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Vapor-Phase Reactions Catalyzed by Ion Exchange Resins

I. Isopropanol Dehydration

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The dehydration of 2-propanol has been studied using ion exchange resin as catalyst, in a gas-phase flow reactor. The temperature was 90°, 100°, and 110°C and the pressure, atmospheric. The production of both propylene and diisopropyl ether have been measured. The Langmuir-Hinshelwood model only fits the data in a limited range of partial pressure of water ($p_w/p_w^0 = 0.20$). The reactions are zero order with respect to alcohol and strongly inhibited by water. The ether did not react in the presence of alcohol and its influence on the velocity of reaction is negligible. No appreciable effect of the partial pressure of propylene has been observed either. A comparative analysis with inorganic catalysts shows that the reaction mechanism should be the same although the ion exchange resin seems to be more active. The controlling step for both reactions is the surface reaction on two adjacent sites.

1. INTRODUCTION

Since the Second World War the study of ion exchange resins as catalysts has increased enormously. Most work has been done in the liquid phase, and good reviews can be found elsewhere (*1–5*). More recently a great number of papers have been published (*6*).

The general idea of the structure of the ion exchange resin allows us to consider it as a special kind of catalyst. It is well known that the adsorption of water depends on both the number of active centers (number of equivalents/g of resin) and the degree of crosslinking. In other words it seems that two "kinds" of water can be present in the catalyst at the same time. Helfferich (*7*) shows that the water first tends to be adsorbed on the H^+ (3 H_2O per H^+) and after this point the relation begins to be dependent on the elasticity of the matrix of the resin.

In a number of works in the liquid phase the velocity of the reaction has been found to be dependent on the particle size of the catalyst. Saletan and White (*8*) presented an outstanding study of this phenomenon. However the diffusion coefficient of an ion exchange resin is not even well known and Frish (*9*) developed a rather interesting model, showing that the effective diffusivity depends not only on the distribution of pore sizes but also on the nature of the matrix.

On the other hand in the gas phase the data are very difficult to correlate and some nonclassical models have been proposed (*10, 11*), although Kabel and Johnson (*12*) succeeded in getting a good fit of their data using a Langmuir-Hinshelwood model, on the dehydration of ethyl alcohol at 120°C.

In this part of the paper, the dehydration of 2-propanol is presented, including the

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influence of reactants and products, with special emphasis on the water, in a range of temperature close to the normal boiling point of this substance, where its influence is critical. A comparison of the mechanism, activity, and selectivity with published data for the same reaction on inorganic catalysts has been attempted.

2. NOTATION

a, b, c, d, e	Regression coefficients
$\bar{E}$	Activation energy (*k*cal/mole)
F	Flow rate (mole/hr)
k	Reaction rate coefficient (mole/hr g cat)
K	Equilibrium or adsorption constant (atm^{-1})
m	Mass (g)
M	Dried mass of catalyst (g)
p	Partial pressure (atm)
PM	Molecular weight (g/mole)
t	Time (hr)
X	Conversion
y	Dependent variable
σ	Standard deviation
Suffixes	
A	Alcohol
E	Ether
L	Liquid state
P	Propylene
W	Water
1 and 2	First and second reaction, respectively
I and II	First and second condensate trap, respectively
Superscripts	
^{0}	Saturation conditions
Overline	
$\bar{\ }$	Mean value

3. EXPERIMENTAL

Apparatus. A schematic representation of the system is given in Fig. 1. It is convenient to divide it into three different parts: (a) feed of chemicals, (b) evaporator–reactor unit, and (c) sample condensation traps.

The liquid reagents (mixtures of 2-propanol and water or 2-propanol and ether) were fed from a vessel (A) above which has been placed a tube (B) filled with calcium chloride, at the air inlet. The liquid passed through a flow regulator (C), formed by a piece of capillary tube (1-mm ID, approximately 20 cm long), in which was inserted a stainless steel wire, whose diameter was only a few tenths of a millimeter smaller than that of the capillary tube. The flow rate was very sensitive to the wire length inserted. From here the liquid passed to a flow meter (D) and afterwards to the reactor (H).

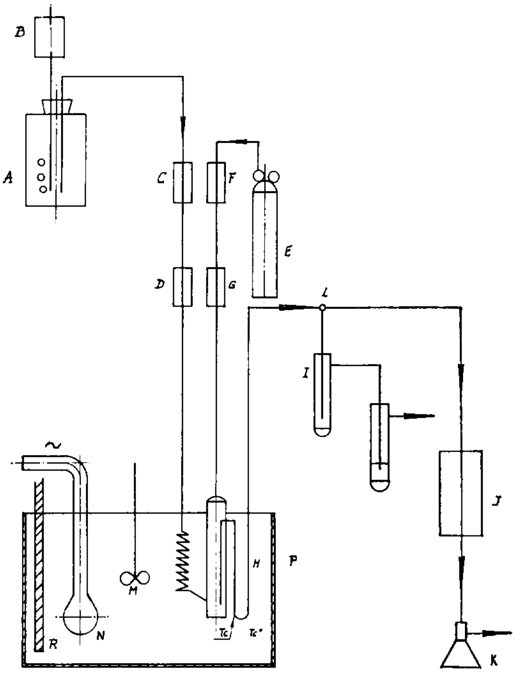

FIG. 1. Schematic flow diagram.

The gases (nitrogen and propylene) were fed from tubes through a bed of calcium chloride (F) and a flow meter (G), to the reactor (H). In all the cases where both gases were fed simultaneously they were mixed after the flow meters (in Fig. 1, only one gas line is shown).

The output of the reactor passed through a tube heated electrically to avoid condensation. Normally the stream of gases was directed to (K). The water cooling jacket (J) was placed to minimize the escape of condensables to the atmosphere. Operating the three-way glass stopcock key (L) appropriately, it was possible to force the stream to pass through two condensation traps (I). They were submerged in baths of solid CO_2-acetone (the temperature being approximately —72°C); the first trap was empty while the second always contained a known amount of 2-propanol to increase the effectiveness of the condensation of propylene carried by the nitrogen stream. This method was checked by circulation of gas mixtures of known composition. Furthermore no appreciable amount of propylene was detected when a third trap containing 2-propanol was added to the system. When water had to be analyzed the trap tubes were kept in a dry nitrogen atmosphere before their assembly.

The more important part of the equipment was the evaporator–reactor unit described in Fig. 2. It had two coils: one (B) for the liquid flow evaporation, and the second (not shown) for preheating the gas stream. The internal diameter of both coils was 8 mm. Both streams were mixed in (D), in which is indicated the entrance of the gas stream (C). The internal diameter of the mixer tube was 4 cm and it was filled with glass spheres of 2 mm diameter. It has been proven experimentally that this tube was necessary to provide a steady evaporation of the liquid stream. The gas mixture passed to the reactor (F) through a small tube. The reactor was made by a glass tube of 6 mm ID, in U shape. While the gasket (E) allowed the introduction of a thermocouple, through the other gasket (H) it was possible to place the catalyst between two layers of glass powder of the same mean size as the catalyst itself. The reacted gases left the reactor through the gasket (G) which was connected to the condensation system. The arrows in Fig. 2 indicate the direction of the stream.

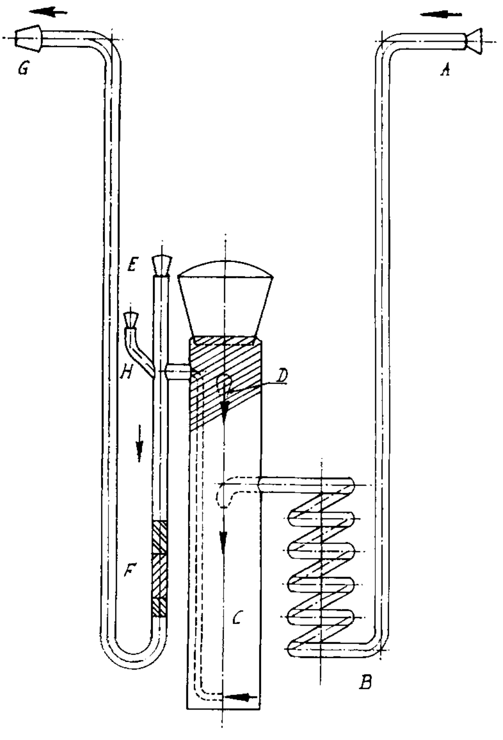

FIG. 2. Reactor–evaporator assembly.

The whole unit was placed in a thermostated electrically heated oil bath, the precision being 0.1°C over the working temperature range. A more detailed description of the apparatus is given elsewhere (*6*).

Analysis of the Samples. Propylene and diisopropyl ether were analyzed in a Perkin-Elmer 800 chromatograph (flame-ionization detector) which used two columns (Carbowax 20-M) 2 m long. The carrier was nitrogen gas, the flow rate in both columns, 35 cc/min; temperature, 100°C; samples from 1 to 10 μl.

Water content was analyzed in an F.M. chromatograph (catharometer detector) using a column 2 m long (diglycerol supported on Chromosorb P silanized). Temperature of the columns: 70–100°C; the filament operated between 80 and 120 mA; samples injected, from 10 to 100 μl.

Catalyst and chemicals. The catalyst was Amberlite I.R. 200 (Rohm & Haas) in the acid form. The resin was acidified in the usual way and when no traces of Cl^- were observed in the washing water, the catalyst was dried under vacuum condition and stored in a vessel of constant humidity after being size-clasified. The size used was Tyler mesh 20–40. The experimental value of the number of equivalents per unit mass of dried catalyst was 4 meq/g.

Whenever the catalyst was fed into the reactor another sample was taken and the content of water determined (15–20%). All the data are referred to the dry weight of the resin.

The specific surface was determined by

the N_2 adsorption isotherm method to be 40 m^2/g.

The chemicals used were as follows: 2-propanol pure (Sintorgan) (0.21% water, less than 1% of ethyl alcohol); distilled water; propylene Matheson (99.9%); diisopropyl ether (Baker Analyzed) (this chemical was repeatedly extracted with sulfuric acid until the content of 2-propanol and other alcohols was less than 0.5% and dried on sodium); and nitrogen gas (Autogena).

Reaction system and range of variables. The reaction system can be represented by the following reactions:

$$2A = E + W \quad (1)$$
$$A = P + W \quad (2)$$
$$E = 2P + W \quad (3)$$
$$E = A + P \quad (4)$$

In a differential reactor, fed with pure alcohol, the last two reactions can be neglected. Furthermore in those runs in which ether was added in feeding stream, no appreciable changes in the rate of production of propylene were observed; while when pure ether was fed this rate was found to be approximately 3 times less with respect to pure alcohol feeding under the same conditions.

The reverse reaction (4) has been taken into account, as is shown later.

The influence of each variable was studied for fixed conditions of all the others (the N_2 was used as inert gas).

The range of variation of each variable is given in Table 1.

TABLE 1

Variables	Range
p_A (atm)	0.340–0.992
p_W (atm)	0.001–0.497
p_E (atm)	6×10^{-6}–0.428
p_P (atm)	10^{-6}–0.519
T (°C)	87–112
M (g)	0.520–1.145
F (mole/hr)	0.480–1.925

The total number of runs considered satisfactory was 109.

Preliminary tests. No appreciable conversion was observed when the reactor was operated without catalyst. The temperature was 112°C.

In other runs the conversion was 0.015 and no appreciable difference in temperature with respect to the oil bath was observed when a thermocouple was inserted in the reactor. Thus in later runs when the conversion was always less than the above value, the thermocouple was omitted. The stoichiometry of reactions (1) and (2) was checked when pure alcohol was fed.

The time necessary to reach steady state was approximately 30 min. A substantial modification of the flow rate, after this was achieved, needed another 30 min to again reach steady state. In all the cases a minimum time of 1 hr was allowed before taking samples.

4. CALCULATIONS

The rate for reaction (1) was calculated according to

$$r_1 = 2F_L X_L/M \quad (1)$$

providing that no ether was observed in the second trap (this happened in most of the runs).

For the second reaction (2)
but

$$r_2 = F_L X_P/M \quad (2)$$

$$X_P = (X_P)_I + (m_A/PM_A F_L t)(X_P)_{II} \quad (3)$$

where the suffixes I and II refer to the first and second trap, respectively; t is the time in which the (m_A/PM_A) moles of isopropyl alcohol placed in the second trap have been exposed to the impurified nitrogen stream. It is clear that the error of the measurement of the second rate of reaction is greater than the first one.

When ether or propylene were fed water was analyzed instead of one of them.

For all the calculations ideal behavior was assumed and the value of partial pressure given in Table 2 are the arithmetic means throughout the reactor.

Both the external and internal diffusional resistances were neglected after calculations: the latter using the Weisz and Prater (*13*) criteria. Also the Anderson criteria (*14*) were applied before neglecting the

TABLE 2
SUMMARY OF RESULTS

T (°C)	p_A (atm)	p_W (atm)	p_E (atm)	p_P (atm)	$r_1 \times 10^4$ (mole/hr g cat)		$r_2 \times 10^4$ (mole/hr g cat)		
					Expt.	Calc.	Expt.	Calc	(g)
110°	0.928	0.0125	0.0025	0.0016	71.72	83.7	23.49	23.70	0.977
110°	0.601	0.0073	0.0014	0.0014	71.01	77.5	26.70	29.0	0.977
110°	0.649	0.156	0.00065	0.00041	34.66	37.9	10.60	7.7	0.658
110°	0.485	0.0062	0.389	0.0016	77.20	80.0	23.58	23.1	1.145
110°	0.409	0.0025	0.0011	0.328	83.2	71.5	19.9	23.1	1.145
100°	0.856	0.0070	0.0006	0.0003	28.15	27.5	6.84	7.76	0.977
100°	0.515	0.122	0.0002	0.00006	12.41	12.95	2.03	2.66	0.658
100°	0.540	0.0045	0.428	0.0006	18.9	20.1	7.80	8.06	1.145
100°	0.380	0.0012	0.0004	0.519	24.7	25.7	6.65	7.30	1.145
90°	0.992	0.0076	0.0004	0.0002	13.10	10.5	3.06	2.58	0.977
90°	0.484	0.114	0.0004	0.000006	2.60	3.01	0.21	0.27	0.658

possibility of an internal temperature gradient. The equilibrium constants of both reactions were calculated from data of Hougen and Watson (*15*). The values are $K_1 = 92.55$ and $K_2 = 316$ at 90°C.

5. DISCUSSION OF THE RESULTS

A short account of the results obtained is given in Table 2. All the data can be seen elsewhere (*6*).

The influence of the partial pressure of alcohol in both reactions is presented in Fig. 3. The partial pressure of the other components is very near to zero. The same behavior has been observed at 100° and 110°C. Other data, feeding the reactor with pure alcohol, were obtained at temperatures of 96.5°, 107.5°, and 112°C and the apparent energy of activation under these conditions has been determined to be $\bar{E}_1 = 24.0$ and $\bar{E}_2 = 28.6$ kcal/mole. The order of the reaction with respect to the alcohol is very near to zero and the same result has been found when pure ethyl alcohol was fed to the reactor, although in this case no appreciable detection of ethylene was observed.

Both the order of the reaction and the

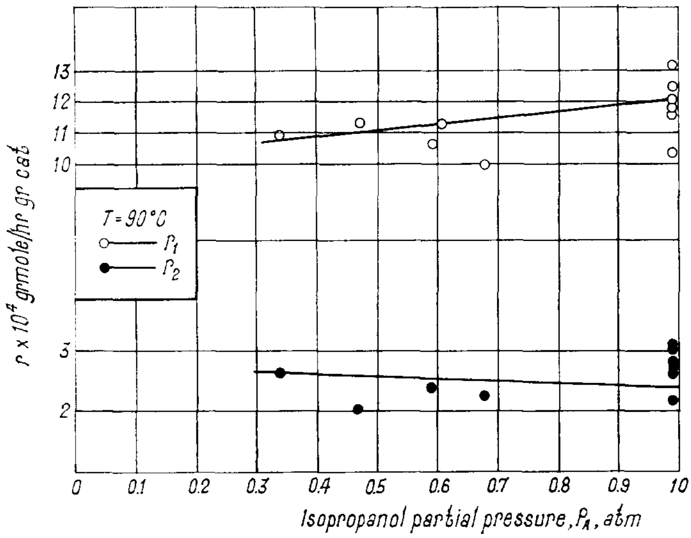

FIG. 3. Influence of isopropanol partial pressure upon reaction rate for both reactions.

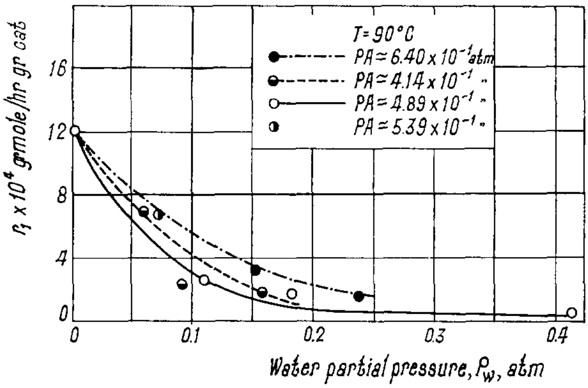

FIG. 4. Influence of water partial pressure upon reaction rate for the first reaction and for different alcohol partial pressures.

energy of activation are in general agreement with Stauffer *et al.* (*16*) and Mourgues *et al.* (*17*).

Keeping in mind a Langmuir-Hinshelwood model we should expect that the only possible mechanisms that can explain the behavior of the partial pressure of alcohol are surface reaction or desorption as controlling steps.

In Figs. 4 and 5 is presented the influence of the water on the rate of reaction for different partial pressures of alcohol. The water strongly inhibited the dehydration, so desorption cannot be the controlling step. This behavior has been observed by many authors working with inorganic catalysts, the more recent one in addition to those mentioned above, being de Boer *et al.* (*18*). Also Kabel and Johnson (*12*), using a synthetic resin as catalyst, observed a strong influence of the partial pressure of water on the velocity of reaction.

On the other hand, when ether was fed, no appreciable change in the rate of production of propylene was observed, and this is also in general agreement with the observations of de Boer *et al.* (*18*), mainly because the ether produced is easily desorbed without any chance of being readsorbed in the presence of the alcohol. Then we conclude that the ether desorption cannot be the controlling step. The influence of the partial pressure of propylene was also found to be negligible.

Taking into account all these arguments, we should expect that a model in which only alcohol and water compete for the active centers must be able to correlate the data.

The similarity of behavior between the ion exchange resin and the alumina as catalysts is also remarkable, and the mechanism is likely to be the same in both of them.

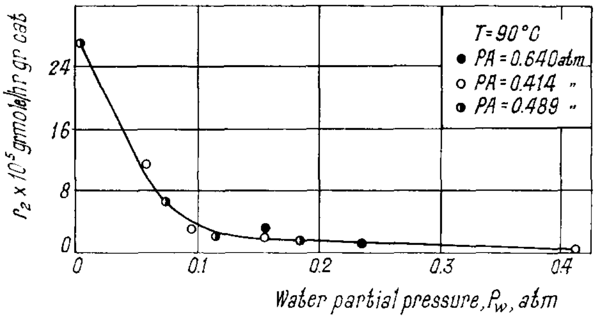

FIG. 5. Influence of water partial pressure upon reaction rate for the second reaction and for different alcohol partial pressures.

TABLE 3

Probable Mechanisms of Reaction (1)

Case	Controlling step	Kinetic expression	Regression equation
1	$A_s + A_s = W_s + E_s$	$r_1 = \frac{kK_A{}^2p_A{}^2}{(1 + K_Ap_A + K_Wp_W + K_Ep_E)^2}$	$y = p_A/(r_1)^{1/2} = a + bp_A + cp_W + dp_E$
2	$E_s = E + s$ $(A_s + A_s = W_s + E_s)$ $(A_s + A + s = W_s + E_s)$	$r_1 = \frac{k_EK(p_A{}^2/p_{WW})}{1 + K_Ap_A + K_Wp_W + KK_E(p_A{}^2/p_W)}$	$y = \frac{1}{r_1} = a\frac{p_W}{p_A{}^2} + b\frac{p_W}{p_A} + c\frac{p_W{}^2}{p_A{}^2} + d$
3	$E_s = E + s$ $(A_s + A = E_s + W)$ $(A_s + A_s = E_s + W + s)$	$r_1 = \frac{kK(p_A{}^2/p_W)}{1 + K_Ap_A + KK_E(p_A{}^2/p_W)}$	$y = \frac{1}{r_1} = a\frac{p_W}{p_A{}^2} + b\frac{p_W}{p_A} + c$

TABLE 4
Regression Coefficients for Different Mechanisms of Reaction (1)

Case	a	b	c	d	$\sigma/\bar{y}$
		Temperature 110°C			
1	−2.37	13.99	37.86	2.59	0.135
2	1,708	−927	2,364	134	0.07
3	1,998	−331	125	—	0.03
		Temperature 100°C			
1	−2.58	21.34	66.4	7.6	0.132
2	−4,049	8,294	7,303	382.1	0.265
3	−8,078	6,096	381.8	—	0.140
		Temperature 90°C			
1	−0.646	28.76	136.3	11.0	0.077
2	−1,474	8,962	21,285	847.7	0.136
3	−9,346	12,728	835.1	—	0.148

6. DATA CORRELATION

All the equations arising from the consideration of the different controlling steps in the Langmuir-Hinshelwood model have been considered for the data correlation. After linearizing them according to Hougen and Watson (*12*), the coefficients were determined using a standard program of the least-squares method on a Mercury-Ferranti digital computer. The reversibility of the reactions was neglected.

A. Reaction (1)

The only mechanisms in which the mean error was less than 50% are given in Table 3 (σ being the standard deviation and $\bar{y}$ is the mean value of the experimental data according to the definition in Table 3). As we have expected the value of the constant of adsorption of ether is very small and can be neglected. All the correlations presented have a negative coefficient (see Table 4). However with a t test, it has been proven (*6*) that the only constant in which the error is greater than its own value was a in case 1. Writing the kinetic expression for this case:

$$r_1 = \frac{k(K_A p_A)^2}{(1 + K_A p_A + K_w p_w)^2} \qquad (4)$$

it will fit the data presented in Fig. 3, only if

$$K_A p_A \ll 1 \qquad (5)$$

Applying Eq. (5), we can rewrite Eq. (4) in the form

$$\left(\frac{1}{r_1}\right)^{1/2} = \left(\frac{1}{k}\right)^{1/2} + \left(\frac{K_w p_w}{K_A p_A}\right) \qquad (6)$$

TABLE 5
Data Correlation for $(p_w/p_w^0) < 0.20$ for Reaction (1)

Case	a	b	c	d	$\sigma/\bar{y}$
		Temperature 110°C			
1	−1.196	13.2	24.4	0.7	0.067
2	1,196	−1,210	1,630	136	0.16
3	−2,060	−756.7	128.1	—	0.06
		Temperature 100°C			
1	0.56	18.1	36.1	0.7	0.055
2	−140	1,046	3,360	394.6	0.03
3	−10,086	6,013	338.5	—	0.129
		Temperature 90°C			
1	0.403	27.8	122.6	9.5	0.092
2	1,738	−16,434	107,606	1,014	0.120
3	−10,086	12,931	838.0	—	0.136

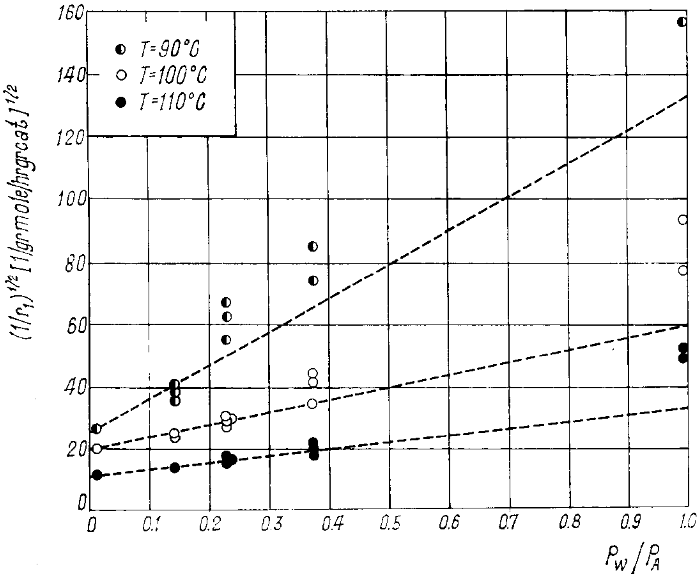

FIG. 6. Correlation of reaction rate with water partial pressure for different temperatures.

In Fig. 6 $(1/r_1)^{1/2}$ vs. (p_W/p_A) is plotted and it is possible to see that Eq. (6) only fits the data in a reduced range of partial pressure of water. Furthermore, it depends upon the temperature, being smaller as the temperature decreases, but reducing the partial pressure of water with respect to its normal pressure at the given temperature it appears that Eq. (6) fits the data for $p_W/p_W^0 < 0.20$.

All the data refered to in the above statement were correlated again and the results are presented in Table 5. Now, it is possible to say that the most probable mechanism is that of case 1 in which the dual surface reaction is the controlling step. The only problem which arose was that the value of the constant a at 110°C was -1.20 ± 1.15. We repeated this calculation setting the value $a = 0.60$ (given by Fig. 6) and the mean error of the calculated data varied from 10% to 12% approximately.

The best explanation we found for this is that the covariance of the data is high, making all the constants heavily dependent one with the others. Watson *et al.* (*20, 21*) presented a very good discussion on this subject and also showed that a better determination of the constants can be found if the experiments were properly designed, although in our case this could not be done, mainly because the reaction kinetics were unknown.

The calculated values of the reaction rate are represented in Fig. 7 vs. the experimental ones, the mean error being 10.5% for all the data excluding those for which $p_W/p_W^0 > 0.20$. No good correlation has been found for all the data, which is in agreement with other authors (*10, 11, 17*) working with resin and inorganic catalysts. It is likely that the water played not only a chemical role but also a physical one, which is not taken into account in a Langmuir-Hinshelwood model. The possibility of condensation in small capillaries and the formation of azeotropes (*22*) cannot be excluded.

B. Reaction (2)

The procedure and the model used to find the best correlation is essentially the same, and the surface reaction on two adjacent sites ($A_s + s = W_s + P_s$) seems to be the most probable controlling step. The kinetic expression is given by

$$r_2 = \frac{kK_Ap_A}{(1 + K_Ap_A + K_wp_w + K_Ep_E + K_Pp_P)^2} \tag{7}$$

and the linearized correlated expression was

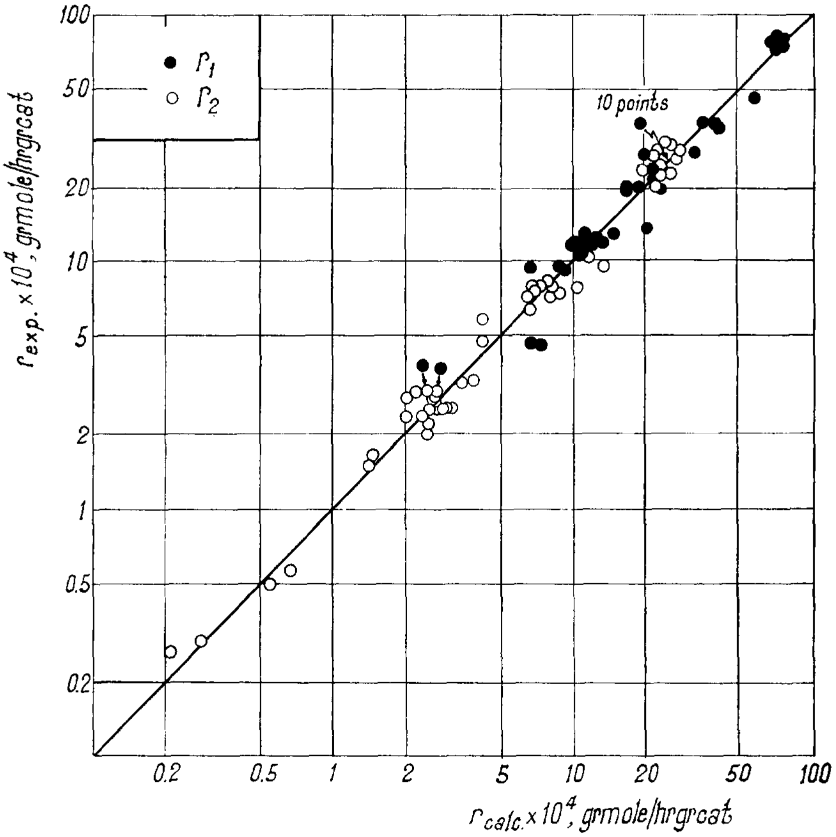

FIG. 7. General correlation of experimental results.

$$(p_A/r_2)^{1/2} = a + bp_A + cp_w + dp_E + ep_P \tag{8}$$

Again the data were separated in two groups according to the value of p_W/p_W^0, and in Table 6 the values of the coefficients are given. In comparison with the data taken as a whole, it seems that in the restricted range $p_W/p_W^0 < 0.20$ the accuracy of Eq. (7) has increased, as is shown by the relation $\sigma/\bar{y}$. We deduce from Table 7 that the values of the adsorption constants of ether and propylene are low enough to be negligible and both water and alcohol adsorption constants have an anomalous behavior with temperature, which again shows the covariance of the experimental data. It could be possible to correct this behavior by means of a nonlinear regression, as proposed by Watson *et al.* (*20*) but we don't think it is worthwhile to perform such complicated

TABLE 6

DATA CORRELATION FOR REACTION (2)

$p_w/p_w^0 < 0.20$

T(°C)	a	b	c	d	e	$\sigma/\bar{y}$
110°	4.46	15.36	93.54	5.05	6.68	0.12
100°	17.34	17.16	168	−3.6	−2.58	0.074
90°	20.8	34.9	849	3.61	7.12	0.158
			All the data			
110°	−3.27	24.4	126.7	13.7	16.2	0.25
100°	2.26	34.4	251.7	13.5	16.0	0.20
90°	16.3	40.3	810	9.1	12.7	0.135

TABLE 7
Kinetic Parameters

T(°C)	Reaction (1)			Reaction (2)		
	90°	100°	110°	90°	100°	110°
$k_1 \times 10^3$ (mole/hr g cat)	1.29	3.03	9.3	1.37	3.35	14.5
K_A (atm^{-1})	69.0	32.6	17.25	1.68	0.99	3.44
K_W (atm^{-1})	304	63.4	34.5	40.7	9.67	20.95
K_E (atm^{-1})	23.6	6.4	−0.6	0.2	−0.2	1.1
K_P (atm^{-1})	—	—	—	0.3	−0.15	1.5

calculations, mainly because in this case a Langmuir-Hinshelwood model cannot fully explain the behavior of the resin catalyst.

The plot of the calculated reaction rate vs. the experimental one is presented in Fig. 7 also; the mean error is 14% for all the data excluding those in which $p_W/p_W^0 > 0.20$.

Finally, it should be of interest to say that Frilette *et al.* (*5*) presented a very simple model to correlate their data, showing good agreement between experimental and calculated results. However, according to their Figs. 3 and 4, the scattering of the experimental points along the regression line seems to increase with water partial pressure.

The two equivalent expressions of reaction rates for our case were tested by us without any success.

7. Conclusions

The dehydration of 2-propanol has been studied at three different temperatures (90°, 100°, and 110°C). Both diisopropyl ether and propylene have been detected.

The activation energy and the order of reaction with respect to the alcohol have been found to be in agreement with the reaction kinetics studied over inorganic catalysts (*17*). No satisfactory correlation of data was found using a Langmuir-Hinshelwood model as has also been found by other authors (*10, 11, 17*). However, it was possible to correlate the data in a reduced range of partial pressures of water (p_W/p_W^0) < 0.20; the controlling steps are the dual surface reactions in both cases. The values of the constants for both kinetic expressions [see Eqs. (4) and (7)] are given in Table 7.

From the fact that the point $p_W/p_W^0 = 0.20$ is reported by Helferich (*7*) to be just the zone where the physical adsorption of water in ion exchange resins begins, we conclude that the water can play an important physical role in the inhibition of the reaction.

Another important conclusion is that the selectivity of the resin for the ether did not change appreciably in the presence of alcohol.

References

1. Bafna, S. L., *Proc. Natl. Acad. Sci. India Sect. A* **23**, Pt. 6, 63 (1954).

2. Glenat, R., *Chim. Ind.* **75**, 292 (1956).

3. Helfferich, F., *Angew. Chem.* **66**, 241 (1956).

4. Lister, B. A. J., *Ind. Chemist* **32**, 627 (1956).

5. Nachod, F. C., Research Council of Israel, Spec. Publ. No. 1, 7, 117 (1967).

6. Gottifredi, J. C., Doctoral Thesis, Facultad de Ciencias Exactas y Naturales (U.N.B.A.), Argentina, 1966.

7. Helfferich, F. "Ion Exchange," p. 107. McGraw-Hill, 1962.

8. Saletan, D. I., and White, R., *Chem. Eng. Progr. Symp. Ser., Reaction Kinetics* **48**, 59 (1952).

9. Frish, N. W., *Chem. Eng. Sci.* **17**, 735 (1962).

10. Ehrreich, I. E., and Metzner, A. E., *A.I.Ch.E. J.* **2**, 496 (1959).

11. Metzner, A. E., Lashmet, P. K., and Ehrreich, I. E., *Actes Intem. Congr. Catalyse, 2e, Paris, 1960,* p. 735 (1961).

12. Kabel, R., and Johnson, L. N., *A.I.Ch.E. J.* **8**, 621 (1962).

13. Weisz, P. B., and Prater, C. D., *Advan. Catalysis* **6**, 143 (1954).

14. Anderson, J. B., *Chem. Eng. Sci.* **18,** 147 (1963).

15. Hougen, O. A., Watson, K. M., and Ragatz, M. A., "Chemical Process Principles," Vol. 2. Wiley, New York, 1948.

16. Stauffer, I. E., and Kranich, W. L., *I.E.C. Fundamentals* **1,** 107 (1962).

17. Mourgues, L. de, Peyron, F., Trambouze, Y., and Prette, M., *J. Catalysis* **7,** 117 (1967).

18. de Boer, J. H., Fahim, R. B., Linsen, B. G., Visserin, W. J., and Vleesschauwer, W. F. N. M., *J. Catalysis* **7,** 163 (1967).

19. Hougen, O. A., and Watson, K. M., "Chemical Process Principles," Vol. 3. Wiley, New York, 1948.

20. Watson, C. C., Kittrel, J. R., and Mesaki, R., *Ind. Eng. Chem.* **57,** 18 (1965).

21. Watson, C. C., Kittrel, J. R., and Hunter, W. G., *A.I.Ch.E. J.* **12,** 5 (1966).

22. Reeds, J. M., and Kammermeyer, M., *Ind. Eng. Chem.* **51,** 707 (1959).

23. Frilette, V. J., Mower, E. B., and Rubin, M. K., *J. Catalysis* **3,** 25 (1964).