

Vapor-Phase Reactions Catalyzed by Ion Exchange Resins

II. Isopropanol-Acetic Acid Esterification

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A kinetic study of the esterification of isopropyl alcohol with acetic acid is presented. The experimental procedure is essentially the same described in Part I. The measurements have been done at three different temperatures (110°, 116°, and 120°C). In this case it was found that the experimental data are explained fairly well by a Hinshelwood-Langmuir model. Water inhibited the reaction but its effect is very much reduced in comparison with the alcohol dehydration studied in Part I. The influence of both reactants is also important and no general order of reaction with respect to them can be deduced, although the order with respect to the alcohol tends to zero as its partial pressure increases. Evidence has been found that both reactions (esterification and dehydration) proceed through the same rate mechanism. A general comparison with published data using inorganic catalysts seems to indicate that it is the acid sites which determine the mechanism of reaction.

1. INTRODUCTION

The esterification of alcohol with acetic acid has been studied intensively both in the liquid and gas phases.

The rate of reaction is very slow without catalyst, and most work in the liquid phase has been done in the presence of mineral acids; some authors (1, 2, 3) have also reported as catalysts F_3B , F_4Si , and acid sulfates.

In the gas phase a number of different oxides (ZrO_2 , TiO_2 , ThO_2 , and WO_3) have been used (4, 5), as well as silica gel (6, 7) and active coal impregnated with phosphoric acid (8, 9).

No previous kinetic information has been found for the esterification of 2-propanol

with acetic acid in the gas phase, catalyzed by ion exchange resins. Neither, Andrianova (4) and Hermann (10) reported a kinetic expression for the correlation of their data.

In Part I of this paper (preceding paper), it was found that the correlation of the data for the dehydration of 2-propanol was very difficult. It is possible that water may play some physical role which is not included in the classical model. The presence of acetic acid could reduce the availability of the active sites for the water, but only if the acetic acid were adsorbed on the surface of the catalyst. In fact, recently Bochner *et al.* (11) studied the liquid-phase esterification of methanol with salicylic acid and found the surface reaction to be the controlling step. They used ion exchange resin as catalyst, which makes the result remarkable in view of the size of the salicylic acid molecules and the excess of methanol present. Several authors have also reported the surface reaction to be controlling step (12), although others have reported the adsorption of the acid to be the predominant mechanism (6, 13). In any case we should

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expect a reduction in the effect of the water in comparison with the dehydration, for the acetic acid is likely to be adsorbed on the surface of the resin.

Making use of the above argument the esterification of 2-propanol with acetic acid has been studied, using the same catalyst reported in Part I, and maintaining the relative partial pressure (p_w/p_w^0) below 0.25. Thus it should be possible to represent the kinetics by a Langmuir-Hinshelwood model.

2. EXPERIMENTAL

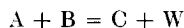
Equipment. The equipment used was essentially the same as that described in Part I, the only difference being that there were two lines whereby 2-propanol and acetic acid were fed to the reactor. This was found necessary because a homogeneous reaction was observed when only one flask was used to feed the reactor; in fact, after a few hours the solution prepared showed an appreciable amount of isopropyl acetate. Thus the reactor was slightly modified. The acetic acid entered the evaporator-reactor unit through the same coil presented in Fig. 2 of Part I, while the alcohol reached the unit through a coil connected to the tube joining the reactor with the container filled with glass spheres.

Analysis of the samples. Both the chromatographs and the operating conditions were the same as described in Part I. The only substance analyzed was isopropyl acetate, and whenever this substance was fed the water was analyzed following the same procedure described in Part I.

Catalyst and chemicals. The catalyst was the same as described in Part I, and the new chemicals used were as follows: acetic acid "Atanor" (no traces of impurities were detected by chromatographic analysis); isopropyl acetate, purified by water extraction and dried over magnesium sulfate (final content of water 0.10%, weight basis).

System of reaction and range of variables. The only reaction detected was the esterification, and no traces of diisopropyl ether

or propylene were observed. The reaction is represented by¹



The influence of each variable was studied, keeping all the others constant. The range of each of them is given in Table 1. The total number of runs considered satisfactory was 86.

TABLE 1
VARIABLES RANGE

p_A (atm)	0.191-0.630
p_B (atm)	0.096-0.490
p_C (atm)	0.0003-0.396
p_W (atm)	0.004-0.407
T (°C)	110-120
M (g)	0.073-0.181
F (mole/hr)	0.80-1.70

Preliminary tests. When the reagents were fed to the reactor in the absence of catalyst, no appreciable amount of isopropyl acetate was detected. No temperature gradient between the reactor and the oil bath for conversion up to 2% was observed. During the experimental measurements conversion was always smaller than this and for this reason the thermocouple was omitted.

A rather interesting phenomenon was observed when the flow of nitrogen was very high or its partial pressure was greater than 0.60 atm. Under this condition a continuous deactivation of the catalyst occurred but by decreasing the nitrogen flow the activity was slowly reestablished. When this phenomenon took place, a loss of catalyst weight was noticed, thus we concluded that the cause must be ascribed to a partial dehydration of the resin. This "deswelling" decreases the sites accessibility and thus the resin deactivates progressively.

The steady state was reached in 1 hr approximately; consequently at least 2 hr elapsed before samples were taken.

¹The notation is the same as given in Part I, the only difference being the new subscripts B and C, referring to acetic acid and isopropyl acetate, respectively.

Calculations. The calculations methods have been indicated in Part I. In these experiments the first trap was submerged in an ice bath to avoid the solidification of acetic acid, and under this condition when the flow of nitrogen was high isopropyl acetate was detected in the second trap.

The value of the equilibrium constant at 120°C has been estimated from thermodynamic data (14) ($K = 3.16$).

A simple calculation showed external diffusion control to be unlikely, although due to the small value of the equilibrium constant internal diffusion can make the reversibility of the reaction important in spite of the differential character of the reactor, as described by Maymo and Cunningham (15). This possibility was checked experimentally by changing the size of the catalyst particles (Tyler mesh 80–100) and found to be negligible. The experimental values of the velocity of reaction for different conditions of partial pressures of reagents changed randomly and the mean difference (about 5%), can be considered within the experimental error, by comparison with the data determined with particle size Tyler mesh 20–40. The internal temperature gradient has been estimated to be negligible.

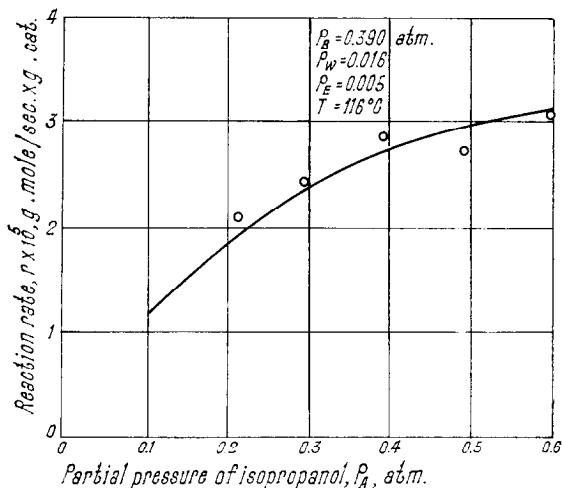


FIG. 1. Influence of isopropanol partial pressure upon reaction rate for different reaction mixture compositions.

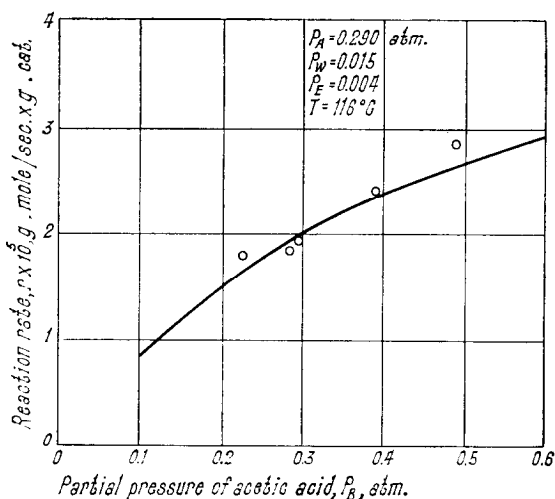


FIG. 2. Influence of acetic acid partial pressure upon reaction rate for different reaction mixture compositions.

3. DISCUSSION OF THE RESULTS

Some of the results are presented in Table 2, and in Figs. 1 and 2 are presented the influence of the partial pressures of alcohol and acetic acid on the rate of reaction at 116°C, respectively.

Using a Langmuir-Hinshelwood model it is possible to deduce that neither the desorption of products nor the adsorption of one of the two reagents are likely to be the controlling step, and the surface reaction over two adjacent sites seems to be the most probable one.

The influence of the partial pressure of water is presented in Fig. 3. It can be seen that the reaction is inhibited, but not so strongly as in the dehydration of isopropyl alcohol presented in Part I, although it is still important. Its effect is approximately the same at the three temperatures at which the reaction has been studied. In this case the possibility of the water inhibiting the reaction is less in comparison with the dehydration reaction (Part I) where the alcohol is the only other substance present; the water now has to compete with two species for the active sites. In fact, the effect of isopropyl acetate is presented in Fig. 4, and turns out to be negligible.

TABLE 2
 SUMMARY OF RESULTS

T (°C)	p_A (atm)	p_B (atm)	p_C (atm)	p_W (atm)	$r \times 10^5$		M (g)
					Expt. (mole/sec. gr. cat.)	Calc.	
120°	0.589	0.289	0.006	0.017	3.22	2.90	0.121
120°	0.391	0.291	0.005	0.015	2.53	2.48	0.121
120°	0.293	0.490	0.004	0.015	3.46	3.28	0.073
120°	0.191	0.191	0.400	0.020	1.23	1.17	0.073
116°	0.590	0.293	0.005	0.015	2.27	2.58	0.121
116°	0.194	0.391	0.003	0.014	2.21	1.89	0.121
116°	0.197	0.196	0.001	0.107	1.03	0.99	0.073
111°	0.592	0.194	0.002	0.011	1.59	1.62	0.121
111°	0.295	0.195	0.002	0.009	1.36	1.17	0.121
111°	0.195	0.194	0.0005	0.414	0.48	0.40	0.121

From Fig. 1 it is possible to observe that after a value of alcohol partial pressure of 0.40, the order of reaction with respect to this substance tends to be zero. This and the fact that the three reactions studied (in Parts I and II) take place over two adjacent sites, are strong indications that both reactions (esterification and dehydration) can be governed by the same mechanism.

In Part I, it has been shown that a general similarity in mechanism exists between ion exchange resin and alumina as catalysts. Taking into account the above arguments and the fact that an ion ex-

change resin only has acid sites it is possible to conclude that the acid sites must be the cause of this similarity. This can be interpreted as a support of the conclusion of Dzisko *et al.* (16).

It is possible that at higher temperatures only one site is involved instead of two, as was found by de Boer *et al.* (17).

4. CORRELATION OF THE DATA

All the possible mechanisms (the total number was 33) have been used to correlate the data and the best one is presented in Table 3. The values of the kinetic coefficients are given in Table 4. As we were

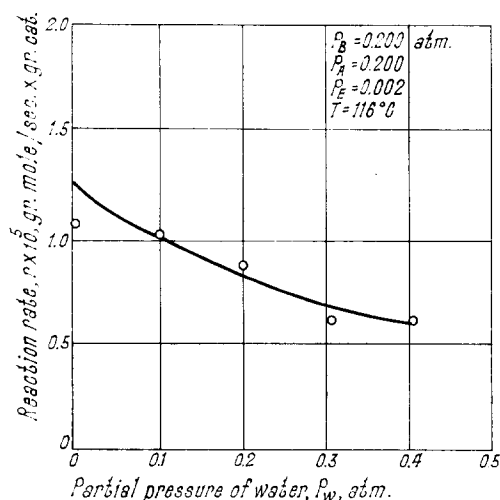


FIG. 3. Influence of water partial pressure upon reaction rate for different reaction mixture compositions.

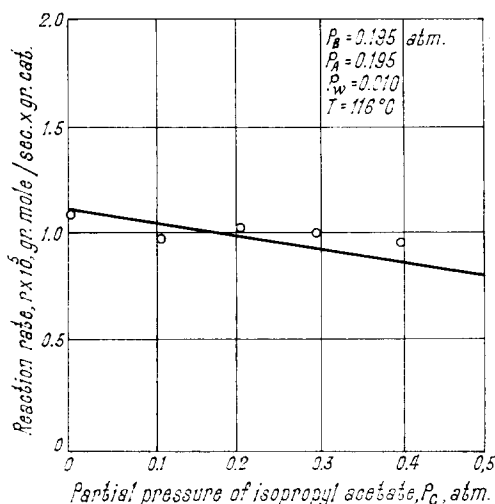


FIG. 4. Influence of isopropyl acetate partial pressure upon reaction rate for different reaction mixture compositions.

TABLE 3
PROPOSED MECHANISM

Case	Controlling step	Kinetic expression	Regression equation
1	$A_s + B_s = C_s + W_s$	$r = \frac{kK_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B + K_C p_C + K_W p_W)^2}$	$\left[\frac{p_A p_B}{r}\right]^{1/2} = a + b p_A + c p_B + d p_C + e p_W$

expecting, the most probable controlling step is the surface reaction on two adjacent sites. In all the cases the reversibility of the reaction was neglected and no problems arose in correlating the data with a Langmuir-Hinshelwood model.

The mean error of the correlation was found to be only 5.4% and the plot of experimental vs. calculated data is presented in Fig. 5.

TABLE 4
KINETIC PARAMETERS

	110°C	116°C	120°C
$k \times 10^4$ (mole/sec g cat)	2.75	4.8	15.4
K_A (atm ⁻¹)	1.07	1.50	1.0
K_B (atm ⁻¹)	1.96	1.03	0.33
K_W (atm ⁻¹)	1.76	1.75	1.12
K_C (atm ⁻¹)	0.39	0.38	-0.11

5. CONCLUSIONS

In the second part of this paper the esterification of isopropyl alcohol with acetic acid has been studied.

Using a Langmuir-Hinshelwood model a fairly good fit of the data has been found. The range of relative partial pressure of water (p_w/p_w^0) was smaller than in Part I of the present work. This in conjunction with the effect of the introduction of a second reactive component for the competition of active centers, explains the main reason for the discrepancies in the model in comparison with Part I.

It has been shown that both reactions (dehydration and esterification) are likely to take place through the same mechanism. Comparison with inorganic catalysts suggests that in general the velocity of reac-

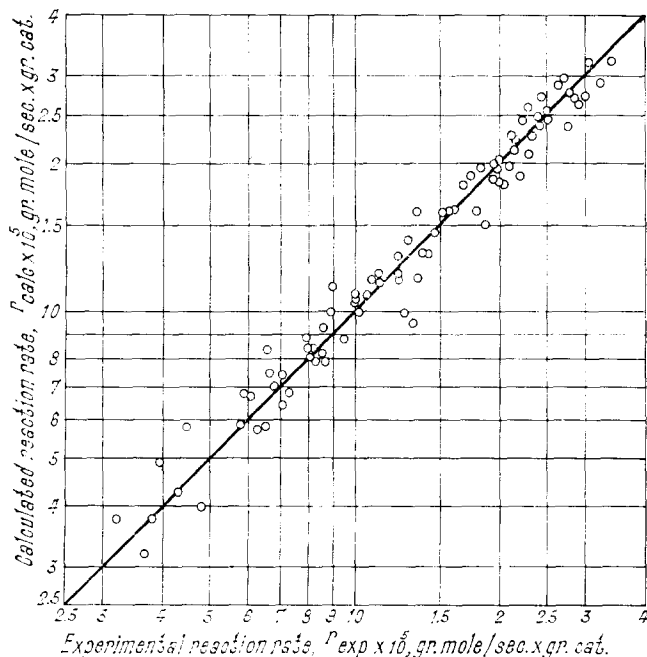


FIG. 5. General correlation of experimental results.

tion must be essentially dependent on the acidity of these catalysts.

In this case, the selectivity of the resins as catalysts was also observed, for no traces of diisopropyl ether or propylene were detected in the chromatographic analysis of the condensate samples.

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