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The Microcatalytic Technique Applied to a Zero Order Reaction

The Dehydration of 2-Butanol over Hydroxyapatite Catalysts

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A comparison has been made between microcatalytic and steady state flow reactor data for the dehydration of 2-butanol over a series of hydroxyapatite catalysts. The conventional steady state flow experiments revealed that the reaction was zero order in 2-butanol, but weakly inhibited by the product water. Unlike first order reactions, where identical results are derived from the two techniques, the microcatalytic results were not identical with those from the steady state experiments. Instead, they indicated that the surface-adsorbed species were not in equilibrium with the gas phase, and that products continued to desorb long after the gas pulse had passed. Thus, plots of conversion vs. reciprocal flow rate did not extrapolate to zero at infinite flow rate. Instead, the finite conversion intercept was a measure of the "site monolayer" from which products desorbed very slowly. This fact was used to count the active sites for dehydration. Together, the two methods yield complementary information, not obtainable from one method alone. The design of a versatile, high-temperature, microcatalytic reactor is given.

INTRODUCTION

The microcatalytic technique has been applied in a variety of ways (*1*) during the last decade. Although it has been used extensively in quantitative work, it has been obvious to us for some time that insufficient attention has been paid to the kinetic interpretation of the results. Bassett and Habgood (*2*) demonstrated that identical results should be obtained from microcatalytic and steady state studies for first order reactions, provided that the adsorption isotherm is linear and that the retention time of the slug can be equated to the volume the adsorbed gas would occupy at the ambient conditions, if it were not adsorbed. However, these assumptions are not always valid. More often than not in real first order systems, the adsorbed amount does not fall to zero at zero pressure; equilibrium cannot be maintained below a critical value of the pressure which, in turn, may be a function of temperature. Advantage has been taken of this situation in studies of the nature and reactivity of the chemisorbed substrate (*1*d,e).The conventional explanation for this behavior is that the heat of adsorption rises steeply as the coverage falls. This may lead to a failure of the second assumption, i.e., that the retention time *of that portion of the gas which reacts* decreases with temperature. The low values of the activation energy for ethylene hydrogenation reported by Hall and Emmett (*1*b) may have been due to this factor. Nevertheless, good first order kinetics were obtained for the isomerization of cyclopropane over a Na^+ zeolite (*2*) and for the dehydrogenation of cyclohexane over a number of catalysts (*3*). Schwab and Watson (*4*) compared results from microcatalytic and steady state flow reactors for the dehydrogenation of methanol over Ag (a first order reaction) and found good agreement could be obtained, but low values of the activation energy resulted when rate constants were based on disappearance of reactant rather than appearance of product.

Recently, Gaziev and co-workers (*3*) treated the pulse (microcatalytic) technique mathematically; again, the authors confined themselves to the case of ideal linear chromatography and derived equations for a square and a triangular pulse for zero, first, and second order reactions. They found, in agreement with Habgood (*2*), that only with first order reactions was the rate constant independent of pulse shape. Merrill (*5*) has reached similar conclusions.

In zero order reactions, desorption of products may be rate-controlling. Thus, products and unconverted reactant cannot maintain equilibrium with the moving pulse and considerable tailing should result, leading to a very asymmetric chromatographic peak. In a practical way, this can become so severe that it is necessary to insert a cold trap between the catalyst and the chromatographic column and to collect the products for a period of time before flashing them onto the chromatographic column. Otherwise, poor resolution of peaks and poor mass balances result. Inherently, this would not seem to be a good way to study catalytic kinetics. However, with proper utilization, the microcatalytic technique affords a way to obtain additional insight into the processes which are occurring. This insight should supplement, not replace, that obtained from steady state kinetics where, in a similar fashion, product molecules may desorb "miles upstream" from the volume increment from which the parent molecules were adsorbed. The present work presents an experimental comparison of some microcatalytic results with steady state kinetics for a zero order reaction, viz., the dehydration of 2-butanol over hydroxyapatite catalysts.

EXPERIMENTAL

Apparatus. At room temperature, the vapor pressure of 2-butanol was inconveniently low; therefore, an apparatus was constructed which could function either as a microcatalytic or as a conventional steady state flow reactor, and the entire apparatus was thermostated at about 100°. The apparatus was similar in function to the glass system described by Hall *et al.* (*1c*), but was constructed almost completely of stainless steel and aluminum. The reactant feed gas mixture was supplied in one of two ways: from a conventional gas saturator in a thermostated bath, or from the mixing tank described below.

The flow sheet for the apparatus is shown in Fig. 1. The mixture (purified He and alcohol) was supplied from either of the two feed systems to a system of multiport spindle valves, A and B (six-port, two-

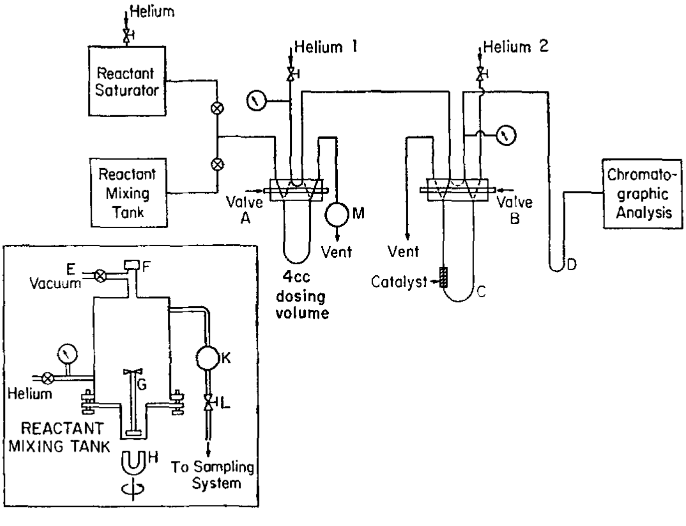

FIG. 1. Flow sheet for the heated microcatalytic reactor.

position valve, Aerograph Instrument & Research Co.). For microcatalytic experiments, valve A, in the position shown (the interconnected valve ports are indicated by solid lines), was arranged to flush a small section of tubing of known volume. A flow controller, M, (Moore Products Co., 63-BU) before the vent, could be used to adjust the pressure in the dosing loop so as to match the pressure in the reactor, which reflected the back-pressure of the chromatographic column. This was normally about 1000 torr. After a prescribed period of flushing, the spindle was moved by a solenoid-controlled piston to the alternate position, indicated by the dotted lines, so that helium carried this slug to valve B where, with the connections shown by the solid lines, the slug passed through a Pyrex tube, C, containing the catalyst. With valve B in the alternate position (dotted lines), the He passed directly over the chromatographic column where the products were separated. As shown, the helium flow 1 is not interrupted in either position of valve A, whereas helium flow 2 is maintained over the catalyst only in the alternate position. The reacted pulse could be trapped in a liquid-nitrogen-cooled trap, D, and flashed onto the chromatographic column by a heater after a prescribed period of collection of products. The whole cycle of operations, repeated at different temperatures, could be controlled by a timing device containing a bank of rotating microswitches operated on a common shaft (*1c*). Each section of the apparatus was heated by thermostated air furnaces, except for the saturator, which was immersed in a temperature-controlled oil bath.

For steady state flow experiments, the connections to valves A and B were rearranged so that the reactant stream passed directly over the catalyst, and the sampling tube was then downstream of the catalyst. Valve B was replaced by an eight-port, two-position Loenco Co. valve for this purpose.

The mixing tank (see insert of Fig. 1) served as an alternate supply system. It was designed with isotopic tracer experiments in mind (where small quantities of reactant are available), but provided a versatile and rapid method for preparing mixed reactant feeds. The 8-liter aluminum tank could be evacuated and filled with helium to a pressure of 3 atm. The desired reactant mixture either could be metered into the tank through a valve system, E (gases), or injected through a rubber septum, F (liquids). A glass stirring rod attached to a bar magnet, G, rotated in a well on the floor of the tank activated by a magnet, H, outside the tank, enabling rapid mixing of the reactant mixture (15–30 min). The flow from the tank to the dosing system was controlled by a Moore Products Co. 63SDL flow controller, K, which maintained a constant pressure upstream of a finely adjustable needle valve, L, despite the gradually dropping pressure in the tank. The number of pulses delivered by the tank, or the length of time of reactant flow, varied with the flow rate, but typically (at 100 cc/min to flush a 4-cc sample tube for 3 min) 35 slugs of 2-butanol could be delivered. Reproducibility in peak height varied between 3.85 and 4.00 chart units.

Gas chromatographic separation of 2-butanol, 2-butanone, and the butene isomers (unresolved) was obtained in 10 min with a 6 ft × ¼ inch column of 15% PEG (Carbowax 1500) on 60/80 mesh firebrick maintained at 75°C.

Materials. The catalyst system was described previously (*6*). The hydroxyapatites, $Ca_{10-n}(PO_4)_{6-n}(HPO_4)_n(OH)_{2-n}$, are homocrystalline basic calcium phosphates whose stoichiometry can be altered by varying the amount of calcium in the lattice. The charge balance is maintained (*6*) by the addition of approximately one proton and the elimination of one structural hydroxyl group for each Ca^{2+} removed. Thus, these catalysts form a series with identical crystal structure and similar morphology, but with varying concentrations of acid phosphate hydrogen. The surface concentrations of acid phosphate hydrogen have been estimated (*6*) by hydrogen assay and by spectroscopic measurement of the formation of carbonium ions from triphenylcarbinol indicators. It is these acid hydrogens which presumably are the active sites for the dehydration of alcohols in the experiments described below.

The preparation and properties of the catalysts have been described (*6*). The general formula was $Ca_{10-n}(PO_4)_{6-n}(HPO_4)_n(OH_{2-n}$ and the calcium-to-phosphorus atom ratio varied from 1.67 for stoichiometric hydroxyapatite to 1.58. The catalysts were crystalline and the surface areas varied from 70 to 50 m^2/g and approximately equaled the sum of the areas of the small single crystals. In the kinetic studies, Fisher highest purity 2-butanol was used without further purification.

RESULTS

Both dehydrogenation and dehydration occurred over stoichiometric hydroxyapatite; dehydration was the only significant reaction over the nonstoichiometric samples. The data presented herein concern the kinetics of the dehydration reaction. Dehydrogenation and questions of selectivity on the catalyst surface will be discussed in a later paper.

The Microcatalytic Technique

In the microcatalytic experiments, successive slugs of alcohol were passed over the catalyst sample and the conversion to olefin was plotted as a function of slug number. Extrapolation of the conversion to zero slug number gave the intrinsic conversion. A typical plot is shown in Fig. 2, giving the conversion at constant flow rate and at a series of temperatures. Under these conditions, as shown in Table 1, the rate of dehydration was nearly independent of initial alcohol pressure, indicating that dehydration obeys zero order kinetics.

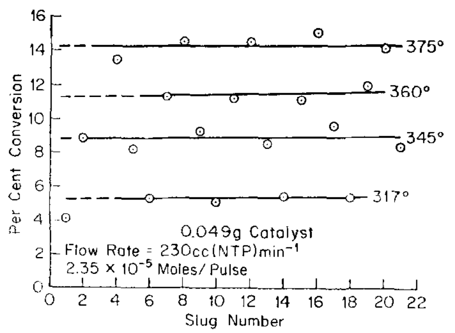

FIG. 2. Dehydration of 2-butanol over hydroxyapatite (Ca/P = 1.67) using the microcatalytic technique.

TABLE 1
RATE OF DEHYDRATION OF 2-BUTANOL WITH CHANGING INITIAL ALCOHOL PRESSURE IN THE MICROCATALYTIC SYSTEM[a]

Initial 2-butanol vapor pressure (mm Hg)	Rate of dehydration [cc(NTP) min^{-1} g^{-1}]
A. *Catalyst Ca/P = 1.67 at 327°*	
34	5.0
62	4.6
118	6.3
233	6.0
B. *Catalyst Ca/P = 1.58 at 343°*	
35	20
58	24
135	18

[a] Helium carrier gas flow rate was 33 cc(NTP)/min in A and 34 cc(NTP)/min in B. In A and B, 0.063 and 0.050 g, respectively, of catalyst were used. The pulse size was 4.3 cc(NTP) and the total pressure was 1000 mm Hg.

A plot (Fig. 3) of conversion against reciprocal space velocity was obtained by varying the size of the catalyst sample, and hence the space velocity, at constant flow rate. These curves are consistent with

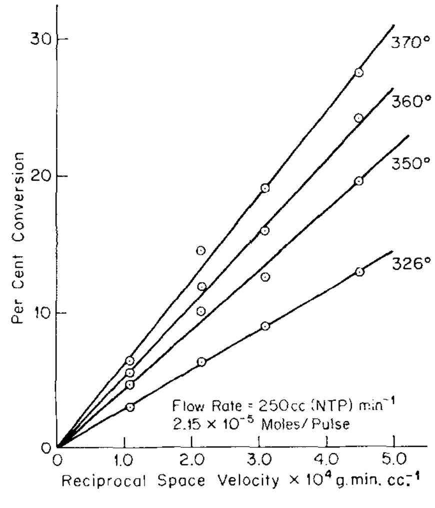

FIG. 3. Dehydration of 2-butanol over hydroxyapatite (Ca/P = 1.67) using the microcatalytic technique. Space velocity was varied by catalyst weight.

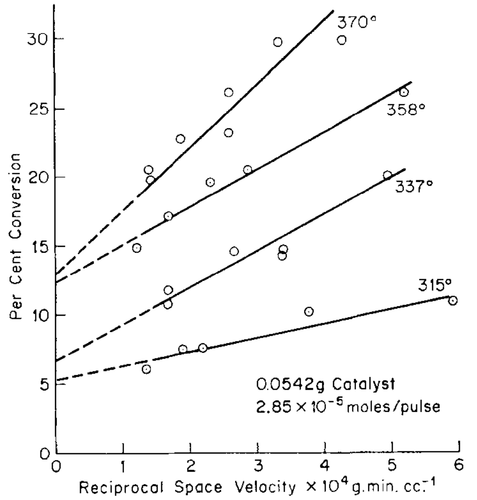

FIG. 4. Dehydration of 2-butanol over hydroxyapatite (Ca/P = 1.67) using the microcatalytic technique. Space velocity was varied by flow rate.

zero order kinetics in that they were straight lines over the entire range of the variables. Note that these curves all passed through the origin. The activation energy corresponding to these data was 14.5 kcal/mole.

The space velocity could also be altered by varying the flow rate of the helium carrier gas. For these experiments, the reactor was so arranged that the carrier gas stream over the catalyst was vented to the atmosphere. In this way, the reactor pressure could be maintained close to 1 atm at all flow rates. Products from the reactant slug were trapped downstream in a —195° trap, which could then be flashed onto the analytical column in a separate helium stream. Plots of conversion against reciprocal space velocity for two catalysts are shown in Figs. 4 and 5. Although the conversion decreased with increasing space velocity, the curves did not extrapolate through the origin; rather, a finite intercept at infinite flow rate is indicated. This is an unacceptable conclusion. Evidently the conversion did not fall properly with increasing carrier gas flow rate. It is suggested that gas is adsorbed as the slug passes and that products desorb at much the same rate regardless of flow rate.

With the calicum-deficient hydroxyapatite (Fig. 5), the intercept on the conversion axis reached a maximum value of 25% conversion of the standard slug as the temperature was increased. With the less active stoichiometric hydroxyapatite (Fig. 4), such a maximum could be said to occur at about 12.5%, but it was not possible to check higher temperatures where dehydration on the walls of the catalyst tube became appreciable.

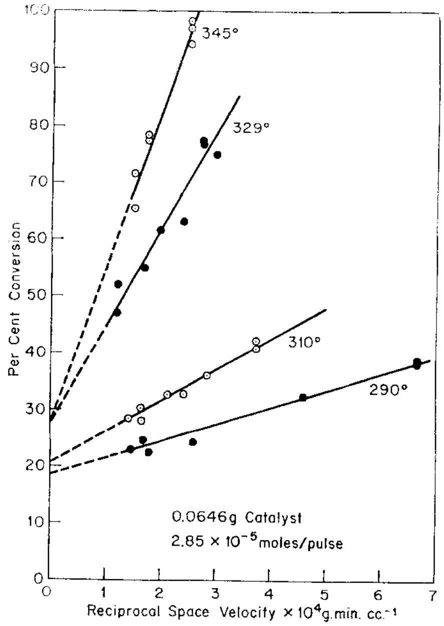

FIG. 5. Dehydration of 2-butanol over hydroxyapatite (Ca/P = 1.58) using the microcatalytic technique. Space velocity was varied by flow rate.

Steady State Flow System

The heated reactor could be arranged to give conventional steady state flow conditions. In some experiments, the flow was stopped while the chromatograms developed, to conserve the reactor feed from the tank. During this time, the catalyst was in contact with the static reaction mixture. However, comparison between continuous flow and stopped flow experiments showed them to be equivalent. In the flow system, dehydration was shown to be nearly zero order in initial alcohol pressure (Table 2). A typical plot of conversion vs. reciprocal space velocity is shown in Fig. 6. From the slopes of these curves at

TABLE 2
RATE OF DEHYDRATION OF 2-BUTANOL WITH CHANGING INITIAL ALCOHOL PRESSURE IN A STEADY STATE FLOW SYSTEM[a]

Initial 2-butanol vapor pressure (mm Hg)	Rate of dehydration [cc(NTP) min^{-1} g^{-1}]
A. *Catalyst Ca/P = 1.67 at 366°*	
38	3.5
70	4.3
100	5.1
138	5.1
B. *Catalyst Ca/P = 1.58 at 308°*	
20	7.9
47	9.1
70	11.1
122	13.7

[a] Helium carrier gas flow rate was 170 cc(NTP)/min in A and 31 cc(NTP)/min in B. In A and B, 0.063 and 0.050 g of catalyst were used at 1000 mm Hg total pressure.

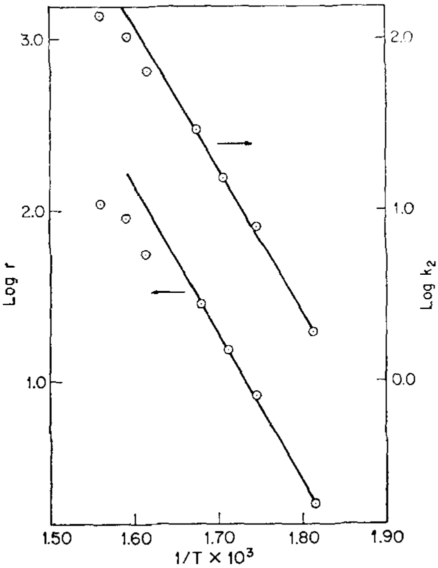

FIG. 7. Arrhenius plots for dehydration of 2-butanol over hydroxyapatite (Ca/P = 1.58) in flow reactor.

various temperatures [differential reaction rates, $dx/d(W/F) = r$), an Arrhenius plot was obtained giving the zero order activation energy (Fig. 7). This plot (log r vs. $1/T$) deviated from linearity at high temperatures, but a value of 39 kcal/mole was derived for the low-temperature range. This behavior could be due to a change in the order of the reaction with temperature, but supplementary experiments showed the reaction to be zero order over the whole range of temperature. However, the experiments reported in Fig. 8 revealed that the reaction was weakly inhibited by H_2O, but not by butene. Therefore, the deviation probably corresponded to poisoning by products.

The conventional Langmuir-Hinshelwood rate law for inhibition due to products is

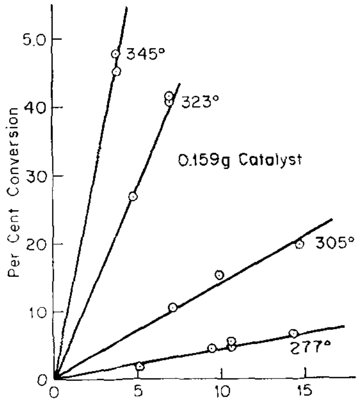

FIG. 6. Dehydration of 2-butanol over hydroxyapatite (Ca/P = 1.58) using the steady state flow technique. Space velocity of He + 12.5% 2-butanol was varied by flow rate.

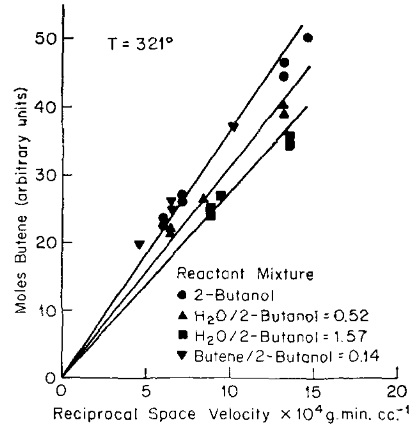

FIG. 8. Inhibition of the dehydration of 2-butanol over hydroxyapatite (Ca/P = 1.58) by products in a steady state flow experiment.

$$r = \frac{k_2 K_1 P_{\text{alc}}}{1 + K_1 P_{\text{alc}} + K_3 P_{\text{H}_2\text{O}}} \tag{1}$$

where k_2 is the rate of reaction of adsorbed alcohol and K_1 and K_3 are the adsorption equilibrium constants of alcohol and water defined by

$$\text{ROH (g)} \overset{K_1}{\rightleftharpoons} \text{ROH (s)}$$

$$\text{H}_2\text{O (g)} \overset{K_3}{\rightleftharpoons} \text{H}_2\text{O (s)} \tag{2}$$

Since the initial rates of reaction were zero order in alcohol pressure, $K_1 P_{\text{alc}} + K_3 P_{\text{H}_2\text{O}} \gg 1$. Hence,

$$r \approx \frac{k_2 K_1 P_{\text{alc}}}{K_1 P_{\text{alc}} + K_3 P_{\text{H}_2\text{O}}} \tag{3}$$

which, on rearrangement, gives

$$\frac{1}{r} = \frac{1}{k_2} + \left(\frac{K_3}{k_2 K_1}\right)\left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{alc}}}\right) \tag{4}$$

This equation could be checked using the data of Fig. 8, where the initial rates of dehydration at three different initial partial pressures of water are given. The slope and the intercept obtained from these data, when plotted according to Eq. (4), yielded K_3/k_2K_1 and $1/k_2$. Plots such as these were not of great accuracy, but did establish that K_3/K_1 was a small fraction (0.26 ± 0.09 at 395° and 328°). The small values for K_3/K_1 were consistent with the weak deviations from the zero order plot contained in Fig. 7.

The integrated form of the rate expression

$$\frac{W}{F} = \frac{C_0}{k_2}\left(x - \frac{K_3}{K_1[x + \log(1 - x)]}\right) \tag{5}$$

where C_0 is the concentration of reactant in moles/cc and x is the percent conversion. From plots of Eq. (5) at various temperatures, values of k_2 were obtained. These are plotted in Fig. 7, where the results may be compared with the simple plot of log r vs. $1/T$. It is apparent that the data have been corrected, but not completely. Considering the crudeness of the data, however, it appears likely that product inhibition is mainly responsible for the deviation, and that the activation energy for the reaction is about 39 kcal/mole. The activation energies were constant at this value over the series of hydroxyapatites of varying Ca/P ratio.

DISCUSSION

The kinetic data for dehydration under steady state flow conditions followed satisfactorily a conventional Langmuir-Hinshelwood treatment. Evidently the reaction occurred with full surface coverage of adsorbed alcohol, but with some competition for active sites from product water at high conversion. The activation energy (39 kcal/mole) was consistent with the previously reported (*7*) value (38 kcal/mole) for the dehydration of isopropanol over tricalcium phosphate. Diffusional effects were not important; a catalyst (Ca/P = 1.67) ground to smaller particle size, i.e., from 60 to 140 mesh, gave the same conversion in a pulsed system, as the larger particle size. This was as expected from the fact that the catalyst samples were comprised of nonporous single crystals (*6*).

Since the reaction was described by zero order kinetics for the flow system, the anomalous conversion curves and low activation energies for the pulsed reactor should also be explained on this basis. In the case of a zero order reaction, the evaluation of rate constants from the equations of Gaziev *et al.* (*3*) is dependent upon the shape of the reactant pulse. For a square pulse, which may be approximated in our system, however, the same functional relationship between conversion and reciprocal space velocity was predicted for the microcatalytic and the conventional flow methods. The data of Figs. 4, 5, and 6 showed that this prediction was not fulfilled and that it was the microcatalytic system which deviated from expectation. In Gaziev's derivation (*3*), equilibration of the reactant with the surface was assumed. For zero order reactions, desorption of reactant may be too slow for equilibrium to be maintained with the moving pulse, and this seems to be the situation in present experiments. At high space velocities, secondary reactions were eliminated, but a monolayer of reactant was adsorbed, no matter how short the contact time be-

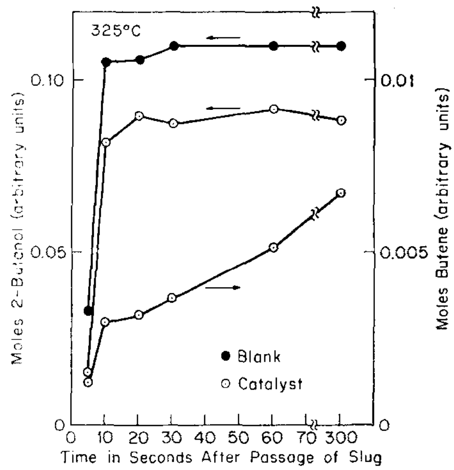

FIG. 9. Elution of product butene from hydroxyapatite catalyst (Ca/P = 1.67).

tween pulse and catalyst. Products then desorbed slowly and were collected in the trap downstream of the catalyst. This was shown by the following experiment. The multiport valve downstream of the catalyst could be operated so that the effluent either passed to the cold trap and the chromatographic column or could be vented to the atmosphere. By venting the effluent to the atmosphere at varying times after the slug passed the catalyst, it was possible to determine the composition of the product mixture as it desorbed from the catalyst. The data of Fig. 9 show that most of the unreacted alcohol had passed from the catalyst in 10 sec while less than 50% of the products had yet appeared. Desorption of products did not become quantitative until about 5 min after the passage of the pulse, whereas the calculated residence time of the slug was about 1 sec. The anomalous behavior of the pulse experiments, and the low values of activation energies derived therefrom, must thus reflect the indeterminate residence time of the reactant pulse. Nevertheless, some new insight concerning the reaction can be obtained from these results, e.g., it may be supposed that in a steady state flow reactor, products desorb "miles upstream" from the volume increment from which the parent alcohol molecules were adsorbed.

The intercept of the conversion vs. reciprocal space velocity curve is related to this slow desorption and, perhaps, to the number of sites active for alcohol dehydration. The value of the intercept could reach a maximum with temperature at the point where a "site monolayer" of reactant was adsorbed, and every active site yielded a product molecule. This point would correspond to about 25% conversion of the standard pulse in Fig. 5, while a less well defined maximum could be taken at 12.5% in Fig. 4. The number of sites per cm² of catalyst surface calculated from such experiments are listed in Table 3. It is instructive to compare these sites densities with those obtained from other measurements.

The active site for dehydration, by analogy with dehydration in solution (*8*), may be an acidic hydrogen on the catalyst surface and, indeed, the rates of dehydration correlated with calcium deficiency and with increasing surface POH concentration (*6*). Values of the latter, estimated by two dif-

TABLE 3

SITE DENSITIES FOR DEHYDRATION OVER HYDROXYAPATITES MEASURED BY VARIOUS METHODS

Hydroxyapatite Ca/P	No. per cm² × 10^{-13}				
	Theoretically expected POH[a]	Trianisylcarbonium Ions		Absolute reaction rate	Microcatalytic intercept
		290°[b]	500°[b]		
1.67	0	0.053	0.0095	3	5[c]
1.63	5.5	0.26	0.053	23	—
1.61	9.8	0.24	0.065	31	9[d]
1.58	14.5	0.29	0.087	48	12[d]

[a] Based on hydrogen content measurements (ref. *6*).

[b] Pretreatment temperature (ref. *6*).

[c] Intercept at 370°.

[d] Intercept at 345°.

ferent methods, are listed in Table 3, viz., the surface POH concentration obtained from spectrophotometric measurement of carbonium ion formation from triphenylcarbinol indicators, and the theoretically expected values, based on the stoichiometry of the hydroxyapatites $Ca_{10-n}(PO_4)_{6-n}(HPO_4)_n(OH)_{2-n}$. The number of sites active for dehydration was also calculated from the steady state flow kinetics, using absolute reaction rate theory. The zero order rate constants is given by the equation

$$k_2 = C_a(kT/h)(f^\ddagger/f_g)\exp(-E_a/RT) \quad (6)$$

where C_a is the number of active sites per cm^2 of surface. Assuming the partition function ratio is unity, and taking a value of 39 kcal/mole for E_a, the site concentrations for the series of hydroxyapatites were calculated, and the results are included in Table 3.

The carbonium ion measurements yielded site densities more than an order of magnitude below those theoretically expected, while the absolute reaction rate values were in reasonable agreement with prediction, when it is remembered that implicit in the absolute reaction rate calculation is the assumption that the partition function ratio is unity. If this were not true, high values would be calculated when one or more vibrational modes are restricted in the transition state, i.e., the partition function ratio would become larger than unity so that true values of site densities would be lower than calculated. The values derived from the intercepts of the microcatalytic experiments are independent of the partition function ratio and afford an independent comparison. These values were in reasonable agreement with those calculated from Eq. (6), as well as those derived from the stoichiometry. If, however, these measure site densities, what causes the much lower values from the triphenylcarbinol indicators? Apparently carbonium ion density is limited by some factor other than the availability of protons. This might be the mutual repulsion of the positively charged carbonium ions or a limiting charge density on the catalyst surface. In this respect, it may be significant that the maximum carbonium ion concentrations per cm^2 on hydroxyapatites and on silica-alumina (*10*) are very similar.

In conclusion, the microcatalytic technique, applied to zero order reactions, may supply information not readily available from conventional kinetic methods. It reveals a situation not apparent from steady state flow experiments, i.e., that the monolayer of reactant on the catalyst surface is not in rapid equilibrium with the gas phase, but has a residence time on the surface which is independent of that calculated from the carrier gas flow rate. Under favorable conditions, this phenomenon can be employed to estimate catalytic site densities without the assumptions of the absolute reaction rate theory.

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