Catalytic Vapor Phase Esterification

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The kinetics of vapor phase esterification of n-propyl alcohol with acetic acid over a silica gel catalyst were studied in a differential reactor to determine the apparent rate controlling step for the reaction and the role of water as a catalyst promotor. The surface reaction, which probably occurs between alcohol adsorbed on the hydrated surface and acid in the gas phase, is the rate controlling step, and water promotes the reaction by hydrating the surface. Acid is apparently excluded from the surface because of the preferential adsorption of the longer chain alcohols.

INTRODUCTION

The purpose of this study was to investigate the vapor phase esterification of acetic acid with n-propyl alcohol over a silica gel catalyst in a differential flow reactor. Esterification of methanol (1), ethanol (2, 3), n-propyl alcohol (4), and n-butyl alcohol (5) with acetic acid in the vapor phase over silica gel has been studied in integral flow reactors, but the apparent rate controlling steps thus determined are inconsistent. The basic cause of the difficulty is apparently the fact that water acts as a catalyst promotor, since water apparently increases the concentration of hydroxyl groups on the surface (6). Since water is a reaction product, the water concentration (and catalyst activity) varies in an integral reactor. Thus, the effect of water on the catalyst activity and the rate controlling step must be determined simultaneously from integral reactor data by trial integration of assumed functional relations.

In this investigation, a differential reactor was used so that the effects of water on catalyst activity and on the rate controlling step could be determined separately. The experimental program was designed to determine explicitly the effects of acid and alcohol partial pressures, water partial pres-

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sure, and total pressure on the reaction rate. Using the results of this study, we could then recorrelate earlier results to develop a consistent pattern of rate controlling steps for the normal alcohol series and we could compare the implied modification of the surface by water to results of NMR (6), infrared (7–9) and adsorption (10, 11) studies of the effect of water on silica gel.

METHODS

The vapor phase esterification of n-propyl alcohol with acetic acid over silica gel was studied at one to seven atm total pressure over the temperature range from 200° to 260°C using the differential flow reactor system shown in Fig. 1. Acid and alcohol were metered separately with constant displacement pumps, vaporized, mixed, heated, contacted with the catalyst, condensed, and collected in dried receivers. The reactor was a 2 in. NPS jacketed stainless-steel pipe 78 in. long containing a catalyst bed approximately 6 in. deep that was supported on a stainless steel screen located 18 in. from the reactor entrance. Temperature of the reaction zone was controlled to within ±0.5°C by circulating Dowtherm A through the jacket, and pressure was controlled manually to within ±2%. If reaction products were to be added to the reactor
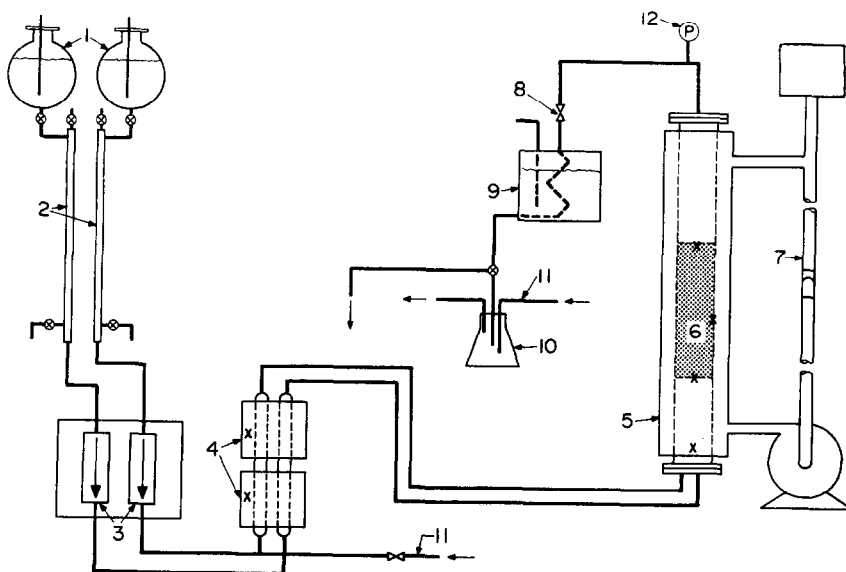
FIG. 1. Flow Diagram of Reactor System: 1, feed storage; 2, feed burets; 3, constant displacement pumps; 4, vaporizers and superheaters; 5, reactor; 6, catalyst bed; 7, Dowtherm circulation; 8, pressure control valve; 9, condenser; 10, sample receiver; 11, nitrogen purge; 12, pressure gauge.

feed, water was premixed with the acid feed and ester with the alcohol feed.

Specially dried glacial acetic acid and n-propyl alcohol were used. The catalyst used in this study was a 6–8 mesh quartered sample of silica gel purchased from Joliet Chemicals, Inc. that was guaranteed to show no loss in activity for this reaction if not heated above 300°C.

Product sampling was begun after thermal steady state had been established. Samples were taken at approximately fifteen minute intervals and were analyzed immediately. When results of three successive analyses agreed within experimental error and exhibited no trend, steady state was assumed to have been attained, the run was terminated, and the average results of the last three analyses were taken as the product composition. The reactor was then purged with dry nitrogen for one hour before starting the next run.

The conversion of the limiting reagent was determined from a material balance for water when using anhydrous (about 0.1% water) feeds. The water concentration of reactant and product streams was determined by Karl Fisher titration, which was conducted automatically using a Beckman

KF-2 aquameter. Each sample was analyzed in duplicate as rapidly as possible by titrating to an end point, adding excess reagent, and backtitrating with a very dilute solution of water in methanol. Extreme care was exercised to prevent contamination of the samples with the atmosphere. Karl Fisher titration has been found in one study (12) to give results equivalent in accuracy to a more complicated chromatographic analysis for a similar system.

When water was added to the reactor feed, the conversion was determined by analyzing the reactor product for unreacted acid. Weighed aliquots of the sample were diluted with water and titrated with 0.15 N standard NaOH solution using a Sargent–Malmstadt potentiometric titrator. Samples were analyzed in duplicate.

Results

Since low conversion data were to be taken, the effects of the homogeneous reaction, catalysis by the reactor, and side reactions could be magnified. Also, since the effect of water on catalyst activity was to be studied, other factors affecting catalyst activity had to be eliminated.

Some preliminary runs were made with

no catalyst in the reactor and the conversions were zero, within experimental error. Similar results have been reported for esterification of ethanol (2) and methanol (1) with acetic acid. Also, in one study (13), no homogeneous reaction was found to occur in a mixture of ethanol and acetic acid vapors below 450°C. However, the results of a more recent study (14) do not support this. No side reactions, with or without catalyst, were noted at temperatures below 275°C. At 275°C, dehydration of the alcohol began to be noticeable. Therefore, the upper operating temperature for the study was set at 260°C. Resistances to heat and mass transfer between the bulk stream and the catalyst surface were shown to be negligible by calculation and by experimentally measuring the effect of flow rate on reaction rate at constant catalyst-to-feed ratio. It was demonstrated that particle size of the catalyst does not affect the reaction rate and the calculated Thiele Modulus was quite high. Also, after an initial decline, the catalyst was found not to be subject to progressive fouling or poisoning in this system, as shown in Fig. 2. Therefore, the catalyst activity could be considered to be constant after about 20 hr exposure in the reactor. Since the reaction temperatures were below the critical temperatures for all components involved, condensation in the catalyst pores could occur at higher pressures. To prevent this, the pressure was

limited to about 50% of the saturation pressure of acetic acid, the component with the lowest vapor pressure at all reaction temperatures, and the lower temperature limit for the study was set at 200°C. Finally, acetic acid dimerizes in the vapor phase, and the acid partial pressure in all runs was corrected for this by using the equilibrium relation for dimerization as determined by Essex and Clark (15). Only the monomeric acid was assumed to participate in the reaction.

Esterification runs with no water added to the feed were made at 200, 230, and 260°C. The majority of the data were taken at 230°C. The effects of acid partial pressure, alcohol partial pressure, and total pressure over the ranges from 0.4 to 2 atm, 0.4 to 4 atm, and 0.98 to 7 atm, respectively, were determined explicitly. The effect of acid mole fraction at constant pressure on the rate was also determined for fractions ranging from 0.2 to 0.75 at pressures of 0.98, 1.0, and 2.0 atm.

To determine the effect of water on the reaction rate, the relation between conversion and catalyst-to-feed ratio (W/F) was determined for several levels of water concentration, holding the reactant ratio constant at 1.0 and the sum of the partial pressures of acid and alcohol constant at about 1.0 atm. A set of such curves for data at 230°C is shown in Fig. 3.

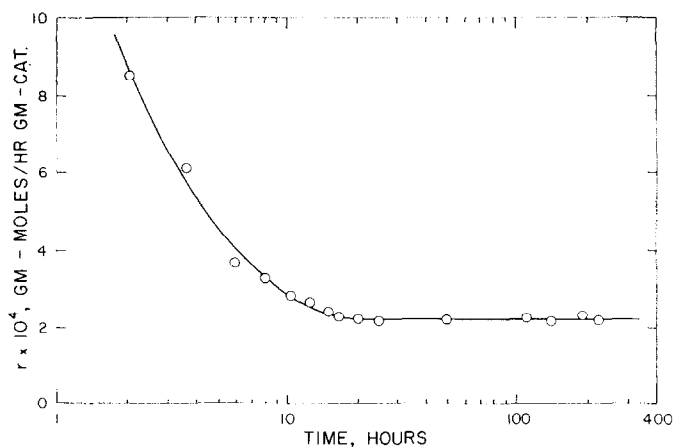The effect of water on the reaction rate

FIG. 2. Activity decline of fresh catalyst during esterification of equimolar reactant mixture at 230°C and 0.98 atm.
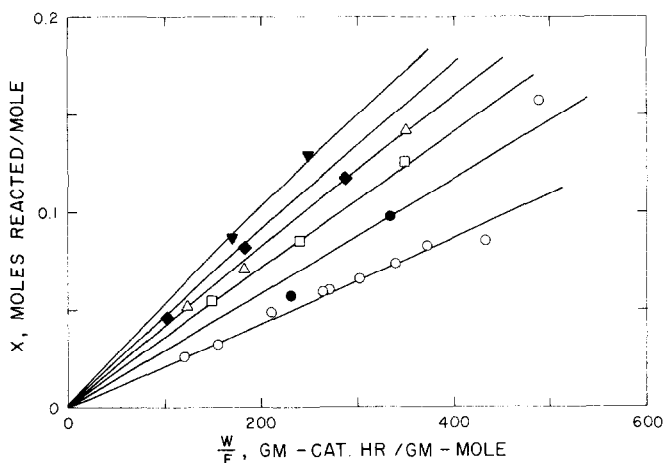
FIG. 3. Integral conversion curves for esterification of equimolar reactant mixture at 230°C and 1.0 atm, reactant pressure with water mole fraction in feed of: O, $N_w = 0$; ●, $N_w = 0.0917$; □, $N_w = 0.167$; △, $N_w = 0.231$; ◆, $N_w = 0.334$; ▼, $N_w = 0.502$.

was determined by taking slopes of the X vs W/F curves. These slopes, which are the reaction rates, were plotted as shown in Fig. 4, and the best curves were drawn. As can be seen, water increases catalyst activity very strongly. For example, the rate increases almost 200% when the water pressure is increased from 0 to 1.0 atm at 230°C.

Data was taken at conversions of the limiting reagent ranging from 3 to 7% in most cases with no water added to the feed so that the reaction rate corresponding to arithmetic mean conditons in the reactor could be calculated as

$$r = \frac{\Delta X}{(W/F)} \tag{1}$$

where r = reaction rate; ΔX = fractional conversion of limiting reagent; W = catalyst mass; F = flow rate of the limiting reagent.

However, the mean water partial pressure for these runs varied from 0.01 to 0.11 atm, and the variation in catalyst activity over such a range is too large to ignore. Therefore, the experimentally determined rates were corrected to zero water partial pressure by using a factor developed from the general expression for the reaction rate.
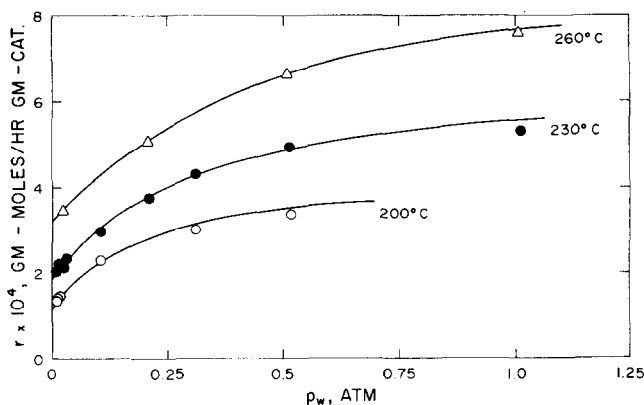

FIG. 4. Effect of water on the esterification rate of equimolar reactant mixture at 0.98 atm reactant pressure.

The general expression for catalytic reactions may be written as

$$\text{rate} = \frac{(\text{kinetic term}) \ (L) \ (\text{driving force})}{(\text{adsorption term})^n},$$

(2)

where L = concentration of active sites on the catalyst surface; n = number of adjacent active sites that participate in the reaction. Since all terms except L in Equation (2) are affected very little or not at all by small variations in water partial pressure, the ratio of the general rate expression at zero water partial pressure to the expression at some small water partial pressure can be taken as

$$r_0/r = L'/L,$$

(3)

where r_0 = reaction rate at zero water partial pressure; L' = concentration of active sites at zero water partial pressure. Since the increase in reaction rate is nearly linear with increase in water partial pressure to approximately 0.1 atm, the concentration of active sites can be approximated by

$$L = L'[1 + \alpha p_w],$$

(4)

where α = initial slope of rate vs water partial pressure relation, p_w = mean water partial pressure. Substitution into Equation (3) yields

$$r_0 = r[1/(1 + \alpha p_w)]$$

(5)

which was used to correct the rate data. A later recalculation using the actual functional relation determined for the effect of water yielded only very slight differences. Data presented in Figs. 5–10 were corrected in this manner. The curves presented in Figs. 5–11 were calculated using the final correlation corresponding to reaction between adsorbed alcohol and acid in the vapor phase as the rate controlling step.

The effect of alcohol pressure on reaction rate is shown in Figs. 5 and 6. The rate is virtually constant with increasing alcohol concentration above about 0.30 atm, indicating that the surface becomes saturated with alcohol at very low pressures. The reaction rate is proportional to the acid partial pressure, as shown in Fig. 7; therefore, either acid adsorption is very weak or the reaction takes place between adsorbed alcohol and acid in the gas phase. This is further illustrated in Fig. 8, since the rate is very nearly proportional to acid mole fraction over a wide range at constant pressure. To distinguish clearly between reaction of adsorbed species and reaction of one adsorbed and one unadsorbed species, it is necessary to determine the effect of total pressure on the rate. This effect is shown in Figs. 9 and 10. Within the experimental range, the rate increases without limit with increasing total pressure; however, the maximum pressure that can be
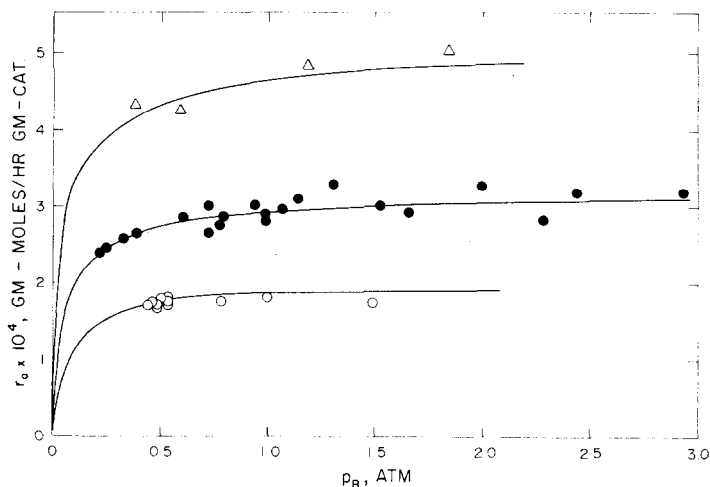

FIG. 5. Dependence of reaction rate upon alcohol pressure at 230°C and various acid pressures: $\bigcirc$, p_{A_1} = 0.40 atm; $\bullet$, p_{A_1} = 0.63 atm; $\triangle$, p_{A} = 1.0 atm.
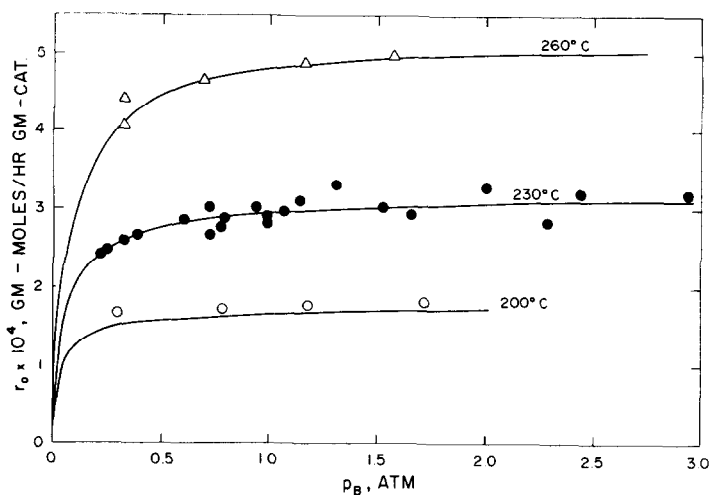
FIG. 6. Dependence of reaction rate upon alcohol pressure at $p_{A_1} = 0.63$ atm and various temperatures.

used experimentally is limited to about 50% of the saturation pressure of the acid.

By inspection of the experimental rate curves, all steps can be rejected as rate controlling, except the surface reaction or acid adsorption. Rate expressions for acid adsorption controlling with (1) Langmuir ad-

FIG. 7. Dependence of reaction rate upon acid pressure at $p_B = 0.8$ atm and various temperatures.

sorption of both reactants, (2) Temkin adsorption of both reactants and alcohol preferentially adsorbed, and (3) Temkin adsorption of acid and Langmuir adsorption of alcohol were derived and applied to the data. Also, it has been shown that none of these expressions yields the best correlation for esterification of methanol (1) or ethanol (2) with acetic acid. Furthermore, acid adsorption controlling would require that the rate decrease continuously with increasing total pressure. This is not the case, as can be seen in Fig. 9 and Fig. 10. Therefore, acid adsorption was rejected as the rate controlling step.

There are several types of surface reaction possible, but the expression that yields the best correlation of the data:

$$r_0 = C[p_{A_1}p_B]/(1 + K_{p_B}) \qquad (6)$$

where C, K_B = constants; p_{A_1} = mean partial pressure of monomeric acid; p_B = mean partial pressure of alcohol is an expression that can be derived for reaction between acid and alcohol adsorbed an exclusive sites, for reaction between adsorbed alcohol and acid in the gas phase, or for reaction between adsorbed acid and alcohol in the gas phase. It is not possible to distinguish between these from the kinetic data alone; however, data from other kinetic and adsorption studies can be used
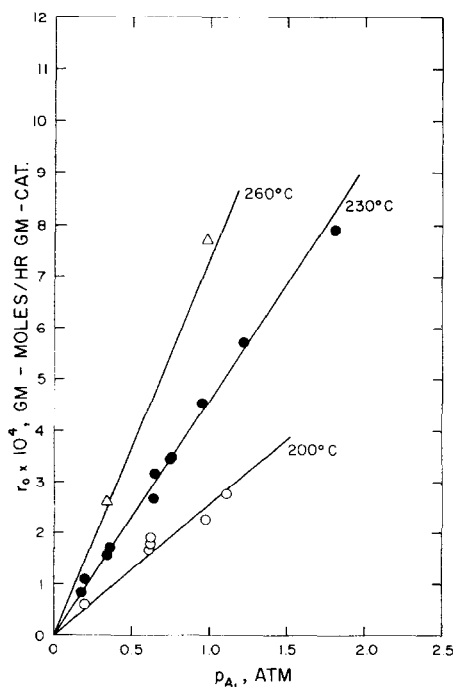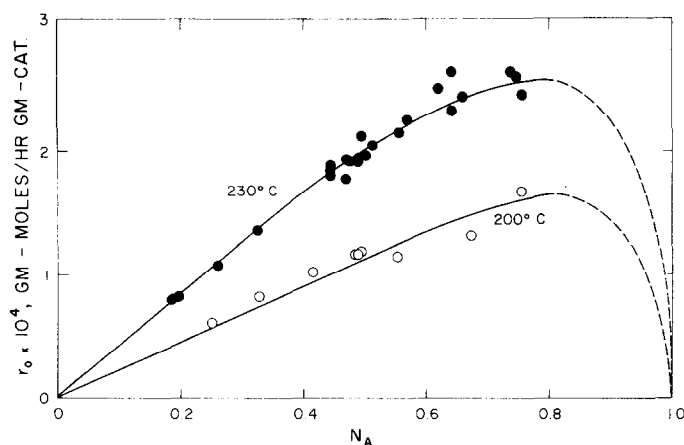
FIG. 8. Dependence of reaction rate upon acid mole fraction at $\pi = 0.98$ atm.

as a guide in selecting the most probable mechanism.

There is no justification for assuming that acid and alcohol are adsorbed on different sites. In fact, just the opposite is probably true; therefore, reaction between acid and alcohol adsorbed on exclusive sites was rejected.

Selection between the other two is more difficult. If the reaction is between adsorbed acid and alcohol in the gas phase, it has been pointed out (16) that the activated species can be postulated to be the conjugate acid which is the reactive species for liquid
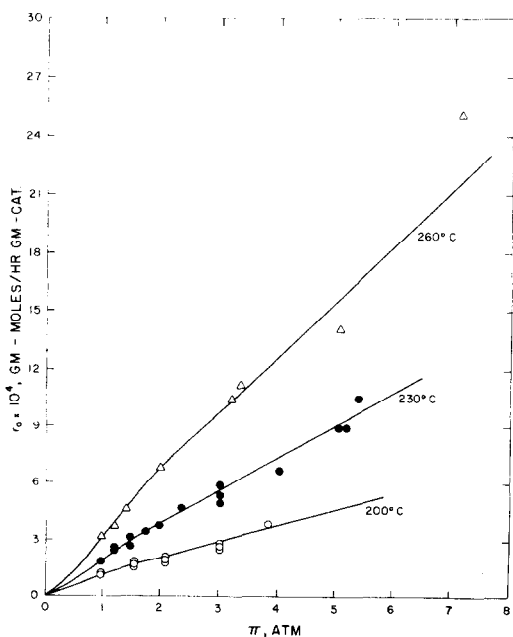

FIG. 9. Dependence of reaction rate upon total pressure for equimolar reactant mixture at various temperatures.
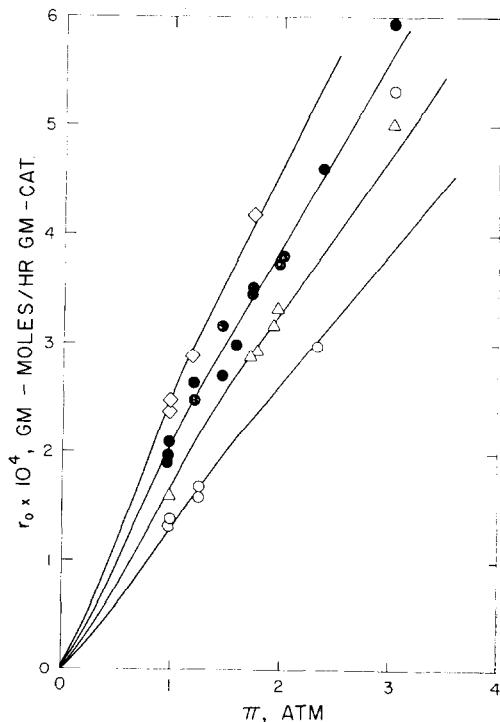

FIG. 10. Dependence of reaction rate upon total pressure at 230°C for various acid mole fractions: $\bigcirc$, $N_A = 0.33$; $\triangle$, $N_A = 0.39$; $\bullet$, $N_A = 0.5$; $\diamondsuit$, $N_A = 0.64$.

phase esterification. However, consideration of the results of esterification of other systems presents difficulties. Vapor phase esterification of methanol with acetic acid (*1*) is apparently a surface reaction between adsorbed species. Also, it has been shown (*17*) that the degree of adsorption of alcohol increases with increase in alcohol chain length. Therefore, if adsorbed acid is involved in the esterification reaction of *n*-propyl alcohol, then the mechanism should be reaction between adsorbed species, since *n*-propyl alcohol is more readily adsorbed than methyl alcohol, all other things being equal, and surface reaction between adsorbed species does not fit our data. Reaction between adsorbed acid and alcohol in the gas phase is difficult to accept as a mechanism, since this would require that *n*-propyl alcohol be adsorbed to a lesser degree than methyl alcohol in the presence of acetic acid, a behavior that is opposite to that observed for adsorption of

formed and are not available. After considering these factors, reaction between adsorbed alcohol and acid in the gas phase was chosen as the most probable apparent mechanism. Equation (6) can be rearranged to give

$$p_{A_1}p_B/r_0 = 1/C + [K_B/C]p_B, \qquad (7)$$

where K_B = equilibrium adsorption constant for alcohol. A correlation of the initial rate data by Eq. (7) is shown in Fig. 11.

The complete rate expression for the reaction must contain some functional relationship capable of representing the increase in rate resulting from the presence of water. Results of independent adsorption studies are helpful in selecting a proper relation. It has been reported that dehydration of silica gels decreased surface hydroxyl concentration markedly, and that rehydration restored the concentration to nearly the initial level (*9*). According to Zhdanov (*18*), the hydration reaction is

$$\ce{-Si-O-Si-} \;\overset{\displaystyle O}{\triangle}\; + \ \ce{H2O} \longrightarrow \ce{-Si(OH)-O-Si(OH)-} \qquad (8)$$
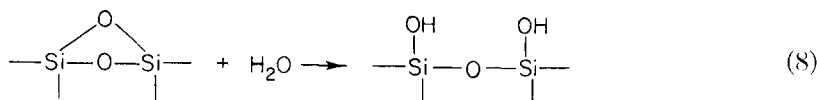
alcohols in the absence of acetic acid. Therefore, reaction between adsorbed acid and alcohol in the gas phase was rejected as a possible mechanism.

The third possibility, reaction between adsorbed alcohol and acid in the gas phase, would seem to be the best choice. As the alcohol chain length is increased, adsorption is expected to increase, possibly excluding the acid from adsorption. This interpretation would explain why the apparent mechanism changes from reaction between adsorbed species for methanol to reaction between one species adsorbed and one in the gas phase for *n*-propyl alcohol without postulating that the adsorption behavior of alcohol in the presence of acid be the opposite of the adsorption behavior of pure alcohol. Acceptance of this mechanism presents severe problems in proposing a reasonable activated species; however, product analyses and isotopic studies required to specify an activated species were not per-

Results of many adsorption studies (*8*), (*11*), (*19*), (*20*), emphasize the influence of hydroxyl concentration on adsorption of polar molecules on silica gel. Finally, Filimonov (*21*) observed that surface hydroxyl groups can act as adsorption sites for molecules having electron donor atoms. Therefore, it was reasonable to assume that the sites for surface reaction are hydroxyl groups and that water increases the rate by increasing the hydroxyl group concentration. If this were true, the concentration of active sites would be

$$L = \phi[(L'/\phi) + f(p_w)], \qquad (9)$$

where ϕ = concentration of gross adsorption sites; $f(p_w)$ = an adsorption isotherm for the adsorption of water on silica gel. The term L'/ϕ is justified by the fact that some hydroxyl groups remain on the surface even after harsh dehydration treatment (*22*).
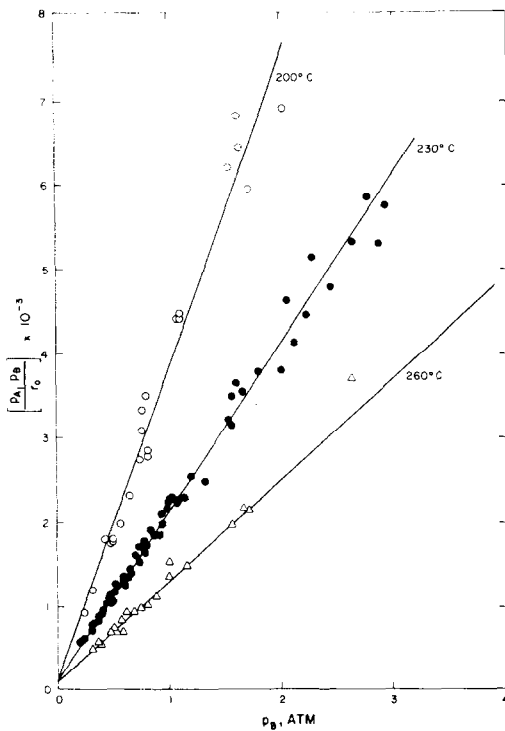
Using constants determined from the

FIG. 11. Correlation of reaction rate according to Eq. 7.

initial rate data at zero water concentration, attempts were made to fit various isotherms to the rate data for higher water concentrations, such as shown in Fig. 4. The best fit was obtained by considering that water is adsorbed in two layers and that adsorption on each layer follows a Langmuir isotherm. The first adsorbed layer produces active sites and water is adsorbed on the second layer in competition with the reactants. The resulting form of the complete rate expression is

$$r = \frac{Ek_s K_B \phi \left[\dfrac{L'}{\phi} + \dfrac{K_w p_w}{1 + K_w p_w} \right] p_A p_B}{1 + K_B p_B + K'_w p_w}, \quad (10)$$

where E = catalyst effectiveness factor; k_s = surface reaction rate constant; K_w, K'_w = equilibrium adsorption constants for water for the first and second layers adsorbed, respectively.

The constants determined from the initial rates were treated as first approximations. Final values for the constants of Equation (10) at each experimental temperature were determined by analyzing each set of isothermal data using a nonlinear correlation procedure, the "Princeton–IBM Non-Linear Estimation Program." Each data point was treated as an integral reactor datum and the parameters of the rate expression were determined to minimize the sum-of-squares of errors in

$$\frac{W}{F} = \int_{x_1}^{x_2} \frac{dx}{r}. \quad (11)$$

Values of the constants determined from the data are given in Table 1 and are shown in Fig. 12 as Arhennius relations. The determined rate expression was then used to generate the calculated curves shown in Figs. 3–11.

DISCUSSION

Since the rate equation correlates the data successfully, interpretation of the results of the correlation may provide an understanding of the basic nature of the reaction, if the choice of mechanism is correct. Adsorption behavior assumed for each component involved does not represent true behavior; however, thermodynamic quantities associated with the assumed adsorption behavior are consistent with the assumption of molecular adsorption, i.e., enthalpies are exothermic and entropy changes are negative.

Independent studies (7, 9, 10) have shown that silica gel can adsorb two layers of

TABLE 1
CONSTANTS FOR EQ. (10)

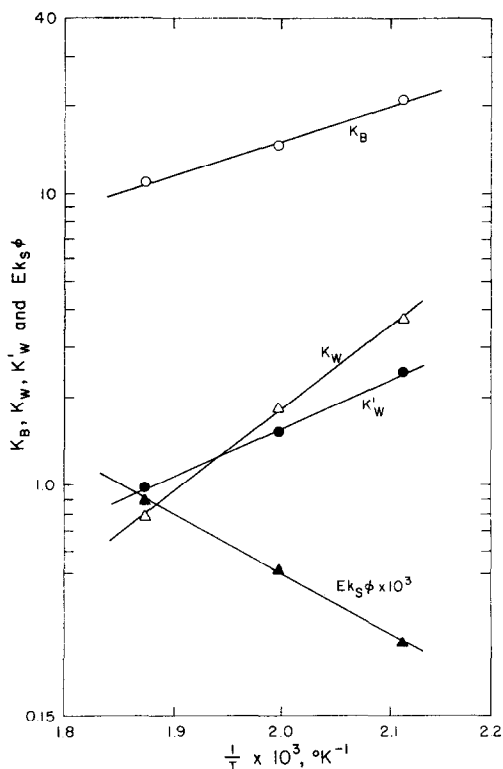| T	L'/ϕ	$Ek_s K_B \phi$	K_w	K'_w	K_B	$Ek_s \phi$ ($\times 10^3$)
200	0.2533	0.0225	3.717	2.447	21.05	1.069
230	0.2533	0.0293	1.849	1.530	14.82	1.977
260	0.2533	0.0360	0.7813	0.9883	10.93	3.294

FIG. 12. Arhennius relations for constants for Eq. 10.

water; the first layer is strongly chemisorbed with strong surface bonding, and the second layer is less strongly adsorbed and retains much of the character of free water. The heat of adsorption has been shown to decrease linearly from —28 to —16 kcal/g mole for the first layer and from —16 to —10 kcal/g mole for the second layer (10). By comparison, the heats of adsorption derived from the kinetics data are —12.9 kcal/g mole and —5.3 kcal/g mole for the first and second layers, respectively. The quantitative agreement with the adsorption results is poor, but the results are consistent. As further support, the entropies for adsorption derived from the kinetic data are —19.6 cal/g mole°K and —9.7 cal/g mole°K for the first and second layers, respectively. This indicates that the first layer is much more strongly adsorbed than the second.

The enthalpy and entropy of adsorption of n-propyl alcohol derived from the data are —7.6 kcal/g mole and —9.7 cal/g mole°K. Since the enthalpy and entropy of condensation of n-propyl at 230°C are —4.5 kcal/g mole and —9.0 cal/g mole°K, it appears that it is weakly adsorbed on the surface, retaining much of the character of liquid alcohol. Even more striking is the fact that entropies of adsorption for water and n-propyl alcohol are the same, indicating that the same type of bond may be formed in the two cases.

Adsorption enthalpies and entropies derived from Hinshelwood type correlations seldom agree, of course, with direct measurements, and little confidence can be placed in the numerical values. However, the results are thermodynamically consistent for the proposed mechanism. Therefore, the derived thermodynamic quantities serve as additional support for the proposed mechanism.

Acetic acid should also be adsorbed by silica gel. However, it is known that adsorption of alcohol increases as the chain length increases, and steric hindrance by longer chain alcohols may effectively prevent the adsorption of acid.

From the above comparison with adsorption data, it is reasonable to conclude that esterification in this case takes place by reaction of adsorbed n-propyl alcohol with acetic acid from the gas phase. Also, water apparently promotes the reaction by increasing the surface concentration of hydroxyl groups, which are most probably the active sites for the reaction. This model fits high conversion data, also. It was used successfully to recorrelate the integral reactor results of Heath (4) for the n-propyl alcohol and acetic acid reaction. This model reproduced Heath's results as well as the model he proposed, as can be seen from Fig. 13. Since the present model is less complex, requires fewer constants, and is apparently more consistent with adsorption studies than Heath's, it is preferred.

The alcohol structure has a profound effect on esterification. Only normal alcohols can be esterified, and the rate of esterification drops sharply with increasing chain length. The surface reaction is the apparent
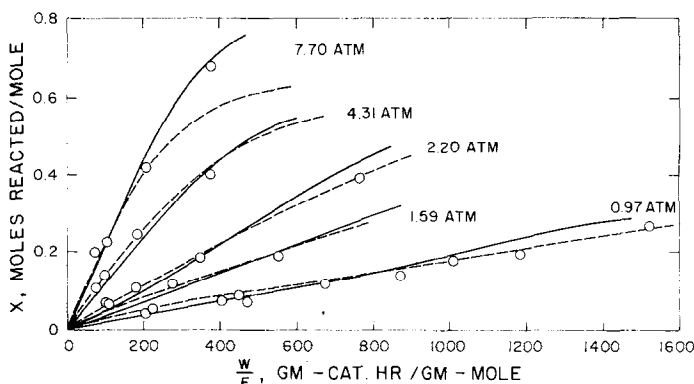
FIG. 13. Recorrelation of Heath's data (4) for equimolar reactant feed at 230°C and various total pressures: - - - Heath's correlation; — recorrelation, this work.

rate controlling step for esterification of methanol (1), ethanol (3), and n-propyl alcohol; but the mechanism changes from a dual site mechanism for methanol to a single site mechanism for n-propyl alcohol. One interpretation that explains this change is that steric hindrance by n-propyl alcohol prevents adsorption of acid, which changes the apparent mechanism and lowers the reaction rate.

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