K_c = controller gain; see Equation (8)
n = reaction order
q = flow rate
R = gas constant
T = temperature
t = time
U_a = overall heat transfer coefficient
U_c = heat transfer coefficient
V = reactor volume

Subscripts

av = average
c = coolant
f = feed
s = steady state

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Langmuir-Hinshelwood Kinetics of the Dehydration of Methanol Catalyzed by Cation Exchange Resin

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Rates of the dehydration of methanol to dimethyl ether catalyzed by cation exchange resin (polystyrenesulfonic acid) were measured with a differential flow reactor and gas chromatographic analysis. Reaction temperature was 119°C., pressure was 1 atm., and feeds were methanol and mixtures of methanol with argon, dimethyl ether, and water.

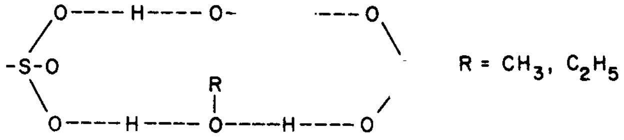
Rate data for the methanol reaction as well as the previously investigated ethanol dehydration reaction are well represented by Langmuir-Hinshelwood kinetics with adsorption parameters in the rate equations approximately equal to corresponding values of Langmuir adsorption equilibrium constants estimated from or available in the literature. The reaction model is consistent with previous conclusions regarding mechanism. Its pertinence suggests that at reaction conditions the ion exchange resin offers a nearly homogeneous array of catalytic sites.

Sulfonic acid ion exchange resins are active catalysts for the dehydration of alcohols to ethers and olefins. At sufficiently low temperatures ether formation from ethanol occurs without side reaction to olefin, as shown by Kabel and Johanson (*1*). In the following report the kinetic investigation of Kabel and Johanson is extended to the similar methanol dehydration.

$$2CH_3OH = H_2O + CH_3—O—CH_3$$

The alcohol dehydrations have a characteristic of general interest in catalytic kinetics, inhibition by a reaction product (water). The polymer catalyst is well suited to experimental investigation as it has a well-defined structure and is stable and of reproducible activity. The resin differs from typical solid catalysts in lacking rigid pores and true internal surface.

The methanol and ethanol dehydration reactions have been investigated with the resin catalyst in various ionic forms (*2*). Catalytic activity for reaction of each pure alcohol increased with catalyst sulfonic acid group concentration, and salt forms lacked activity. It was postulated that a hydrogen-bonded intermediate is formed involving reactant alcohol and catalyst sulfonic acid groups:



Similar bonds are formed between adjacent sulfonic acid groups alone (*3*) and also when water is bridged between sulfonic acid groups (*4*).

The kinetic data for ethanol dehydration have been examined by investigators concerned with statistical methods of parameter estimation and discrimination among reaction models (*5* to *7*). These analyses essentially confirm the

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original choice of a Langmuir-Hinshelwood model and evaluation of the parameters. A valuable check on the appropriateness of the heterogeneous reaction model was provided by adsorption equilibrium data obtained and utilized by Kabel and Johanson in the original ethanol study.

Rate equation parameters were of the magnitude suggested by the independently measured adsorption equilibrium constants for ethanol, ether, and water. The new data for methanol dehydration were measured under similar conditions. They strengthen the earlier conclusions by confirming the appropriateness of Langmuir-Hinshelwood kinetics.

EXPERIMENTAL PROCEDURE

Kinetic data were obtained in a flow reactor system with gas chromatographic analysis of product vapors. The equipment is described in the paper (*2*) concerned with the effects of resin exchange ion concentration on rate of pure alcohol dehydration. The equipment was modified to include one feed line for liquid (alcohol or alcohol-water) and another for gas (dimethyl ether or argon) to be mixed with vaporized alcohol. Gas feed flow rates were measured with rotameters. Other procedures are reported in reference *2*.

The catalyst was 20- to 50-mesh particles of Dowex 50 X-8, supplied in the hydrogen form by the Dow Chemical Company and used without pretreatment. Analysis by titration indicated the resin hydrogen exchange ion concentration was only 97% of the total exchange capacity. It is presumed the remaining exchange ions were sodium. The exchange capacity was 5.20 meq./g. of resin (weighed after dehydration under vacuum at 100°C.).

Kinetic measurements were made at steady state conditions with methanol, methanol-argon, methanol-dimethyl ether, and methanol-water feeds. Reactor pressure was atmospheric; corrections (always less than 2%) were made to account for deviations in pressure from 1 atm. Linear dependence of conversion on pressure was assumed. Reported rates are for reaction at 119°C.; additional rate data for lower temperatures are presented with the complete results and a detailed description of methods (*8*).

RESULTS AND DISCUSSION

Neither side reaction nor uncatalyzed reaction was observed. Periodic tests at standard conditions demonstrated the absence of catalyst activity loss in all but the noted instances. Most of the data were obtained at low conversions for the nearly irreversible reaction (*9*) to determine initial reaction rates. Some integral conversion data are presented in reference *8*. The influence of diffusion on rate has been shown to be negligible at the conditions of highest rate (*2*).

Representative data for low conversions are shown in Figure 1 for reaction of methanol feed at several temperatures. Data for methanol and methanol-water feeds at fractional conversions less than 0.07 were fitted with least-squares straight lines passing through the origin, with the slopes equal to initial rates, the results discussed here.

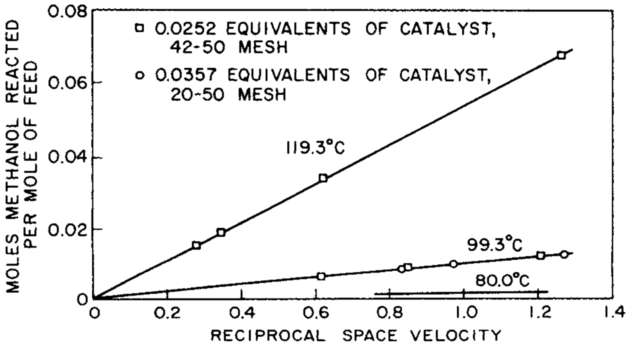

Fig. 1. Conversion data for methanol reaction.

For pure methanol feed the initial rates are precise within less than ±5%, the best precision of any of the data. Errors are the result of imprecision in individual product analyses (±3%), flow rate determinations (±1%), and catalyst titrations (±1%). Errors resulting from heat of reaction effects and departure from the assumed differential conversion are negligible.

Data for methanol-argon feed mixtures are presented in Figure 2. The precision was reduced somewhat as each reaction rate was calculated from only one conversion datum; it was not convenient to vary the feed flow rate while holding the ratio of methanol to argon flow rates constant. There are errors of more than +10% corresponding to temperature increases resulting from heat of reaction; compensating errors are the result of first a loss of catalyst activity, about −5% (probably caused by thermostat oil leaking to contact the catalyst), and second the assumption of differential conversion somewhat beyond the range of applicability, 0 to −5%. Net errors are estimated to be less than ±10%.

Results for methanol-dimethyl ether feeds are also shown in Figure 2. The large scatter is a consequence of imprecise analysis with feeds containing ether; conversion of methanol was determined from the difference of two nearly equal numbers. The data are reasonably well represented by the curve for methanol-argon feeds, suggesting that the effect of dimethyl ether is nearly the same as that of argon. The statement that dimethyl ether affects the rate as a diluent implies it does not compete with reactant methanol for catalytic sites. For the ethanol dehydration reaction Kabel and Johanson (*1*) concluded that the effect of diethyl ether was also essentially that of a diluent. Confirmation of the nonadsorbing nature of dimethyl ether is provided by a single adsorption datum at 100°C. and a dimethyl ether partial pressure of 0.92 atm. (*10*). Adsorption was observed corresponding to a Langmuir adsorption equilibrium constant for dimethyl ether which is less than 1% of the value found for water (*1*). This result is consistent with those of Kabel and Johanson and of Herlihy (*11*),

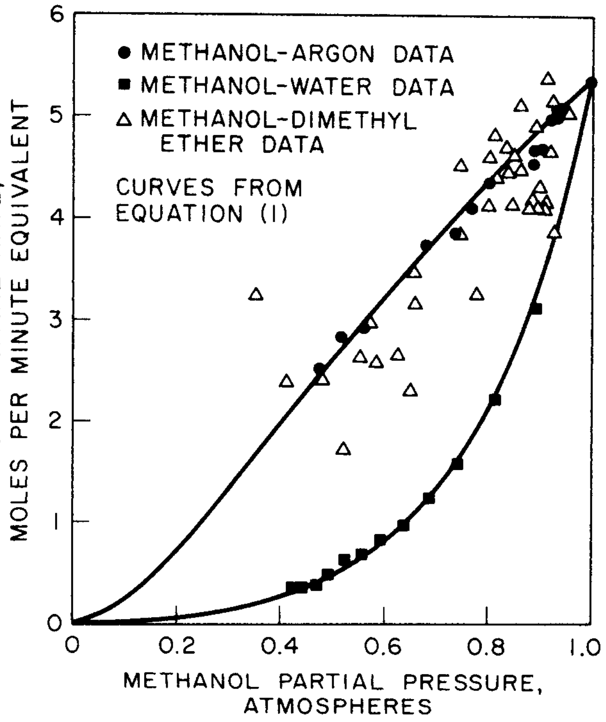

Fig. 2. Initial rate of methanol reaction at 119.3°C. Curves from Equation (1) with parameter values of Table 1.

who observed that the chemically similar diethyl ether is essentially not adsorbed by the catalyst at reaction conditions.

Results for methanol-water feeds are shown in Figure 2. Heat of reaction effects and approximately compensating catalyst activity losses influenced the precision of these data, which is estimated to be ±5%. Comparison with the methanol-argon data shows that water strongly depresses the rate and implies that water is bound to catalytic sites in competition with methanol. Confirmation of the conclusion is provided by the adsorption data of Kabel and Johanson and of Herlihy, which demonstrate that water and ethanol are both strongly chemisorbed by the catalyst at reaction conditions. Similar behavior is inferred for methanol as follows.

A single semiquantitative measurement of methanol adsorption by the catalyst was made at 100°C. and 0.54 atm. methanol partial pressure (*10*). An upper limit to adsorption was found corresponding to a Langmuir adsorption equilibrium constant for methanol considerably greater than the values obtained for the ethers, but somewhat less than the value obtained for ethanol (*1*). The bonding of methanol and ethanol vapors to resin sulfonic acid groups at 25°C. has been studied by Ulbricht (*12*), who made calorimetric and dielectric measurements and found methanol to be somewhat more strongly bonded than ethanol. Reichenberg and Wall (*13*) measured absorption by strongly hydrated resin of ethanol, *n*-propanol, and *n*-butanol from aqueous solutions at 25°C., and found almost no effect of alcohol chain length on degree of alcohol absorption. These results suggest that methanol and ethanol are adsorbed to approximately the same extent at reaction conditions.

APPROPRIATENESS OF THE LANGMUIR-HINSHELWOOD MODEL

The depressive effect of water on the methanol reaction rate suggests the applicability of a heterogeneous reaction model. Ideal (Langmuir) kinetics account for reaction on catalytic sites which can be saturated by competitively combining reactants and products. The Langmuir-Hinshelwood equation selected by Kabel and Johanson (*1*) for the ethanol reaction corresponds to the rate determining combination of two adjacently adsorbed alcohol molecules:

$$r = \frac{kK_A^2 p_A^2}{(1 + K_A p_A + K_E p_E + K_W p_W)^2} \tag{1}$$

This equation also provides a good representation of the methanol rate data* (Figure 2) with parameter values estimated by an unweighted linear least-squares procedure (*8*) with K_E, the adsorption equilibrium constant for ether, set equal to zero in agreement with ether's diluent effect. The parameters are given in the top line of Table 1; they are approximately equal to the corresponding estimates (*1*, *10*) of Langmuir adsorption equilibrium constants for reactant and products. This agreement is interpreted as evidence of the appropriateness of the reaction model. Further evidence is provided by the model's correspondence to the previously stated conclusion (*2*) that the rate determining reaction step occurs between two alcohol molecules bonded to adjacent sulfonic acid groups in the resin catalyst.

The overall compatibility of the data with the simple, ideal (Langmuir) reaction model is somewhat surprising. The ideal models have widespread applicability, but adsorption parameters in rate equations are generally not simply related to bulk adsorption constants since surfaces are heterogeneous and adsorption non-Langmuir. The success of the model with the polymer catalyst is perhaps understandable. At reaction conditions alcohol is adsorbed to the extent of approximately one molecule per sulfonic acid group (*11*), and for most of the run conditions it is expected that water was not present to a greater extent. The sulfonic acid groups are evidently both the adsorption sites and the catalytic sites (*2*). The agreement of adsorption constants with rate parameters suggests that the array of resin sulfonic acid groups may constitute a nearly ideal, homogeneous "surface," and that in this sense the ion exchange resin at these conditions may be considered a model catalyst.

TABLE 1. SUMMARY OF RATE EQUATION PARAMETERS AND ADSORPTION EQUILIBRIUM CONSTANTS

Temperature, °C.	k	K_A (methyl)	K_A (ethyl)	K_W	K_E (methyl)	K_E (ethyl)
Rate parameters						
119.3	0.17	1.3	—	4.4	0	—
120.0	0.044*	—	3.4*	7.0*	—	0*
Adsorption constants						
116	—	—	2.5*	7.6*	—	0*
100	—	≅1†	8.9*	13.6*	<0.1†	0*

*Results of Kabel and Johanson (*1*).
†Results of Gaudette (*11*).

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NOTATION

k = reaction rate constant, moles of alcohol converted/min. equivalent of catalyst
K = Langmuir adsorption equilibrium constant, atm.$^{-1}$
p = partial pressure, atm.
r = reaction rate, moles of alcohol converted/min. equivalent of catalyst

Subscripts

A = alcohol
E = ether
W = water

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*The data were compared (*8*) to other plausible rate equations suggested by Kabel and Johanson (*1*). The data are consistent with an equation corresponding to the rate determining combination of an adsorbed methanol molecule with one from the vapor phase. The adsorption parameters for methanol and water in this equation, in contrast to those in Equation (1), are not of the order of magnitude of the independent estimates of adsorption equilibrium constants.