

## n-Propanol-Acetic Acid Esterification Catalyzed by Silica Gel

RUSSELL MAATMAN, PETER MAHAFFY AND  
RAYMOND MELLEMA

*Department of Chemistry, Dordt College, Sioux Center, Iowa 51250*

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The vapor phase *n*-propanol-acetic acid esterification catalyzed by silica gel was studied in a flow reactor between 170 and 230°C. Catalyst activities were determined in a system in which the total pressure was always 1 atm and the partial pressures of the reactants were varied with and without the addition of nitrogen, an inert diluent. After the steady state activities are corrected for an unexpected increase in activity associated with the introduction of nitrogen, there is satisfactory agreement with the results reported by Fricke and Altpeter, who did not use a diluent. Six more or less conventional mechanisms are rejected because the corresponding rate laws predict the opposite of what was observed when nitrogen was introduced. Another mechanism, a more complicated one postulated by Fricke and Altpeter, takes into account both the production and the poisoning of sites by the water which is produced in the reaction, and can perhaps account for the nitrogen effect. The number of active sites per unit area, the site density, is calculated for the Fricke-Altpeter catalyst. The calculated site density is shown to be consistent with the mechanism they postulate.

	NOTATION		
A,B	Alcohol or acid reactant	$R$	Gas constant
C	Reaction intermediate	$S_Y$	Concentration of "Y" sites
D,G	Reaction products	$T$	Temperature, degrees K
$E$	Catalyst effectiveness factor	$W$	Weight of catalyst, g
$F$	Flow rate, moles reactant hr <sup>-1</sup>	X, Y	Adsorption sites
$I$	Inhibitor	A1, B2	Reactants adsorbed on different sets of sites
$I_x, I_y,$ and $I_z$	Moments of inertia of the acetic acid molecule	AX(a), BX(a), AY(a), CY(a)	Adsorption complexes
$K$	Equilibrium constant for adsorption of gas molecule	$\Delta H_a$	Heat of activation for the $k_s$ step
$K'$	$k_1k_3k_5/k_2k_4k_6$	$c_s$	Concentration of active sites, sites cm <sup>-2</sup>
$K_w$	Equilibrium constant for the adsorption of water in the first layer	$h$	Planck constant
$K'_w$	Equilibrium constant for the adsorption of water in the second layer	$k$	Boltzmann constant
$L'$	Concentration of active hydroxyl groups after harsh dehydration treatment, moles g <sup>-1</sup>	$k'_2$	Rate constant for bimolecular reaction
		$k_s$	Surface rate constant in Fricke-Altpeter mechanism
		$m$	Mass of acetic acid molecule
		$p$	Partial pressure
		$w$	Water
		$\phi$	Maximum concentration of active sites, moles g <sup>-1</sup>

$\sigma, \sigma^\ddagger$  Statistical factors depending upon the orientation of adsorbed acetic acid and activated complex, respectively

#### INTRODUCTION

Vapor phase esterification is catalyzed by silica gel. We began work with this reaction because of our interest in determining the concentration of active sites on the surfaces of solid catalysts, their site densities, in various heterogeneous catalytic systems. Our earlier experimental work on the site density question was limited to unimolecular decomposition [cumene cracking (1, 2), *n*-butanol dehydration (3), and cyclohexane dehydrogenation (4, 5)] and it seemed of interest to extend the study to the more complicated esterification reaction. We have already described our methods in determining site density and reviewed the site density question (6, 7).

This is a report of our study of the reaction between *n*-propyl alcohol and acetic acid catalyzed by silica gel in a flow reactor. Fricke and Altpeter (8) studied this reaction extensively and frequent reference to their work will be made. Some of our results, particularly the effect we found as a consequence of using nitrogen as an inert diluent, seem at first to be quite different from theirs. The apparent differences between their results and ours can be explained, and the explanation may aid in elucidating the reaction. We have been able to make conclusions concerning site density. Our conclusions with respect to site density and the nitrogen effect tend to confirm the model of the reaction presented by Fricke and Altpeter.

#### EXPERIMENTAL METHODS

The silica gel (6-12 mesh; surface area, 616 m<sup>2</sup> g<sup>-1</sup> (BET); pore volume (water uptake), 0.41 ml g<sup>-1</sup>) and its preparation, insuring a clean surface (9), was described earlier (10). The gel used was prepared at the same time as the gel used for the project described in Ref. (10). The two batches used in the present project, 1 and 2, differed only in that the second batch had a slightly greater contact with water vapor during

storage. Acetic acid and *n*-propyl alcohol were both reagent grade. The water initially present in the acetic acid (~1 mole%) was not removed, while the alcohol was dried over 3A Linde molecular sieve.

The flow catalytic reactor, with a Sage pump for liquid feed, an inlet for introduction of nitrogen into the vapor feed stream, and provisions for direct introduction of product into a gas chromatograph, was described in connection with a study of cyclohexane dehydrogenation (4). Special care was taken to introduce the hygroscopic feed into the pump-driven syringe without contacting air.

In a typical run 2.000 g of silica gel was placed on a flat tray which was then placed in the horizontal reactor. Before the catalyst contacted reactant, nitrogen (purified over hot copper and dried) flowed over the catalyst for 30 min at 300°C. During this pretreatment a few microliters of the feed in the syringe were removed and injected directly into the gas chromatograph, bypassing the reactor, and analyzed for water. At the end of the pretreatment the reactor and the preheater attained the desired temperature in about 20 min. The liquid reaction mixture was fed at the rate of  $1.81 \times 10^{-3}$  ml liquid/sec. The liquid boiled in the preheater and in some runs the vapor was mixed with a nitrogen stream before passing over the catalyst to reduce the partial pressure of the reactants. The desired dilution was achieved by adjusting the nitrogen flow rate; the liquid flow rate was never changed. The partial pressure of the reactants was determined from either the gas chromatogram or the flow rates; the values agreed. The effluent gas was normally sampled at 45 min and at 30 min intervals thereafter and analyzed for water, using a column of 10% ethofat on 60-80 Chrome T held at 122°C. At the end of the run the reactor was flushed with nitrogen for at least 1 hr at 430°C. The contents of the syringe were once again sampled and analyzed for water, by-passing the reactor by direct injection of a few microliters of liquid into the chromatograph. The average of the before-and-after water analyses was taken as the amount of water in the reactant feed stream. Percent-

age conversion and activity were calculated by subtracting out the initial amount of water from the water found in the product. It was not possible to analyze the product for ester on the chromatograph because of peak overlap, but under favorable conditions positive qualitative identification of the ester was made on the chromatograph.

In all runs the total pressure was atmospheric, taken as 1 atm for our purposes. Except where noted, 2,000 g of 6-12 mesh was used, the catalyst stream was undiluted, and the reactor temperature was 230°C.

### RESULTS

With 2,000 g of catalyst steady state conversions for equimolar mixtures at 230°C were  $\sim 2.5$  mole% with respect to *n*-propanol. Catalyst activity dropped significantly as a run proceeded. Activity as a function of time in a particularly long run, carried out to ascertain when a steady state is attained, is given in Fig. 1. Steady state activities are taken to be the average of the results obtained after about 160 min. The scatter in the steady state part of the activity vs time plots of the runs indicated the average error to be about  $\pm 5\%$ .

In comparing 2,000 g samples of 6-12 and 100-200 mesh catalyst in several runs the steady state values of the activities apparently belonged to the same population. It was therefore concluded that particle size is not a factor. The 6-12 mesh cata-

lyst was used in the remainder of the work. Likewise, there was no systematic variation in activity when the catalyst weight was varied from 0.5 to 3.0 g and therefore it was concluded that activities based on runs in which 2,000 g catalyst are used are valid.

Silica gel catalyzes the dehydration of alcohols at sufficiently high temperatures. At 230°C we found less water produced using a reaction mixture of 75 mole% *n*-propanol and 25 mole% acid (0.16 mole% water) than with pure *n*-propanol (0.47 mole% water). We do not understand why there is less water produced when some acetic acid is present, but it does seem safe to assume that alcohol dehydration does not complicate the results when the acid concentration is at least 25 mole%. Almost all of our results were in the range in which the acid concentration in the feed was at least 25 mole% and we did not work above 230°C.

Activity as a function of reactant mixture concentration, with no inert diluent, at a total pressure of 1 atm, is given in Fig. 2. An Arrhenius plot of the activities for equimolar reactant mixtures is given in Fig. 3. The apparent activation energy is  $\sim 11$  kcal mole<sup>-1</sup> for Catalyst 1 and  $\sim 9$  kcal mole<sup>-1</sup> for Catalyst 2.

The concentration of one reactant could be varied while the other was held constant by diluting the reactant stream with nitrogen. In Fig. 4 activity is given as a function of alcohol concentration with the

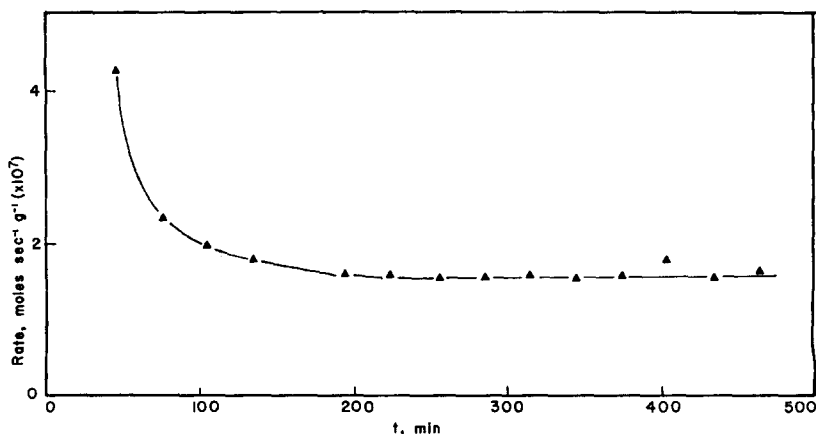


Fig. 1. Activity at 230°C of Catalyst 1 as a function of time using an equimolar reactant mixture.

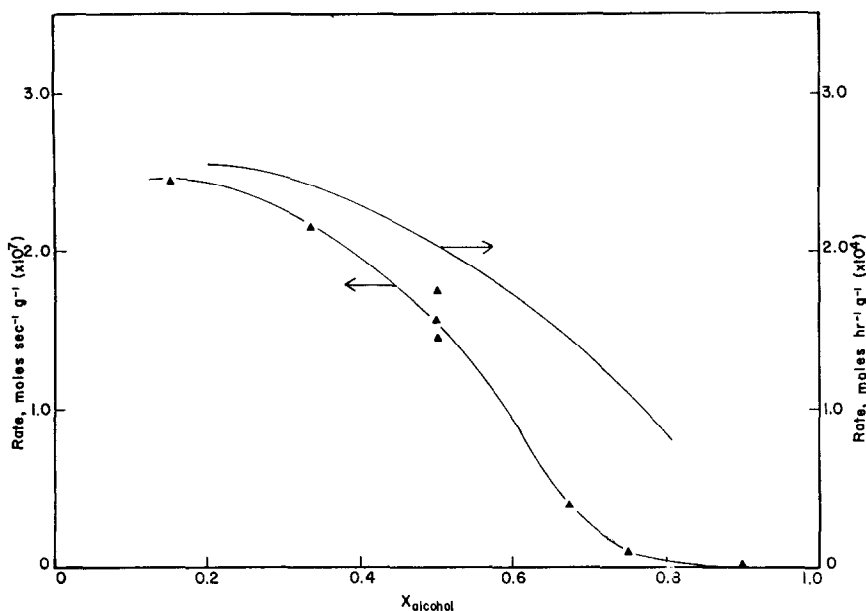


FIG. 2. Activity of Catalyst 1 as a function of mole fraction of alcohol; total pressure, 1 atm, with no nitrogen dilution. Upper curve, results of Fricke and Altpeter.

partial pressure of the acid held at 0.5 atm. Figure 5 shows activities when the acid concentration varies with the alcohol partial pressure held at 0.5 atm. The experimental results of Figs. 4 and 5 cannot be analyzed until it is known how nitrogen effects activity. In Fig. 6 the nitrogen effect is shown.

DISCUSSION

Although the results of the present work seem at first to contradict some of the results of Fricke and Altpeter (8), there are complicating factors in making the comparison. In our experiments, unlike theirs, the partial pressure of the reactants was

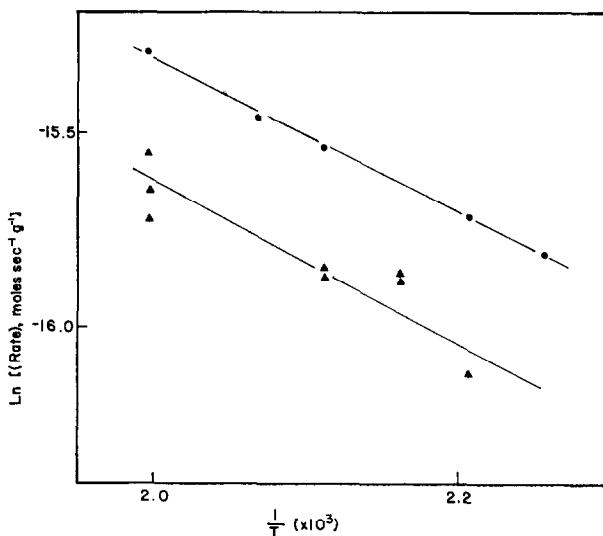


FIG. 3. Arrhenius plots between 170 and 230°C, using an equimolar reactant mixture; (▲) Catalyst 1; (●) Catalyst 2.

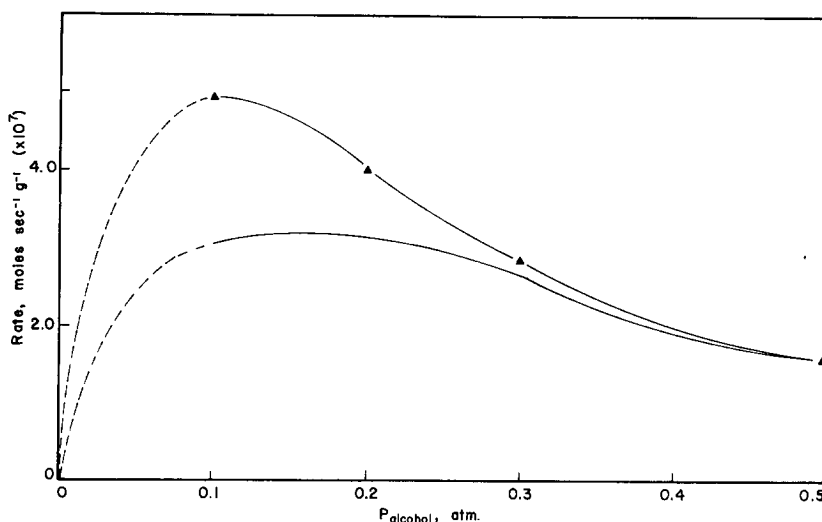


Fig. 4. Activity of Catalyst 1 at 230°C as a function of alcohol partial pressure with the partial pressure of acid at 0.5 atm; total pressure, 1 atm, with nitrogen used as diluent. The lower curve is the corrected curve; see text.

reduced by introducing nitrogen and it is precisely when nitrogen was introduced that the more unexpected results were obtained. For example, in Fig. 6 it is shown that the lower the partial pressure of the reactants in an equimolar mixture, the *greater* is the activity of the catalyst. Any elucidation of the mechanism must account for this most unusual observation.

We now examine various mechanisms, in each case assuming a rate limiting step. The corresponding rate laws are given and the mechanism is rejected wherever the rate law cannot account for our results. We find it convenient to ask first for each rate law

whether or not it can account for the rate increase with a decrease in reactant partial pressure shown in Fig. 6. The first five cases can be considered together. Their rate laws are derived in Ref. (11).

**Case 1. Reaction between two adsorbed molecules on the same set of sites.** The rate is then given by

$$\text{Rate} = \frac{k'_2 K_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2} \quad (1)$$

**Case 2. Reaction between molecules adsorbed on different sets of sites.**

$$\text{Rate} = \frac{k'_2 K_{A1} K_{B2} p_A p_B}{(1 + K_{A1} p_A)(1 + K_{B2} p_B)} \quad (2)$$

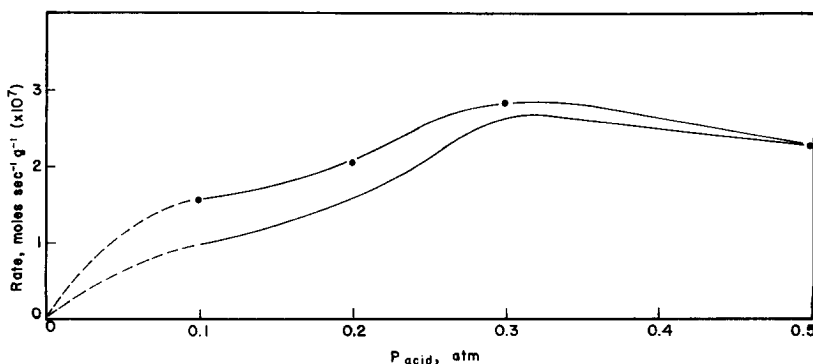


Fig. 5. Activity of Catalyst 2 at 230°C as a function of acid partial pressure with the partial pressure of alcohol at 0.5 atm; similar to Fig. 4.

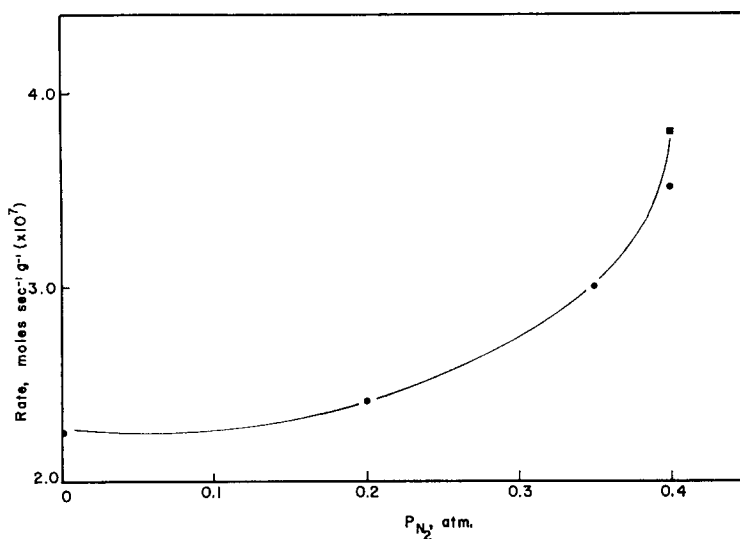


FIG. 6. Activity of Catalyst 2, using an equimolar reactant mixture, as a function of nitrogen partial pressure, with a total pressure of 1 atm; (●) partial pressure of nitrogen varied within one run; (■) value for a second run.

**Case 3. Reaction between an adsorbed molecule and a gas molecule.**

$$\text{Rate} = \frac{k'_2 K_A p_A p_B}{1 + K_A p_A + K_B p_B} \quad (3)$$

An equation of this form can be used regardless of whether the alcohol or the acid is the adsorbed molecule.

**Case 4. Reaction between two adsorbed molecules on the same set of sites, but inhibited by an adsorption poison introduced with a reactant.** If there were irreversible poisoning, the activity would drop to zero, contrary to what is shown in Fig. 1. If the poisoning is reversible, the rate is given by

$$\text{Rate} = \frac{k'_2 K_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B + K_I p_I)^2} \quad (4)$$

**Case 5. Reaction between an adsorbed molecule and a gas molecule, inhibited by an adsorption poison introduced with a reactant.** Assuming again that such poisoning must be reversible, the rate is given by

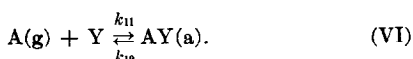
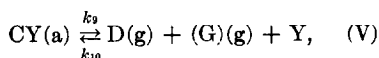
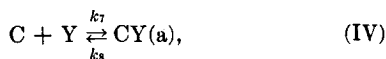
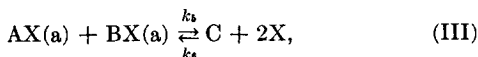
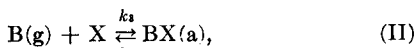
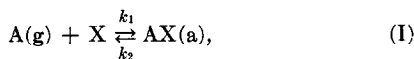
$$\text{Rate} = \frac{k'_2 K_A K_B p_A p_B}{1 + K_A p_A + K_B p_B + K_I p_I} \quad (5)$$

Although the reaction is between a gas molecule and an adsorbed molecule, it is still possible that both molecules adsorb. Therefore, equilibrium constants for both

molecules adsorbing on the active sites are included.

Each of the five postulated mechanisms can be ruled out for the same reason. Inspection of Eqs. (1)–(5) indicates that a simultaneous decrease in  $p_A$  and  $p_B$  causes the numerator of the right side to decrease more than the denominator because of the constant term in the denominator if for no other reason. Therefore, the rate decreases with dilution of reactants, such as the dilution we carried out with nitrogen, regardless of the values of the pressures and the constants. Such a behavior upon dilution is contrary to the results shown in Fig. 6. Questions concerning how much of the surface is covered or whether one molecule adsorbs better than the other are not relevant.

**Case 6. Reaction between two adsorbed molecules forming an intermediate which decomposes on a different kind of site.** Analysis of the first five cases suggests that a simple model cannot account for the results. One might expect intuitively, however, that the formation of an intermediate which decomposes on sites *on which there is adsorption competition with a reactant* could account for the peculiar results of Fig. 6. Therefore, we analyzed this model. The reaction scheme is



From Reaction (V) we have

$$\text{Rate} = k_9[CY]. \quad (13)$$

Combining Eqs. (6), (8), (10), (12), and (13),

$$\begin{aligned} \text{Rate} &= k_9 S_Y \frac{p_A p_B}{\frac{k_8 + k_9}{k_7 K'} + \frac{k_8 + k_9}{k_7 K'} \left( \frac{k_{11}}{k_{12}} \right) p_A + p_A p_B}. \end{aligned} \quad (14)$$

No assumption is made concerning whether or not the intermediate, C, enters the gas phase. D and G are the products, water and ester. In what follows B could just as well be postulated to be the competitor. We assume that Reactions (I)–(III) are in fast equilibrium, that Reaction (IV) can be neglected in formulating an approximate equilibrium constant for the first three steps, and that conversion is low enough to make it possible to neglect the  $k_{10}$  step.

Then

$$p_C = K' p_A p_B. \quad (6)$$

Since the  $k_{10}$  step is neglected,

$$\begin{aligned} \frac{d[Y]}{dt} &= -k_7 p_C [Y] + k_8 [CY] + k_9 [CY] \\ &\quad - k_{11} p_A [Y] + k_{12} [AY]. \end{aligned} \quad (7)$$

In the steady state

$$[Y] = S_Y - [AY] - [CY] \quad (8)$$

and

$$\frac{d[Y]}{dt} = 0. \quad (9)$$

Equation (7) then becomes

$$[CY] = \frac{k_7 p_C [Y] + k_{11} p_A [Y] - k_{12} [AY]}{k_8 + k_9}. \quad (10)$$

In the steady state we have from reaction (VI),

$$[AY] = \frac{k_{11} p_A \{S_Y - [AY] - [CY]\}}{k_{12}}. \quad (11)$$

Then it follows from Eq. (11) that

$$[AY] = \frac{k_{11} p_A S_Y - k_{11} p_A [CY]}{k_{12} + k_{11} p_A}. \quad (12)$$

If  $p_A$  and  $p_B$  are decreased simultaneously by the same factor, the rate will, as seen by inspection of Eq. (14), always decrease.

We have examined other mechanisms, and except for the mechanism proposed by Fricke and Altpeter, which we discuss below, the same negative results as obtained with Cases I–VI were obtained.

We now digress from the discussion of the mechanism to discuss certain results and conclusions of Fricke and Altpeter. First, our experimental results must be compared with theirs. In our system, the steady state was achieved in  $\sim 2.5$  hr (see Fig. 1) whereas in theirs it took about 20 hr to achieve the steady state. However, they present data showing that the partial pressure of water in the system and the number of active sites are related. With their much larger catalyst bed (a 6 in. bed vs 2.000 g in our system), they made considerably more water initially. It is therefore to be expected that the steady state would be achieved much more slowly in their system than in ours. The apparent activation energies we obtained using an equimolar mixture between 170 and 230°C, 9–11 kcal mole<sup>-1</sup>, are in good agreement with the value of  $\sim 9$  kcal mole<sup>-1</sup> we calculate for a similar system of Fricke and Altpeter between 200 and 260°C.

We show activity as a function of gas phase alcohol concentration, with enough acetic acid to make a total pressure of 1 atm, in Fig. 2. For comparison, the results obtained by Fricke and Altpeter in a similar system are shown. The shapes of the curves are remarkably similar. Our activities were generally greater than theirs, probably because the surface area of our

catalyst (616 m<sup>2</sup> g<sup>-1</sup>) was significantly greater than the commercial catalyst (surface area not given) which they used. Since the product water itself affects the activity, the agreement between the two curves is particularly good.

In an attempt to understand the effect of dilution with nitrogen, we have attempted to correct the experimental curves of Figs. 4 and 5. Thus, as an approximation,

tion of nitrogen dilution. Fricke and Altpeter postulate a Rideal-Eley mechanism, with gaseous acetic acid monomer reacting with adsorbed *n*-propanol. Water increases the number of sites which are initially present by forming surface silanol groups. However, water also adsorbs in the second layer, competing with reactant and thereby acting as a poison. They show that the rate law for such a mechanism is

$$\text{Rate} = \frac{Ek_s K_B \phi \{ (L'/\bar{\phi}) + [K_w p_w / (1 + K_w p_w)] \} p_A p_B}{1 + K_B p_B + K'_w p_w} \quad (15)$$

it is assumed that the "true" activity in Fig. 6 is a constant, the value obtained when no nitrogen was present. The curves then calculated are the lower curves on Figs. 4 and 5. Almost all of the data of Fricke and Altpeter are for pressures higher than the range of Figs. 4 and 5, but their results do suggest that activity increases with either increasing acid or alcohol pressure, with a more rapid increase in the acid case. Since our method of correction is crude and our results also suggest a more rapid increase in activity with increasing pressure of acid than with increasing pressure of alcohol, we conclude that the results of Figs. 4 and 5 do not conflict with those of Fricke and Altpeter. (They also found that activity decreases linearly with total reactant pressure below 1 atm. If such an effect did not exist in our system, then to compare with their results, our activities for runs below 1 atm should be proportionately decreased. If this operation is carried out, our activities are even more easily seen to increase with either acid or alcohol pressure.)

In a further attempt to understand the experimental results and to answer certain basic questions, especially concerning site density, we now examine the mechanism and rate law postulated by Fricke and Altpeter. Later we shall return to the ques-

where A = acetic acid and B = *n*-propanol, and that this rate law is consistent with their data.

We have shown (6, 7) that in a surprising number of catalytic systems that the site density of the catalyst is at least a few orders of magnitude less than what has usually been supposed. But often when mechanisms are postulated it is assumed that the site density of the catalyst is high, i.e., that the surface is within one or two orders of magnitude of being completely covered. Obviously, it is desirable to ascertain the site density whenever a mechanism is postulated. Fricke and Altpeter assumed a high site density in the formulation of their mechanism; they identified the active sites with the surface silanol groups and they related their catalytic results to certain gross properties of those groups. If the site density is very low, there is then no necessary relation between the gross properties of the silanol groups and the activity of the catalyst. It is therefore of interest to calculate from their data an approximate value of the site density of their catalyst. The method we use utilizes transition state theory.

The rate of the surface reaction is given by  $k_s \phi$  of Eq. (15). Fricke and Altpeter report values of  $E k_s \phi$ ; assuming  $E$  is the order of unity, it can readily be shown that

$$k_s \phi = \frac{3.6 c_s (kT/h) (1/\sigma^\ddagger) e^{-(\Delta H_s/RT)}}{RT \left[ \frac{(2\pi m kT)^{3/2}}{h^3} \right] \left[ \frac{8\pi^2 (8\pi^3 I_x I_y I_z)^{1/2} (kT)^{3/2}}{\sigma h^3} \right]} \quad (16)$$



The first bracketed term in the denominator on the right side of the equation is the translational partition function of the monomeric acetic acid gas molecule and the second bracketed term is its rotational partition function. It is assumed in deriving Eq. (16) that the molecule loses its transitional and rotational degrees of freedom as it forms the activated complex. If it can be assumed that the number of sites did not change rapidly with temperature at 230°C in their experiments, an Arrhenius plot of the  $E_{k_s}\phi$  values which Fricke and Altpeter report gives  $\Delta H_a = 9.44$  kcal mole<sup>-1</sup>. Then, if  $\sigma$  and  $\sigma^\ddagger$  cancel and the values for the moments of inertia  $I_x$ ,  $I_y$ , and  $I_z$  given by Loubser (12) are used, Eq. (16) gives for  $c_s$  a value of  $2.3 \times 10^{21}$  sites g<sup>-1</sup>. (The slightly different moments given by Tabor (13) give for  $c_s$  a value of  $2.1 \times 10^{21}$  sites g<sup>-1</sup>.) If the surface area of the catalyst can be assumed to be between 100 and 500 m<sup>2</sup> g<sup>-1</sup>, a value of  $10^{14}$ – $10^{15}$  sites cm<sup>-2</sup> is obtained. Thus, the surface coverage is high, consistent with the mechanism which Fricke and Altpeter suggest, and their identification of properties of the active sites with gross properties of the surface seems justified. West, Haller and Burwell (14) have suggested that reactions catalyzed by silica gel will turn out in most cases to depend upon impurities; apparently the esterification reaction is not such a reaction.

We now look again at the question of the mechanism of the reaction. Every mechanism we have discussed, except for the Fricke–Altpeter mechanism, we rejected because the rate laws do not predict a rate increase when the reactant mixture is diluted with nitrogen. Is it possible that the Fricke–Altpeter mechanism, which takes into account the dependence of site density on the partial pressure of water, is consistent with the nitrogen dilution effect?

We are not certain of the answer to that question. The following analysis may, however, show that the Fricke–Altpeter mechanism can account for the nitrogen effect in our experiments. With both methods of reducing the partial pressure of reactant the amount of reactant which passes over the catalyst bed per unit time does not

change as the partial pressure of the reactant mixture is reduced. Therefore, the reactant residence time decreases as its partial pressure decreases. Likewise, water which is produced and water which is in the feed stream also have a decreased residence time. Fricke and Altpeter postulate that second-layer water acts as an adsorption poison as it competes with reactant. Perhaps with the right set of conditions a decreased residence time for water—even though its partial pressure does not decrease any more than the partial pressure of reactant—would actually be the cause of an increase in activity because of a decrease in its ability to adsorb competitively. Further, if there were such an effect it would be more likely to occur in a series of experiments in which the longest residence time is short, than in a series in which all residence times are long. Our flow rate was indeed about five times larger than the largest flow rate which Fricke and Altpeter report. (Their smallest  $W/F$  value was  $\sim 100$  g cat hr/mole reactant; whenever we used 2.000 g catalyst, our  $W/F$  value was  $\sim 20$  g cat hr/mole reactant.) If this explanation accounts for the increase in activity when nitrogen was used to dilute, then the effect is not so much a nitrogen dilution effect as a residence time effect. It may also be possible that the inert nitrogen molecules help sweep away competitor water molecules. In any case, it seems that the complex mechanism described by Fricke and Altpeter is more likely to be the mechanism which can be used to explain the nitrogen dilution effect than any of the conventional mechanisms.

#### ACKNOWLEDGMENT

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#### REFERENCES

1. HORTON, W. B., AND MAATMAN, R. W., *J. Catal.* **3**, 113 (1964).
2. MAATMAN, R. W., LEENSTRA, D. L., LEENSTRA, A., BLANKESPOOR, R. L., AND RUBINGH, D. N., *J. Catal.* **7**, 1 (1967).

3. MAATMAN, R. W., AND VANDE GRIEND, L., *J. Catal.* **20**, 238 (1971).
4. MAATMAN, R. W., MAHAFFY, P., HOEKSTRA, P., AND ADDINK, C., *J. Catal.* **23**, 105 (1971).
5. MAATMAN, R., RIBBENS, W., AND VONK, B., *J. Catal.* **31**, 384 (1973).
6. MAATMAN, R. W., *J. Catal.* **19**, 64 (1970).
7. MAATMAN, R. W., *Catal. Rev.* **8**, 1 (1973).
8. FRICKE, A. L., AND ALTPETER, R. J., *J. Catal.* **25**, 33 (1972).
9. AHRLAND, S., GRENTHE, I., AND NOREN, B., *Acta Chem. Scand.* **14**, 1059 (1960).
10. MAATMAN, R., POEL, M., AND MAHAFFY, P., *J. Colloid Interface Sci.*, in press.
11. LAIDLER, K. J., in "Catalysis" (P. H. Emmett, Ed.), Vol. 1, p. 119. Reinhold, New York, 1954.
12. LOUBSER, J. H. N., *J. Chem. Phys.* **21**, 2231 (1953).
13. TABOR, W. J., *J. Chem. Phys.* **27**, 974 (1957).
14. WEST, P. B., HALLER, G. L., AND BURWELL, R. L., *J. Catal.* **29**, 486 (1973).