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Kinetics of the Catalytic Dehydration of 2-Propanol

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The dehydration of 2-propanol is chosen as an activity test of oxide catalysts. The thermal kinetics of the decomposition are studied. Catalytic kinetics are examined on silica, alumina, thoria, and modified silica-aluminas. In the range $T = 100 - 160°C$, p (2-propanol) $= 8 - 23$ mm Hg, the reaction is zero order with respect to alcohol, inhibited by water and acetone, but not by propene. Silica-alumina catalysts have a higher activity than alumina, silica or sodium silica-alumina.

INTRODUCTION

The decomposition of 2-propanol has been chosen as a catalytic test to study dual function catalysts made of nickel-impregnated silica-alumina. A secondary alcohol was preferred because it gives propene and acetone, and acetone is thought to be less troublesome than the propionaldehyde which condenses on silica-alumina.

This paper will be concerned with dehydration only. The measure of the activity of different silica-aluminas in the 2-propanol dehydration was our first goal, but we have been led to study also the thermal reaction, the kinetics, and the activity of other solids such as alumina and silica.

Alcohol dehydration has been previously investigated by many people. A broad survey of the question was published by Winfield in 1960 (*1*a). The two major issues seem to be the mechanism of the reaction and the types of active sites of the catalysts. Some results have been given for ethanol, but very few for 2-propanol. So we have used the results on ethanol to get an overall view of the problem.

About the mechanism the two main questions concern the role of water and the simultaneous or consecutive formation of ether and olefin. While the inhibition of the rate of alcohol dehydration by water is recognized by everybody, the explanation of "how it works" is not satisfying. (*1*b, *3*, *4*). A mechanism of consecutive reactions has been proposed for the production of olefins. Others think it is a set of simultaneous reactions (*1*c, *7*). Quite often the proposed mechanisms don't take into account the role of water. Still the problem has not been solved.

For catalysts the question is whether dehydration uses acid or nonacid sites, and still, there is no agreement. Topchieva (*4*) thinks that protons of the alumino-silicate structure do not play an appreciable part in the reaction, but Dzisko *et al.* (*8*) have concluded that: "dehydration velocity of isopropyl alcohol is essentially dependent on the acidity of the catalysts, therefore this is an acid process."

This paper includes a study of the kinetics of the formation of propene, the influence of several factors, and the comparison of the activities of different catalysts.

EXPERIMENTAL

The experiments were carried out in a flow reactor (Fig. 1) with a carrier gas. The 2-propanol sent to the reactor is

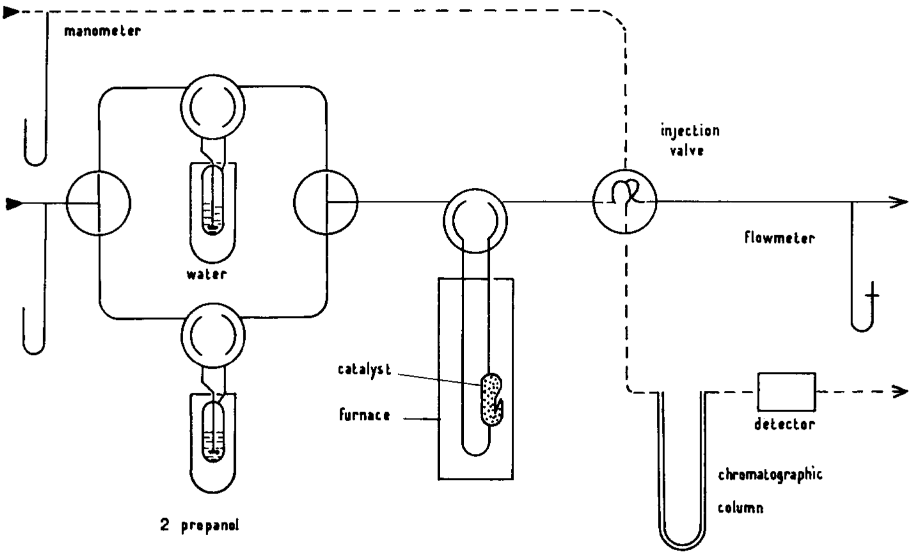

FIG. 1. Schematic diagram of the apparatus.

picked up in a system of two bubblers. The second one is at lower temperature and determines the pressure of 2-propanol. By changing its temperature (0–15°C), the pressure of 2-propanol is modified so that the order of the kinetic reaction can be calculated. The reactor is in an electrically heated, temperature-regulated furnace. Two kinds of reactors are used: In the first one the catalyst is deposited in a small tray, the vessel is horizontal and the gas flows over. In the second one the glass reactor is vertical, contains a sintered glass support to retain the catalyst, and the gas flows through. A small glass cavity allows the introduction of a thermocouple close to the catalysts to measure the reaction temperature. At the outlet of the furnace, the pipe is connected to the gas sample valve of a chromatographic apparatus, which uses a column of Carbowax 20 M (20%, 1 m) that separates propene, diisopropyl ether, acetone, and 2-propanol.

Chromatographic data: Carrier gas, nitrogen; flow rate, 0.5 ml/sec; detector, flame ionization; column T, 100°C; injection volume, 1 ml.

Reactor circuit data: Carrier gas, nitrogen; flow rate, 0.2 to 2 ml/sec; reactor T, 80° to 200°C, weight of catalyst, 0.1 g; 2-propanol pressure, 3-8-23 Hg mm.

Conditions of a Run

For each experiment, three characteristics are examined: initial rate, kinetic order with respect to the reactant, and activation energy.

Initial rate. The production of propene (ether does not exceed 10% and is not taken into consideration) is measured at constant 2-propanol pressure and constant temperature of the reactor with different flows. The origin tangent of the curve of production versus the inverse of the flow gives the initial rate.

Order. The same experiments are run again with different 2-propanol pressures (8.5–23 Hg mm). The order of the reaction is determined.

Activation energy. The temperature of the reactor is regularly changed and the activation energies are determined over a temperature range of 60°C, using conversions less than 0.05.

THERMODYNAMIC DATA

The equilibrium constant of the dehydration is related to the temperature by the relation: $\log_{10} k_p = 6.060 - 1950/T$ which is valid for T between 448° and 523°K (175–250°C) and at 1 atm (*1*d, *2*).

Though our experimental conditions are

different [p(atm), 0.01–0.03; T(°C), 100–180°], this relation shows that the dehydration is practically total. At 127°C, if p(alcohol) $= 0.03$ atm the fraction of unreacted alcohol is 0.03.

THERMAL REACTION

The kinetics of 2-propanol decomposition are measured with two reactors. One is that used for catalytic studies, which contains sintered glass whose volume is 1.5 cc. The second one is larger (17.3 cc) but without sintered glass. Both are made of Pyrex.

Chromatographic analysis reveals propene and acetone. These products are used to measure the rates of the two reactions: dehydration and dehydrogenation.

The rate of formation of propene with a 2-propanol pressure of 22 Hg mm at 373°C is 10^{-9} moles/sec cc of the reactor.

The orders of the dehydration are fractional and vary slightly with temperature: n (373°C) $= 0.41$ while n (396°C) $= 0.55$.

The activation energies are between 28 and 23 kcal/mole.

These results lead us to think that the thermal reaction will not interfere with the catalytic reaction since the rate is far smaller than the observed rates with catalysts. More experiments are necessary to explain the fractional orders.

CATALYTIC DEHYDRATION

This section is divided into two parts: A, the evaluation of the activity of different catalysts; and B, the investigation of the reaction itself, and particularly the influence of water.

A. Activity of Different Catalysts

This section includes at first a comparison of different oxides, then a study of the evolution of the activity of a silica-alumina catalyst as a function of various treatments.

1. Classification of Oxides

The materials which appear in the Table 1 are described here. The silica was prepared in the Institute of Catalysis by cationic and anionic exchange from a dilute solution of sodium silicate. This solution is warmed in order to form the gel which is directly dried at 120°C. This silica is very pure (less than 30 ppm of Fe).

The alumina was prepared in the Institute of Catalysis from aluminum nitrate and ammonia. The alumina gel was washed until it was free of ammonia, then dried 24 hr at 120° and calcinated at 500°C. X-Rays show it is a γ alumina.

The thoria was prepared in the Institute of Catalysis by decomposition of thorium nitrate at 500°C in an air current. The X-Rays show diffuse and broad lines.

The two silica-aluminas (13%, 25% alumina) are commercially manufactured by Ketjen and their trade names are Ketjencat.

TABLE 1

INITIAL RATES V, ACTIVATION ENERGIES E, AND SURFACE AREA A FOR DIFFERENT CATALYSTS[a]

Catalysts	V_{165} (moles/sec g)	E (kcal/mole)	A (m /g)
Silica	0.10×10^{-7}	43.5	650
γ Alumina	4.8×10^{-7}	32	230
Thoria	1.3×10^{-7}	29.5	55
Silica-alumina Ketjen (25% alumina)	13×10^{-7}	32.5	560
Silica-alumina Ketjen (13%)	260×10^{-7}	30	700

[a] For each series a new blank run is made with silica-alumina Ketjen (13%).

The initial rates show a large difference, which cannot be explained by the surface area (last column). From these values the catalysts can be classified in three categories: silica, alumina and thoria, silica-alumina. This last one is much more active than the other catalysts. It is well known that silica-alumina is active in cracking, isomerization, and polymerization, but practically no paper mentions its high activity in dehydration, where alumina and thoria are generally regarded as the best catalysts.

Among these oxides, silica-alumina is known to reveal acid properties which are considered as responsible for the cracking activity. It does seem that acid properties take some part in dehydration, but yet we may think that the sites are not the same, because silica-alumina 25% is much less active than silica-alumina 13% though their activity in cracking is equal (*12*). This is confirmed by the experiments described next.

2. Modification of a Silica-Alumina Catalyst

The very high level of the activity of the silica-alumina (13%) catalyst led us to search for the nature of the sites working in dehydration. Three treatments were investigated.

a. Preheating at different temperatures. The catalysts are heated 16 hr in an air flow then brought back to 130°C and the activity is measured. The results are given in Table 2. Only a small increase of the activity is observed and Barthomeuf had noticed a similar effect for the Bronsted activity (*10*).

TABLE 2
COMPARISON OF THE ACTIVITIES AND THE ACIDITIES OF A KETJEN (13% ALUMINA) AT DIFFERENT TEMPERATURES OF TREATMENT

Preheating temperature (°C):	130°	400°	453°	500°	554°
$V_{130} \times 10^7$ (moles/sec g):	18	18	26	32.5	24.5
Bronsted acidity milliequivalent H^+/g:[a]	0.75	0.88	1.12	1.37	1.5

[a] Reference (*10*).

b. Exchange with sodium salt solutions. In Table 3 are given the results of our experiments and data from the thesis of Barthomeuf (*10*). The amount of exchanged sodium depends on the basicity of the solution.

Two points must retain our attention:

(1) The alcohol dehydration rate is more drastically reduced than the cumene cracking activity. These results confirm the experiments of Boreskov concerning the influence of sodium hydroxide on alumina on the rate of dehydration of ethanol into ethylene at 420°C (*1f*).

(2) With catalysts treated by NaCl solutions, the variations of the dehydration rate is small. This may explain why Topchieva (*6*) and co-workers concluded that sodium does not change the catalytic activity of silica-alumina in the dehydration of ethanol.

c. Removal of aluminum with acetylacetone. Aluminum can be removed from the catalysts by treatment with HCl or with acetylacetone solutions. This last method seems better, because no chlorine is involved and chlorine itself could bring some modifications. The activity variations due to the removal of aluminum are shown in Table 4.

As in the previous paragraph it seems difficult to draw a conclusion from the activation energy, but the initial rate of dehydration is multiplied by a factor of 9 at the maximum.

It is interesting to compare the results

TABLE 3
VARIATIONS OF DIFFERENT PROPERTIES AS A FUNCTION OF THE BASICITY OF THE EXCHANGING SOLUTION

Catalyst	V_{160} (mole/sec g)	E (kcal/mole)	Bronsted acidity (meq H^+/g)	Exchanged Na (meq/g)	Catalytic activity in cumene cracking at 375°C
Ketjen 13% alumina	315×10^{-7}	30.6	0.80	0	2
NaCl-exchanged	174×10^{-7}	30	0.77	0.18	1.3
$NaCH_3CO_2$-exchanged	9.3×10^{-7}	31.1	0.5	0.55	0.2
Na_2CO_3-exchanged	0.3×10^{-7}	32.4	0	1.7	0.1
Na_3PO_4-exchanged	0.2×10^{-7}	29	0	2	0.08

TABLE 4

VARIATIONS OF THE ACTIVITIES AND OF THE ACTIVATION ENERGIES AS A FUNCTION OF THE REMAINING ALUMINA

Catalyst	Al_2O_3 (%)	$V_{100°}$ (moles/sec g)	Activation energies (kcal/mole)
Ketjen 13% untreated	13	1.90×10^{-7}	30.6
Ketjen treated by CCl_4	13	1.39×10^{-7}	31.9
Ketjen treated by CCl_4 + acetylacetone	9.5	6.16×10^{-7}	25
	5.4	11.1×10^{-7}	28
	2.65	11.1×10^{-7}	25
	1.60	17.1×10^{-7}	34.2
	1.30	13.2×10^{-7}	26
	1	4×10^{-7}	26

of Barthomeuf (*11*) with ours (Fig. 2). Though alumina has not been removed by the same method (HCl solutions) the curves reveal a different influence of alumina on the activity when applied to dehydration of alcohols or to cracking of cumene or *n*-octane. It must be pointed out that the catalysts having less than 2% of alumina do not show strong acidity any more.

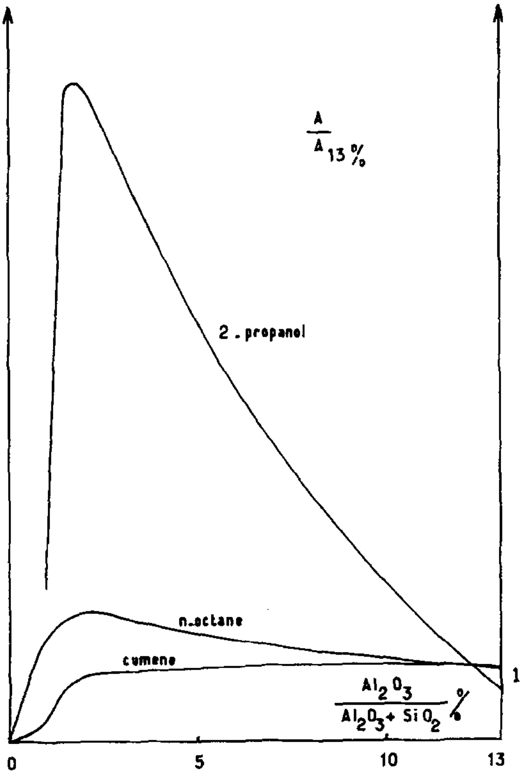

FIG. 2. Relative activities for three reactions as functions of the alumina percentage.

3. Conclusion

The study of these catalysts leads to the following statements:

(1) Some "acid" sites play an active role: Silica-alumina 13% is more active than silica, alumina, thoria, sodium silica-alumina, but silica-alumina 25% is 20 times less active than silica-alumina 13%.

(2) The ratio alumina/silica plays a major role. The activity maximum is reached by modified catalysts with 2% of alumina. We assume that there is another type of active sites, which are complementary to the acid sites. Both of them are necessary, and the number or the efficiency of the sites is closely related to the ratio Al/Si.

In the next part we shall study the mechanism of the dehydration. The existence of two kinds of sites seems confirmed by the experiments concerning the influence of water.

B. Study of the Catalytic Reaction

One of the interesting advantages of this reaction is the stability of the catalysts' activity under the conditions of the test, i.e., at low conversion. Besides, the main reaction produces propene and water; a small amount of ether is produced, which does not exceed 10%.

1. Influence of a Previous Treatment

Generally the catalysts are brought directly to the temperature of the reaction (conversion about 0.01). After they are heated to 400°C for 1 hr, the activity is measured again at the same conditions as before. In most cases no change appears.

2. Influence of the 2-Propanol Pressure

This has been investigated by Dohse and Kalberer (*3*), but the difference between the two orders was not emphasized They reached the following conclusions: (a) the reaction is first order if carried out directly; (b) the reaction is zero order if water is continuously evacuated during the experiment; (c) the reaction is zero order at 120°C with respect to initial pressure.

The data of Dohse (*3*) must be examined with respect to the two previously mentioned aspects of the problem.

Order as a function of initial pressure: At any temperature the reaction is not first order [Dohse, (*3*), p. 136] characterized by a half-reaction time independent of the initial pressure, but close to a zero order; indeed the ratio half-reaction time/initial pressure is practically constant.

Order as a function of the pressure varying in the time: In this case the first order rate of the reaction is fairly well verified with an equation of the form log $a/(a-x) = kt$ [Dohse, (*3*), p. 135] but it is difficult to understand a first order reaction with 2-propanol, and it is more likely that the inhibition by water causes an apparent first order with respect to 2-propanol. Indeed, when water is removed the reaction is zero order.

The same confusion seems to be present in the work of Vasserberg (*4*), who characterizes different catalysts by the half-decomposition time, which is correct only if the reaction has been proved to be first order; but this does not seem to be the case for temperatures and catalysts studied.

Our first work consisted in determining the influence of the initial pressure of 2-propanol.

The preliminary experiments were made with Ketjen 13% alumina; the conditions and the results are collected in Table 5.

These results are transformed into logarithmic form and the curves log $v_0 = f$ (log p_0) are represented in Fig. 3. They clearly prove that the reaction is zero order at a temperature lower than 165°C. Above 165°C the order becomes fractional and tends to one but does not reach it yet at 220°C.

After these experiments the temperature was fixed below 160°C and for practical reasons two pressures, 8.6 mm Hg corresponding to 0°C and 23 mm Hg corresponding to 15°C, were used. Under these

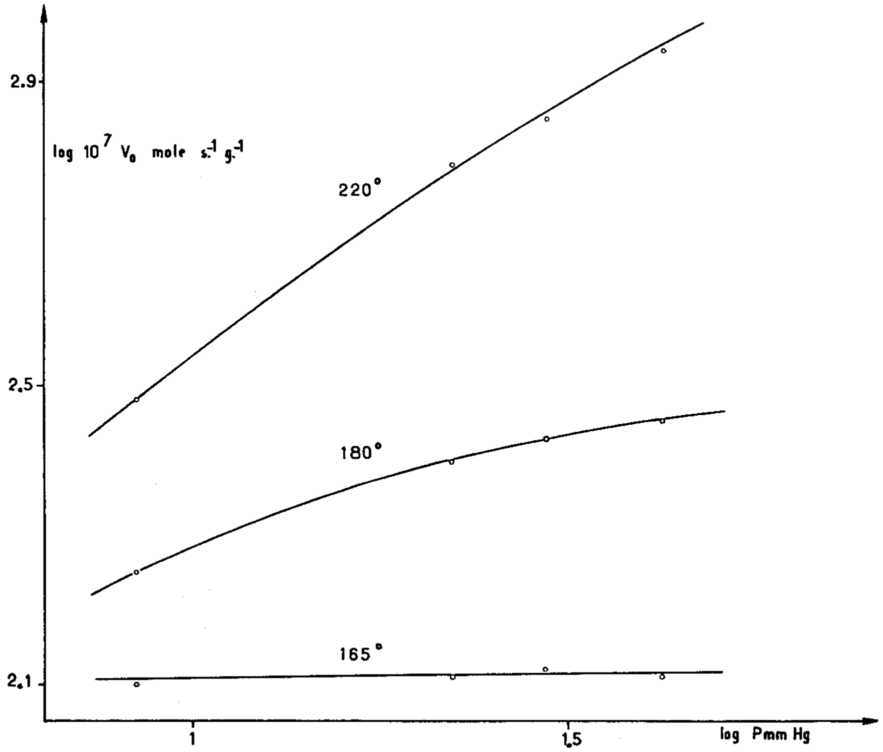

FIG. 3. Reaction order with respect to 2-propanol at different temperatures.

TABLE 5

INITIAL RATES (MOLES/SEC G) AS A FUNCTION OF TEMPERATURES OF THE REACTOR AND OF PRESSURES OF 2-PROPANOL FOR A 13% ALUMINA CATALYST (KETJEN)

2-propanol pressure (Hg mm)	Temperature (°C)		
	165°	180°	220°
8.4	127	177	303
22.2	130	253	612
29.4	132	272	708
42.1	128	280	867

conditions, and for temperatures between 100° and 160°C, the reaction is confirmed to be zero order with initial rates for all the tested silica-alumina catalysts. *So the initial rate has been taken as a measure of the activity of the catalyst.*

3. Influence of Propene

For these experiments the conversion is kept higher than previously (about 0.3) and exceptionally the rate is measured by the disappearance of 2-propanol. A continuous flow of propene under 80 Hg mm pressure is added to the 2-propanol flow (pressure 23 mm Hg). The propene formed by the reaction gives a pressure of 8 mm Hg. The variation of the disappearance of 2-propanol is insignificant.

4. Influence of Water

Water is the product of the reaction which has close physical and even chemical properties with those of 2-propanol. Its influence is strong. Dohse (*3*) has studied it by addition but with only one initial pressure of 2-propanol and one additional pressure of water. In our laboratory this influence has been investigated intensively, in order to establish the kinetic equation. Series of experiments are carried out by adding additional water with a parallel saturator (Fig. 1) at different initial pressures of 2-propanol and of water, and at different temperatures of the reactor:

2-Propanol p (mm Hg): 4.3 11.25
Water p (mm Hg): 0 2.3 6.2 9
Reactor temperature (°C): 113 130 145 155
Catalyst: Ketjen (13% alumina)

With γ alumina the reaction is carried out at 170° only; for Ketjen 13% Al_2O_3 the results are shown in the curves of Fig. 4.

In the range studied, the following conclusions can be drawn: (1) The 2-propanol pressure does not play any role. (2) The water pressure lowers the rate of reaction, but above a certain value of the pressure the rate becomes constant. (3) Curves are similar with γ alumina and Ketjen (13% alumina).

From these experiments, a mechanism with a Langmuir equation and competitive adsorption on the same sites does not fit. It seems better to suggest the existence of two kinds of sites: (a) the A sites, on which alcohol gives an intermediary adsorbate, and which are saturated for 2-propanol pressures as low as 4.25 mm Hg; (b) the W sites, on which water is adsorbed and which are saturated for water pressures of about 2 mm Hg.

The different steps of the reaction would be

$$C_3H_7OH \rightarrow A\text{–}C_3H_7OH \rightarrow W\text{–}H_2O + C_3H_6 \rightleftharpoons H_2O + C_3H_6$$

With no water at all (initial rates), the rate is probably that of the decomposition of the complex A–C_3H_7OH, but limited by the rate of evacuation of the W sites by formed water.

With added water, the rate decreases, then reaches a constant value. Every time one molecule of the complex A–C_3H_7OH decomposes, an empty W site should be available, hence the rate would be the rate of decomposition of W–H_2O.

The hypothesis of the existence of two species of sites allows explanation of why the dehydration activity is increased when Al is removed. It may be assumed that new W sites are created.

The general expression of the rate fits with the equation:

$$V = d(C_3H_6)/dt = K_A B_A \theta_A/(1 + K_W B_W \theta_W)$$

where B_A is the total number of sites which can be occupied by alcohol; θ_A, the coverage of B_A sites; B_W, the total number of sites which can be occupied by water; θ_W,

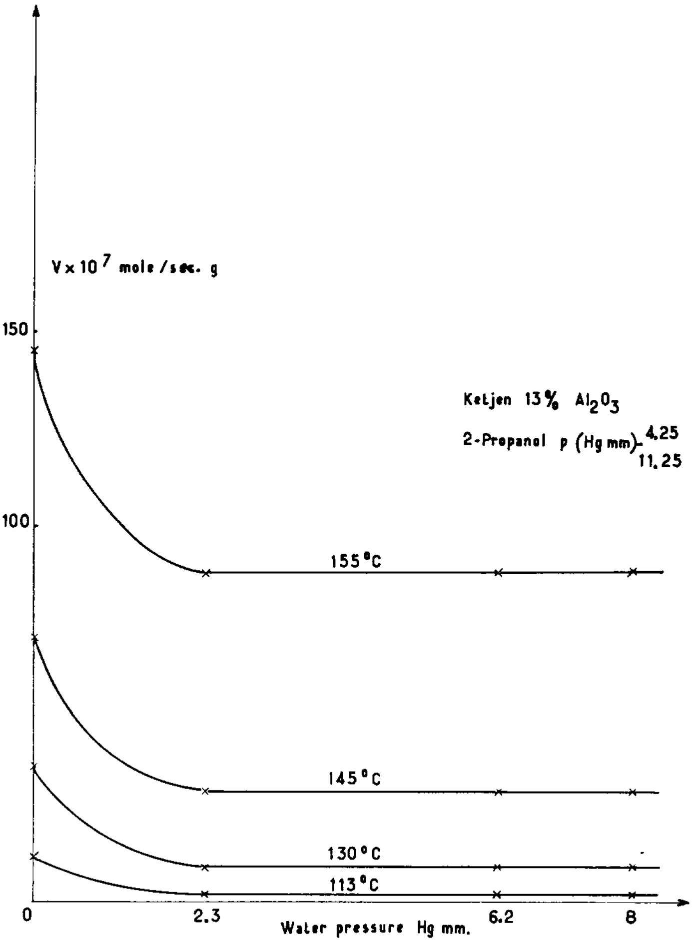

FIG. 4. Influence of water on the dehydration rate. (Curves are exactly the same with the two pressures of 2-propanol.)

the coverage of B_W sites, and K_A and K_B are constants.

5. *Influence of Acetone*

The dehydration of 2-propanol is very sensitive to acetone. An addition of 30 Hg mm acetone pressure to the flow reduces the rate from 100 to 18. The purpose of this experiment was double:

(a) It permits explanation of the negative orders when the feed contains acetone.

(b) If nickel-containing dual function catalysts are used, acetone is formed on the nickel, and may, therefore, poison the active sites of silica-alumina, and this may be one of the causes of the observed drop of the dehydration rate (*3*).

6. *Temperature Influence*

Results found in the literature (*1*) do not agree. Table 6 gives the apparent activation energies for dehydration of 2-propanol into propene with different catalysts. The difference of the last two

TABLE 6
APPARENT ACTIVATION ENERGIES FOR DEHYDRATION OF 2-PROPANOL

Catalysts	Temp. range (°C)	E_{exptl} (kcal/mole)	References
Tricalcium phosphate	262–297°	37.8	(*1e*)
Alumina	350°	16	(*5*)
Alumina	105–145°	26	(*3*)
Alumina	170–200°	39	(*3*)

values is explained by Dohse by the desorption heat of water, which is 13 kcal/mole.

The value of 16 kcal/mole obtained at 350°C might be explained in a similar way. At 350°C the rate of decomposition should normally be first order with respect to propanol, and the apparent activation energy would be the difference between the true activation energy (25 kcal) and the heat of adsorption of 2-propanol. A good approximation of the heat of physical adsorption is given by the 2-propanol heat of liquefaction, which is 10 kcal/mole.

Our results concerning activation energy are given in Tables 1, 3, and 4. Except for silica (43.5 kcal/mole, Table 1) the values for the other catalysts do not allow any conclusion to be drawn. As far as silica is concerned it seems that the active sites, or the steps of the reaction are different, which may explain the gap of about 14 kcal/mole with the other catalysts. It should be mentioned that in all the measurements the reaction is zero order.

CONCLUSION

2-Propanol dehydration certainly is an interesting activity test for the oxide catalysts. The catalysts do not age, the temperatures of reaction are low, and zero order is easy to reach. Moreover the techniques used are simple and rapidly supply initial rate, kinetic order, and activation energy.

It has been shown that the dehydration rate is the highest with silica-alumina catalysts. Acid sites are surely involved in dehydration as it is proved by sodium action, but they seem to be helped by other sites. Aluminum removal experiments, and the influence of water led us to assume the existence of two types of active centers. This is expressed by an equation with two values for the numbers and for the coverages of these sites.

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