The study of catalyst activity as a function of the method of activation was not of interest in this work; therefore all the catalyst used was activated in the same manner. The method of activation consisted primarily of maintaining the alumina at 300°C. in a nitrogen atmosphere for 24 hr. before use. The activity of the alumina catalyst was found to be constant and reproducible after approximately 4 hr. use with this method of activation. For intermittent operation of the equipment it was found that two procedures were necessary in order to reproduce catalyst activity if more than an hour elapsed between two consecutive runs. These procedures were as follows:

1. The catalyst was kept in a nitrogen atmosphere at the temperature at which the next run was to be carried out.

2. Prior to taking conversion data on beginning the next run, the catalyst was stabilized by recycling the feed material to be used at the desired pressure for ten minutes. To equipment was then evacuated and recharged with reactant for the experimental run.

The stabilized activity was essentially constant as evidenced by reproducibility of the results. Check runs were made frequently to verify this.

Analysis

The reactions of ethanol or diethyl ether over alumina catalyst yield a reaction mixture consisting of ethanol, diethyl ether, ethylene, and water. Previously it had been very difficult to work with systems such as this because of the unique analytical procedures involved. It was found that the methods of vapor fractometry afforded a convenient and accurate method for obtaining analyses of

TABLE 1. SAMPLE EXPERIMENTAL DATA

Run: Ethanol feed
Temperature: 294°C.
Initial pressure: 740 mm. Hg
Initial moles charge: 0.05106 g.-moles

Sample no.	Time, min.	Molar composition, g. moles ether	 ethanol	 water	 olefin	Total pressure, mm. Hg
A33-1	3	0.00696	0.03490	0.00942	0.00246	776
A34-1	2	0.00436	0.04090	0.00578	0.00147	760
A34-2	10	0.01498	0.01785	0.01811	0.00314	783
A35-2	9	0.01437	0.01845	0.01802	0.00399	787
A36-1	4	0.01027	0.02850	0.01234	0.00408	796
A36-2	12	0.01563	0.01595	0.01942	0.00378	796
A36-3	20	0.01405	0.01095	0.02317	0.00665	830
A37-1	5	0.00757	0.02970	0.01216	0.00303	784
A37-2	14	0.01596	0.01515	0.01998	0.00402	797
A38-1	1	0.00238	0.04310	0.00546	0.00314	783
A38-2	8.5	0.01277	0.02195	0.01620	0.00342	787
A38-3	16	0.01603	0.01315	0.02162	0.00559	817
A39-1	3	0.00694	0.03690	0.00743	0.00349	790
A39-2	13	0.01534	0.01689	0.01884	0.00355	792
A40-1	6	0.00992	0.02720	0.01394	0.00402	774
A40-2	15	0.01608	0.01360	0.02145	0.00559	819
A41-1	2	0.00393	0.04120	0.00588	0.00196	768
A41-2	9	0.01282	0.02190	0.01631	0.00349	791
A41-3	17	0.01534	0.01432	0.02147	0.00618	830
A53-1	19	0.01717	0.01308	0.02077	0.00361	793
A53-2	27	0.01712	0.01089	0.02305	0.00599	825
A54-3	36	0.01730	0.01168	0.02326	0.00567	820
A54-4	43	0.01733	0.00975	0.02410	0.00631	831
A54-5	51	0.01751	0.00863	0.02486	0.00729	846

this mixture. The rapidity of analyses eliminates any difficulties which might be encountered in storage of samples for slower methods, and the high sensitivity of the method allows the use of samples small enough not to disturb the constant volume nature of the recycling reactor system. Indeed it would be very difficult to carry out kinetic investigations with the recycling reactor without a rapid, convenient method of analysis of very small samples.

In this investigation the fractometer used for the analysis of reaction mixture samples was equipped with a 1/8-in. column 2 m in length and packed with Carbowax 1500. Output from the thermal conductivity measuring device of the fractometer was recorded on a recorder modified for 0 to 1 mv. full scale deflection and equipped with Disc mechanical integrator. A carrier gas pressure of 20 lb./sq. in. gauge and column temperature of 112°C. were used for analyses. At these conditions, with dry helium as the carrier gas, good resolution of all components except water was obtained, elution of components from the column being in the order ethylene, ether, ethanol, and water. A study of the results of thirty analyses carried out on a standard sample indicated that the method was accurate within an average deviation for each component analysis of less than 0.5% (based on the total number of moles of sample).

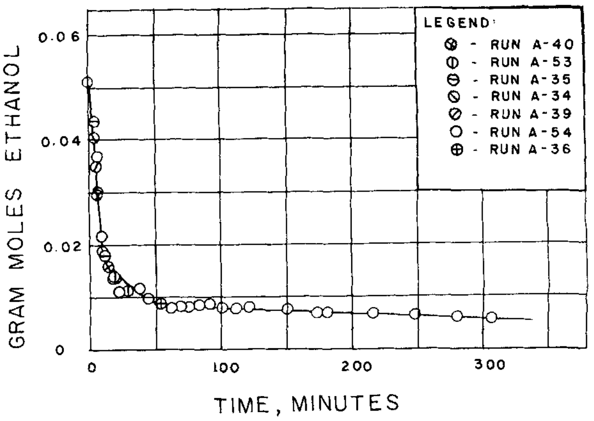

Fig. 2. Reproducibility of experimental data.

DATA

Approximately 120 runs were made, the detailed results of which are given by Butt (2). A sample of the data is given in Table 1. It should be noted that the fundamental measurements made were the compositions of the recirculating gas streams at various times. Conversions and reaction rates were calculated from these. It should also be noted that the conversion per pass is always small and that there can be no appreciable concentration gradient throughout the volume of the recycling system; that is this is essentially a batch reactor.

OBSERVATIONS ABOUT THE DATA AND THE SYSTEM

Isothermal Behavior

The temperature measured over the length of the catalyst bed varied no more than 1°C. throughout each run. The bath temperature was 1 to 1-½°C. above the catalyst temperature in all cases. The temperature of the recirculating gases in other parts of the system, such as the pump, was often appreciably different from that of the catalyst, but this in no way affects the rates. The number of moles of charge is known, and the change in the number of moles throughout the reaction is determined by the analysis. The rates are determined from the number of moles and not from any considerations of volume.

Measurements in the Unsteady State

Most rate measurements are made at steady state conditions, but these are at conditions varying with time. Since rates are influenced primarily by the distribution of adsorbed species on the catalyst, and since these must change during the course of a run, there is a question as to whether the rates could be affected by the time required for necessary adjustments on the catalyst surface. There is no evidence of such an effect, and it appears that the adjustments on the catalyst occur very rapidly. This is best indicated by the following comparison. Runs were made with both pure ethanol feed and an ethanol-water mixture composed of 84% ethanol, as mentioned previously. A comparison of conversion data for the mixed feed runs with those for pure feed indicates that the measured rates of reaction under equivalent conditions of partial pressures and temperature for the two cases are equal. Thus the rate of adjustment of the catalyst to the unsteady state adsorption of water and ethanol appears to be extremely rapid in comparison with the reaction rates measured.

Sample Volumes

The cumulative volume of samples removed was always less than 1% of the total volume. Accordingly any effects due to sample withdrawal were neglected.

Chemical Reactions and Equilibria

With ethanol as the reactant ether, ethylene, and water were found in the products. With ether as the reactant ethylene, water, and alcohol were produced. These can be explained with the following reactions:

$$C_2H_5OH \rightleftarrows C_2H_4 + H_2O \qquad (A)$$

$$2C_2H_5OH \rightleftarrows C_2H_5OC_2H_5 + H_2O \qquad (B)$$

$$C_2H_5OC_2H_5 \rightleftarrows C_2H_5OH + C_2H_4 \qquad (C)$$

$$C_2H_5OC_2H_5 \rightleftarrows 2C_2H_4 + H_2O \qquad (D)$$

An analogous set of reactions was hypothesized by Langer and Walker (8) to explain their results with dodecanol dehydration.

Cope and Dodge (4) give a good summary of the equilibria in these reactions. Under the conditions prevailing here the equilibria in (A) and (B) above are far to the right. The equilibria in (C) and (D) are not known as accurately, but they are probably well to the right. In the longest time and highest conversion runs made these reactions were still proceeding, although very slowly.

Effects of Materials of Construction

It was feared that pump materials, rubber serum stoppers, and sealing cement might possibly exert catalytic, inhibiting, or adsorption effects on the reactants or products. No evidence of this was found. Runs without catalyst exhibited no conversion, and runs at different flow rates which should exhibit different adsorption behavior (on such surfaces as the pump) showed the same conversions. Reproducibility (see below) was always good.

Considerations of Gas Phase Diffusion

Runs were made at gas flow rates from 0.24 to 1.1 cu. ft./min. (standard conditions). At rates of 0.68 and 1.1 cu. ft./min. conversion data were identical within experimental error, indicating no effect of this variable. Calculations with the mass transfer correlation of Hougen and Wilke (7) showed that the mass transfer rate was four times the reaction rate in the worst case. For most of the cases the mass transfer rate was ten to twenty times the reaction rate. All runs for determination of rate constants were carried out at either 0.68 or 1.1 cu. ft./min.

Consideration of Pore Diffusion

The effectiveness factor defined by Thiele (*14*), calculated according to the method proposed by Weisz (*15*), was shown to be 0.9 or higher even at the highest rates of reaction. These calculations were carried out with an effective diffusivity based on a value of 0.043 sq. cm./sec. for hydrogen with the alumina catalyst at 20°C., as reported by Carberry (*3*).

Reproducibility

In several cases a group of runs was made at identical conditions with sampling at different times for each run. The resulting composition vs. time curves practically coincided as shown in Figure 2.

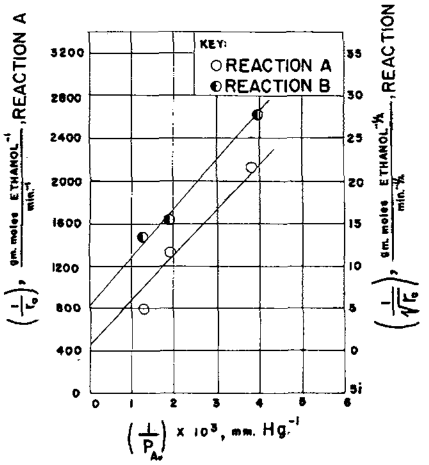

Fig. 3. Initial rate data, dehydration of ethanol at 294°C.

INTERPRETATION OF DATA

Rate Equations

In correlating kinetic data for heterogeneously catalyzed reactions it is necessary to consider the rate of reaction to be controlled by one of a number of steps occurring in the catalytic reaction process. These steps customarily include fluid phase diffusion, pore diffusion, adsorption, surface reaction, and desorption. It has already been pointed out that fluid phase and pore diffusion were very rapid compared with the reaction rate under the experimental conditions here considered; thus they may be disregarded. All further work was done with attention to adsorption, surface reaction, and desorption processes.

The manner of deriving rate equations, based on the adsorption theory of Langmuir (*9*), has been well-described by Hougen and Watson (*6*). A considerable number of such equations may be derived for a reaction system as complex as this one. Equations were written for the cases of adsorption of reactant, surface reaction, and desorption of product controlling. The results described below show that adsorption and desorption steps are not important and that only the surface reaction cases must be considered. The equations were then simplified because ethylene was not adsorbed on the catalyst, as shown by a negligible effect on the rates produced by addition of ethylene to the reactants, and the chemical equilibria are favorable so the reverse reactions can be neglected.

The simplified equations are then written as follows:

(a) first order surface reaction, reaction A:

$$r = \frac{K_{S1} L\, K_A\, p_A}{(1 + p_A K_A + p_w K_w + p_E K_E)} \tag{1}$$

(b) second order surface reaction, reaction B:

$$r = \frac{K_{S2} L\, K_A^2\, p_A^2}{4(1 + p_A K_A + p_w K_w + p_E K_E)^2} \tag{2}$$

Initial Rates

The first quantitative step in the interpretation of data on this reaction system requires the special consideration of initial rates. At the beginning of the reaction no product terms can be important, so the surface reaction equations become:

(a) first order surface reaction, reaction A:

$$r_o = \frac{K_{S1} L\, K_A\, p_{A_o}}{(1 + p_{A_o} K_A)} \tag{3}$$

(b) second order surface reaction, reaction B:

$$r_o = \frac{K_{S2} L\, K_A^2\, p_{A_o}^2}{4(1 + p_{A_o} K_A)^2} \tag{4}$$

The values of initial rates of reaction were determined from experimental data as follows:

1. A parabola was determined according to the method of least squares which related the number of moles of reactant (alcohol or ether) to time. This was limited to the initial portion of the conversion data.
2. The equation was differentiated at $t = 0$.
3. The resultant rate was divided by the weight of catalyst.

The results obtained show that ethanol disappears according to both reactions (A) and (B). The individual rate of reaction (A) can be determined by noting the rate of ethylene appearance and that of reaction (B) in terms of the rate of ether appearance. Thus a plot of the reciprocal of the initial rate so measured for reaction (A) vs. the reciprocal of p_{A_o} was a straight line confirming the first order surface reaction of Equation (3). Similarly a plot of the inverse square root of the initial rate of reaction (B) vs. the reciprocal of p_{A_o} was a straight line, confirming the second order surface reaction of Equation (4). The slopes and intercepts of these straight lines gave preliminary values for the constants appearing in the rate equations. These methods are illustrated in Figure 3 for the data obtained at 294°C.

A similar approach was undertaken with the initial rates of those runs using pure ether as a reactant. Thus the rate of reaction (C) was expressed in terms of alcohol appearance and that of reaction (D) in terms of water appearance. The analysis of these data showed that both reactions (C) and (D) were monomolecular surface reaction controlled, as illustrated in Figure 4 for ether at 294°C. The conclusions reached from Figures 3 and 4 must be considered tentative, since errors in measurement and judgment influence the locations of the lines. The verification of these conclusions depends primarily on the high conversion data discussed below.

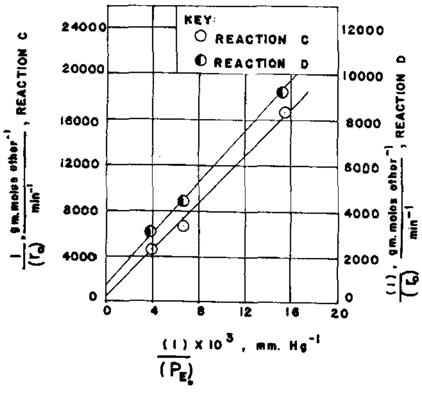

Fig. 4. Initial rate data, dehydration of diethyl ether at 294°C.

The consideration of initial rates is an excellent beginning, but owing to the transient nature of the recycling system at start-up initial rate data are not as accurate as could be desired. Obviously the determination of constants from these data will reflect such inaccuracies. Furthermore the absence of water in initial rate investigations makes impossible the determination of the water adsorption constant; thus it was necessary to carry out an additional series of initial rate evaluations on runs in which water was added to the feed material. These additional data permitted the preliminary evaluation of the water adsorption constants by the methods outlined above.

Initial rate analysis then established that the following rate controlling steps were valid:

Reaction (A): monomolecular surface reaction

Reaction (B): bimolecular surface reaction

Reaction (C) and (D): monomolecular surface reaction

Over-all Rate Equations

In consideration of the reaction process described by Equations (A) to (D) it is necessary to combine the rate equations for the individual reactions in order to define the conversion of any component which takes part in more than one of the reactions. For example if it is desired to write an expression for the net rate of disappearance of ethanol in an ethanol reaction system, the following must be considered:

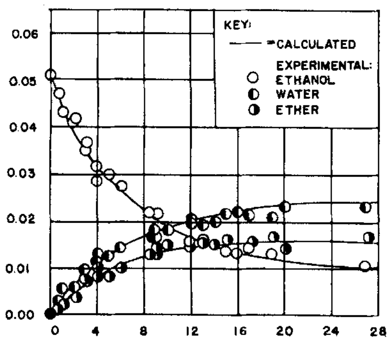

Fig. 5. Comparison of experimental and calculated conversions, ethanol at 294°C.

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad (A)$$

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O \qquad (B)$$

$$C_2H_5OC_2H_5 \rightarrow C_2H_5OH + C_2H_4 \qquad (C)$$

with these reactions now written as irreversible. It is clear that:

Net rate of disappearance of C_2H_5OH = Rate in (A) + Rate in (B) − Rate in (C)

Since the appropriate surface reaction rates are controlling in (A) through (C) then

$$r = \frac{K_{S1}L\,K_A p_A}{D} + \frac{K_{S2}L\,K_A^2 p_A^2}{4D^2} - \frac{K_{S1}L\,K_E p_E}{D} \qquad (5)$$

where

$$D = (1 + p_A K_A + p_w K_w + p_E K_E) \qquad (6)$$

Similar expressions may be written for other components, for both the ethanol and diethyl ether reaction systems.

Analysis of High Conversion Data* and Refinement of the Values of the Constants

The rate expressions which are generally applicable for calculation of conversions beyond the initial region are given by equations of the form of (5). These equations are the final forms used in the correlation of experimental data at high conversions. It was found, on examination of these data, that even the qualitative trends of conversion with time could not be predicted satisfactorily with equations based on adsorption or desorption, confirming that these processes are not rate controlling. The results of the initial rate investigations then can be verified as indicating surface reaction rates controlling in all cases.

Constants for the indicated rate equations calculated from initial rate data are not the best values for fitting both initial and high conversion data. In order to determine the values of reaction rate and adsorption equilibrium constants which best fit both initial and high conversion data according to the surface reaction mechanism, the following procedures were used:

1. The required surface reaction rate equations of the form of (5) were integrated by graphical methods with the preliminary values of the constants and partial pressures calculated from total pressure and molar composition data.
2. The resultant conversion information was compared with the experimental conversion data for the whole range investigated.
3. The preliminary values of the constants were adjusted as indicated by the agreement obtained between the experimental and calculated conversion information.
4. This second set of constants was then checked by the procedures outlined above and the process repeated until the best agreement of calculated with experimental conversion had been obtained.

Two important factors made the above procedure possible.

1. Initial rate data were sufficiently accurate to define fairly well the values of the adsorption equilibrium parameters, thereby reducing considerably the complexity of the trial procedure.
2. The availability of conversion data for each of the components appearing in the reaction mixture allowed the determination of the constants for each reaction independently; thus the over-all conversion of the reactant material could be utilized as a check on the combined rate equation.

The adsorption equilibrium parameters for ethylene and water, determined separately in the initial rate analysis, were also checked by these methods with the high conversion data for the runs with added ethylene and water, respectively.

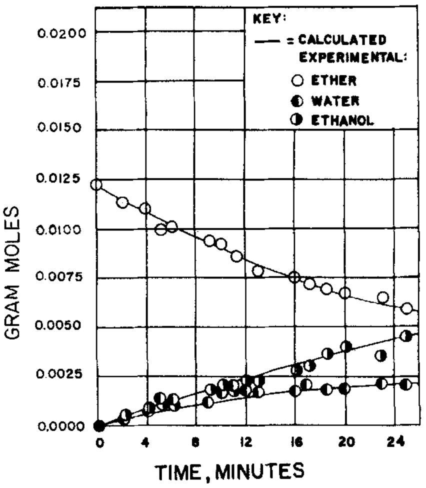

Fig. 6. Comparison of experimental and calculated conversions, diethyl ether at 294°C.

The final values of the constants are given in Table 2 for the three temperature levels investigated. Figures 5 and 6 illustrate the fit of experimental conversion data for an ethanol and an ether run (740 and 250 mm. initial pressure, respectively) at 294°C. with over-all rate expressions such as Equation (5). Similar agreement was obtained for runs at other temperatures and pressures. It was found however that the over-all rate expressions did not agree with alcohol conversion data in that small range of conversions greater than 80%. The data presented in Figure 2 for example indicate that the rate of conversion of ethanol at this point becomes quite slow. The two possibilities to be investigated here are the effects of reverse reactions or changes in the reaction mechanism resulting in a great decrease in reaction rate. In view of the previous comments

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* High conversion data must be dealt with in this way for an array of reactions as difficult as this. The rates of appearance of alcohol, ether, water, and ethylene at high conversions can be found from the data of course, but these cannot be related to the rates of the actual reactions involved because of the requirements of the elemental material balances. Thus the high conversion data cannot be used for the measurements of rates; they can only be used for checking and modifying the generalized rate equations derived from initial rate data.

on the equilibria of this reaction system it is felt that the latter case is much more likely; a change in the mechanism of one or more of the reactions has occurred, and this change is probably associated with the amount of water adsorbed on the catalyst. Unfortunately the data obtained in this research are not of a proper form to proceed with any verification of this hypothesis.

Temperature Effects

The variation with temperature of the rate constants and adsorption parameters given in Table 2 can be represented in linear form by a semilogarithmic plot of their values vs. reciprocal absolute temperature, as suggested by the Arrhenius equation. The activation energies evaluated from this correlation for the reactions investigated are as follows:

Reaction (A);
$E' = 10{,}000$ cal./g.-mole
Reaction (B);
$E' = 25{,}900$ cal./g.-mole
Reaction (C);
$E' = 28{,}500$ cal./g.-mole
Reaction (D);
$E' = 16{,}500$ cal./g.-mole

The temperature dependence of the adsorption equilibrium parameters for ethanol and diethyl ether (determined experimentally) and for water [determined from the data of San la Ville (*12*)] indicated similar behavior of all three substances, decreasing adsorption with increasing temperature. The relative values of these parameters at the temperatures investigated indicate that water is most strongly adsorbed on the alumina catalyst, alcohol is next, and diethyl ether least of the three.

CONCLUSIONS

The results of this work verify the utility of the recycling differential reactor system as a convenient and valuable method for obtaining kinetic data. Conversion data for a wide range of experimental conditions and for a complex system of reactions were obtained and interpreted satisfactorily. The reactions occurring when either ethanol or diethyl ether are passed over an alumina catalyst are

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \tag{A}$$

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O \tag{B}$$

$$C_2H_5OC_2H_5 \rightarrow C_2H_5OH + C_2H_4 \tag{C}$$

$$C_2H_5OC_2H_5 \rightarrow 2C_2H_4 + H_2O \tag{D}$$

The measured rates of these reactions were all found to be controlled by the corresponding surface rates of reaction on the alumina catalyst in the range of temperatures and pressures investigated. Thus reactions (A), (C), and (D) are monomolecular surface reactions and reaction (B) a bimolecular surface reaction. The corresponding rate equations, in terms of disappearance of reactant, were written with values of all the pertinent constants. In addition the effect of temperature on the rates of the reactions occurring has been determined. In general all rates of reaction increase with increasing temperature. The activation energy has been determined for each of the specific surface reaction rate constants. The adsorption parameters for ethanol, water, and diethyl ether were found to have approximately the same temperature behavior over the range of investigation, decreasing with increasing temperature. The relative values of these parameters indicate decreasing adsorption of component on alumina for water, ethanol, and diethyl ether, in that order.

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TABLE 2. FINAL VALUES OF REACTION RATE CONSTANTS AND ADSORPTION PARAMETERS FOR ETHANOL AND DIETHYL ETHER REACTIONS

Rate constant $\left(\frac{\text{g.-moles}}{\text{min., g. catalyst}}\right)$	Value	Temperature, °C.
$K_{s1}L$	0.099×10^{-3}	274
(Reaction A)	0.137×10^{-3}	294
	0.188×10^{-3}	314
$K_{s2}L$	0.627×10^{-2}	274
(Reaction B)	1.41×10^{-2}	294
	3.03×10^{-2}	314
$K_{s1}L$	0.054×10^{-3}	274
(Reaction C)	0.121×10^{-3}	294
	0.261×10^{-3}	314
$K_{s1}L$	0.069×10^{-3}	274
(Reaction D)	0.113×10^{-3}	294
	0.182×10^{-3}	314
Adsorption parameter (mm. Hg^{-1})		
K_A	1.35×10^{-3}	274
	1.00×10^{-3}	294
	0.73×10^{-3}	314
K_E	1.00×10^{-3}	274
	0.80×10^{-3}	294
	0.61×10^{-3}	314
K_W	1.51×10^{-3}	274
	1.22×10^{-3}	294
	1.02×10^{-3}	314

NOTATION

E' = activation energy, cal./g.-mole
K' = chemical reaction equilibrium constant
K = adsorption equilibrium constant, mm. Hg^{-1}
$K_{s1}L$ = monomolecular surface reaction rate constant; reactions A, C, and D, g.-moles/min., g. of catalyst
$K_{s2}L$ = bimolecular surface reaction rate constant; reaction B, g.-moles/min., g. of catalyst
L = concentration of active sites, moles/unit weight of catalyst
P = total pressure, mm. Hg
p = partial pressure, mm. Hg
r = rate of reaction, g.-moles/min., g. of catalyst

Subscripts

A = ethanol
E = diethyl ether
0 = ethylene
o = initial conditions
W = water

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