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The Dehydration of Methanol and Ethanol Catalyzed by Polystyrene Sulfonate Resins*,†

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Initial rates of the reaction of methanol and of ethanol to give water and the corresponding ether were obtained utilizing a packed-bed flow reactor. The reactions were conducted isothermally at 1 atm total pressure, as vapor-phase reactants contacted catalyst at temperatures from 80° to 120°C. The catalyst was a sulfonated styrene–divinylbenzene copolymer (Dowex 50).

The hydrogen form resin was altered by successively replacing hydrogen exchange ions with lithium ions in one series, and with sodium ions in another series. Reaction rate depression became complete at complete replacement of hydrogen ions. Lithium-containing catalysts were more active than sodium-containing catalysts of the same hydrogen content. A bimolecular rate-determining reaction step is indicated, with hydrogen ions being required for catalyst activity. A structure is proposed for the reaction intermediate.

INTRODUCTION

The dehydration reactions of alcohols to yield ethers and olefins are catalyzed by strong acid solutions and by acidic surfaces such as those of alumina and zirconia (*1*). Strongly acidic ion-exchange resins, sulfonated copolymers of styrene and divinylbenzene, have been used for these and numerous other acid-catalyzed reactions (*2*, *3*, *4*). Many of the kinetic results have been influenced by diffusional effects and the presence of reaction-inhibiting water. Little is understood of the resin's catalytic action beyond the fact that the acidic functional groups are responsible for much of the catalytic activity.

The adsorption equilibrium and reaction kinetic measurements of Kabel and Johanson (*2*), who studied the dehydration of ethanol to diethyl ether, suggested the equivalence of reaction sites and ethanol adsorption sites and indicated that the rate-limiting reaction step was the combination of two ethanol molecules, one or both being adsorbed.

The combinations of methanol and ethanol with the resin have been investigated by Ulbricht (*5*), who made calorimetric and dielectric measurements of the systems at 25°C. The results indicated that two alcohol molecules were bound by polar interaction per functional group. Knözinger (*6*) used infrared spectroscopy for further investigation of the methanol–sulfonic acid group interactions at room temperature and proposed that two methanol molecules were hydrogen-bonded to each functional group.

This investigation aimed to provide more evidence of the ion-exchange resin's catalytic nature. Kinetic data for the methanol and ethanol dehydration reactions

$$2\,CH_3OH = H_2O + CH_3{-}O{-}CH_3$$
$$2\,C_2H_5OH = H_2O + C_2H_5{-}O{-}C_2H_5$$

were obtained for various temperatures and concentrations of hydrogen exchange ions in the catalyst.

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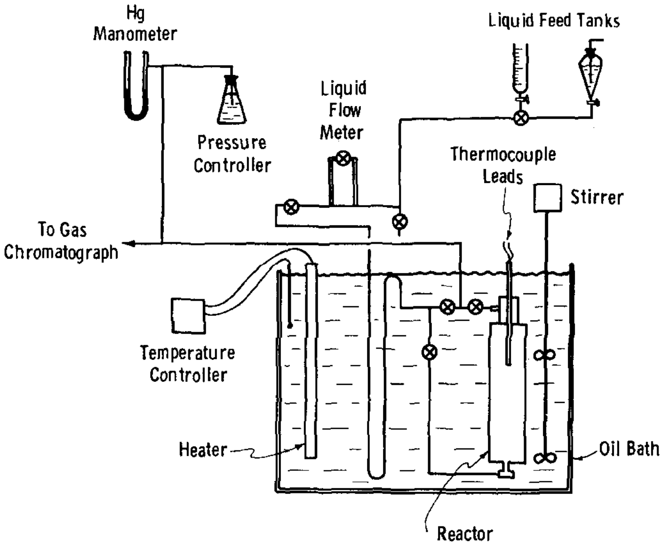


FIG. 1. Schematic diagram of reactor system.

EXPERIMENTAL

Materials. The catalyst was 20- to 50-mesh particles of Dowex 50 X-8 supplied by the Dow Chemical Company. This is a sulfonated copolymer of styrene and 8% divinylbenzene. Reagent grade methanol and ethanol were supplied by Allied Chemical Corporation and U. S. Industrial Chemicals Company, respectively. Helium carrier gas was CP reagent from the Air Reduction Company.

Hydrogen form catalyst was used without pretreatment to afford comparison of results with those of Kabel and Johanson, who used resin from the same batch. Resins of various hydrogen concentrations were prepared by repeated contacting with aqueous solutions of the appropriate ionic compositions (*7*, *8*) followed by repeated washing with distilled water and drying in air. Catalysts were characterized by their exchange ionic compositions and exchange ca-

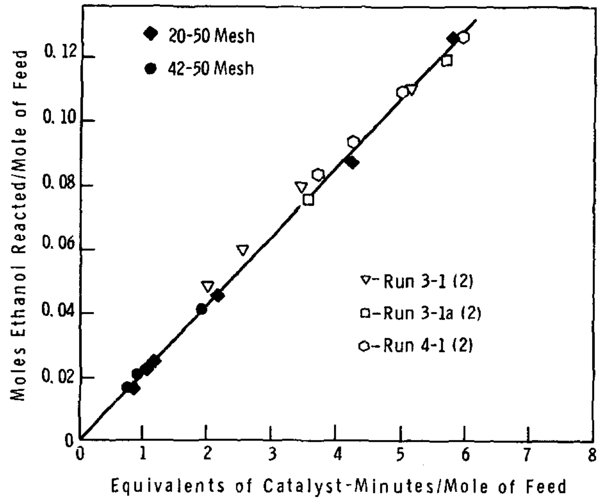


FIG. 2. Conversion data for ethanol reaction at 120°C catalyzed by H^+ form resin.

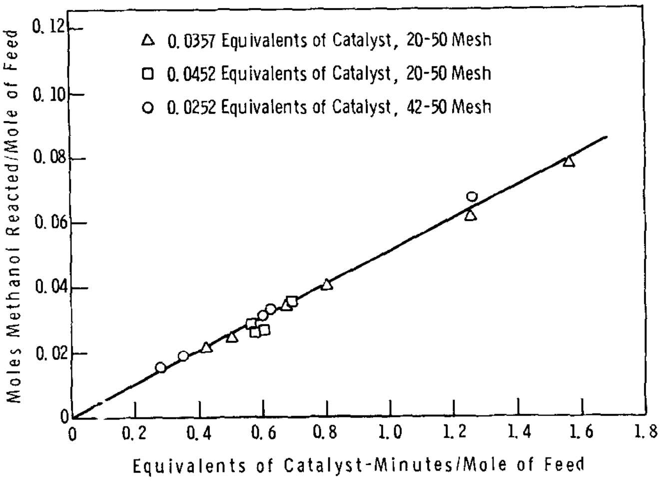


FIG. 3. Conversion data for methanol reaction at 119.3°C catalyzed by H^+ form resin.

pacities, found by titration to determine exchangeable hydrogen ion in the original and completely acidified samples, respectively (*9*).

Apparatus. Initial reaction rate data were determined with a packed-bed flow reactor, the outlet of which was connected directly to the sampling valve of a gas chromatograph used for analysis. Differential conversions were determined using pure methanol and ethanol as feed vapors at atmospheric pressure and temperatures between 80° and 120°C.

The reactor system is shown schematically in Fig. 1. The reactor was a vertical stainless steel tube of 3.4-cm id and 13 cm in length immersed in a well-stirred oil

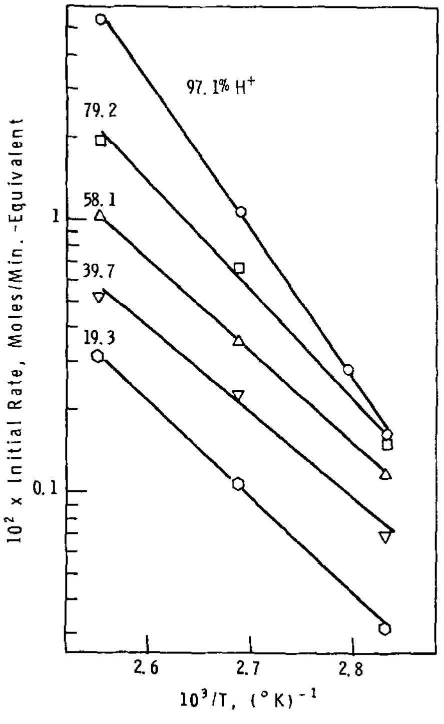


FIG. 4. Arrhenius plot form ethanol reaction catalyzed by H^+-Na^+ form resins.

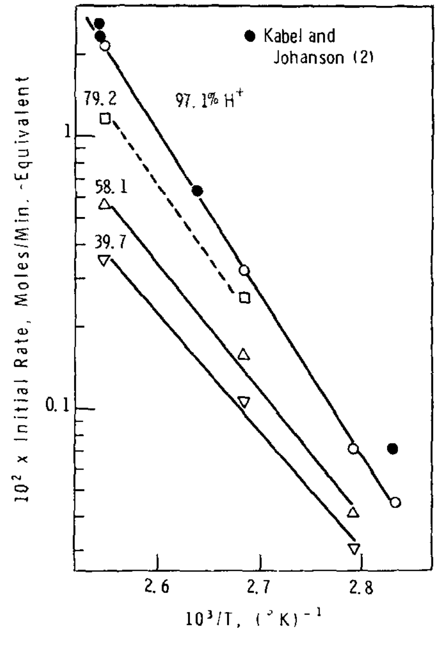


FIG. 5. Arrhenius plot for ethanol reaction catalyzed by H^+-Na^+ form resins.

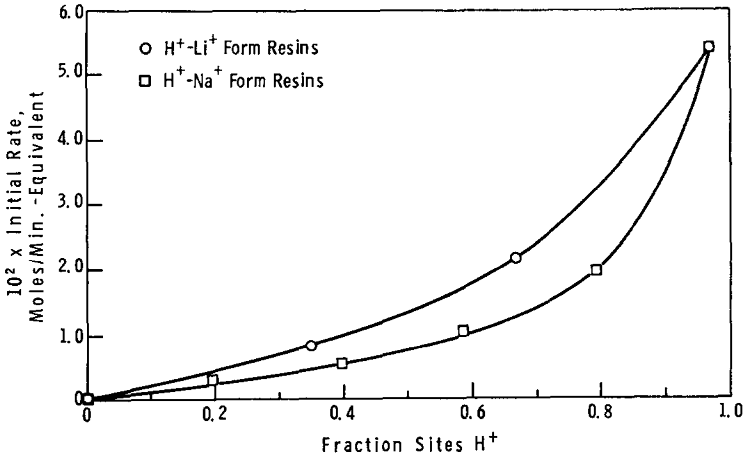


FIG. 6. Dependence of methanol initial rate on resin composition at 119.3°C.

bath. The catalyst particles were mixed with 20- to 24-mesh glass beads to increase rates of heat transfer out of the bed. The length of the catalyst bed was approximately 8 cm; glass beads and glass wool filled the ends of the reactor and allowed for expansion of the resin, which swelled considerably when contacted with reactant vapors. A thermocouple well extended from the top to nearly the midpoint of the catalyst bed. Comparison of readings of the oil bath thermometer and the bed thermocouple indicated that the reported reaction temperatures were correct within ±0.3°C.

The reactor exit tube and vapor-sampling valve were heated to prevent condensation of product vapors. The chromatographic column, thermostated at 105.0°C, was a 6 ft long, 0.25-inch od aluminum tube packed with Carbowax 1540 (polyethylene glycol) (10 wt %) on Fluoropak 80 (powdered Teflon) (90 wt %). A thermistor detector system was used.

Data taking procedure. Conversions of alcohol were calculated from ether-to-alcohol chromatographic peak height ratios; determination of water was imprecise with the chromatographic method utilized. Repeated analyses (usually nine) were obtained at steady state conditions for each alcohol feed flow rate. Feed flow rate was determined by the time required for a certain volume of liquid alcohol to flow from a calibrated feed tank. Periodic

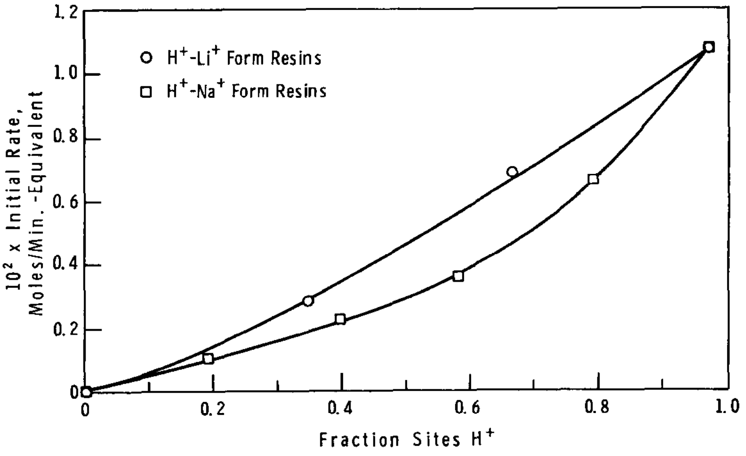


FIG. 7. Dependence of methanol initial rate on resin composition at 99.3°C.

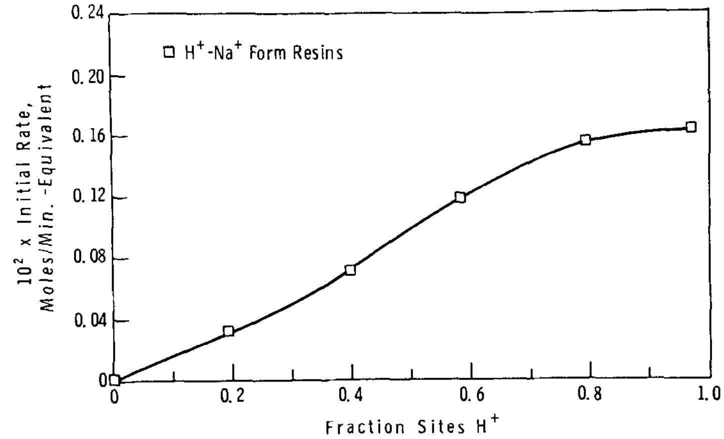


FIG. 8. Dependence of methanol initial rate on resin composition at 80.0°C.

checks were made to confirm the absence of catalyst activity loss from run to run. Further description of apparatus and procedures is presented elsewhere (*10*).

Evaluation and errors. Fractional conversions were plotted as a function of inverse space velocity, defined as the equivalents of catalyst functional groups divided by the feed flow rate. Data were fitted with least-squares straight lines passing through the origin, the slopes of which were initial reaction rates. Decreasing rates were observed for increasing conversions greater than those reported, as product water inhibited the reactions (*10*). Rates were corrected for deviations in pressure from 1 atm.

No side reactions were observed. Variations in analyses and flow rate data indicated that reported rates were precise within less than ±5% at the higher temperatures and somewhat less precise at temperatures less than 99°C.

RESULTS

Some experiments were performed with 42- to 50-mesh particles of the hydrogen form resin to test for a particle-size effect. The average particle diameters of the two batches of catalyst were in the ratio 1.6 to 1. The effect of particle diameter is negligible for the ethanol reaction, as demonstrated by the conversion data of Fig. 2 for reaction at the highest temperature, 119.3°C. The corresponding data for methanol show a slight increase in reaction rate for the smaller particle-size range at this temperature (Fig. 3) and a negligible effect at lower temperatures. The effect is inferred to be negligible for the smaller

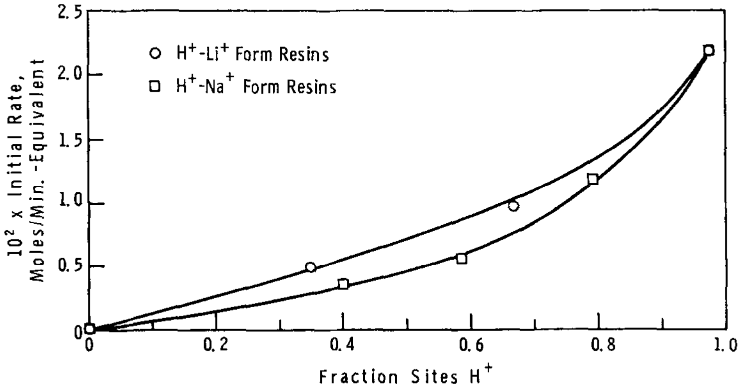


FIG. 9. Dependence of ethanol initial rate on resin composition at 119.3°C.

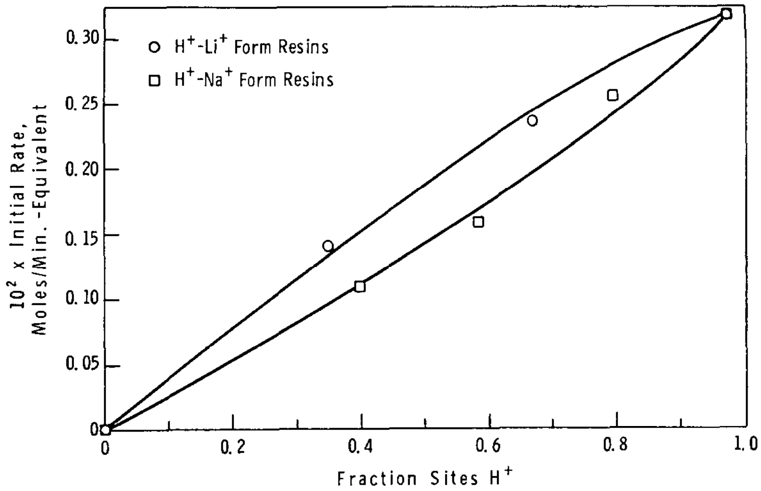


FIG. 10. Dependence of ethanol initial rate on resin composition at 99.3°C.

particles and for the catalysts of other compositions, all of which had lower activities.

The strong temperature dependence of initial reaction rates, shown in the Arrhenius plots of Figs. 4 and 5, is evidence of the lack of a significant diffusional resistance external to the catalyst particles. The conclusion is verified by the lack of an effect on reaction rate of mass velocity at constant space velocity.

Results of Kabel and Johanson are shown for comparison in Figs. 2 and 5.

The initial reaction rate data are presented in Figs. 6–11 for a series of resins containing hydrogen and lithium exchange ions and for a series containing hydrogen and sodium ions. No activity was observed for the lithium and sodium form resins. Activity increased with hydrogen concentration and was markedly different for the two resin series.

The apparent activation energy decreased with decreasing resin hydrogen concentration (Fig. 12), and the compensation effect was observed for each reaction (Fig. 13).

Similar results were observed for the two reactions, indicating that they proceeded through equivalent mechanisms.

DISCUSSION

The results for the resins in various ionic forms demonstrate the necessity of the hydrogen exchange ions for catalytic activity. The marked difference in effect of lith-

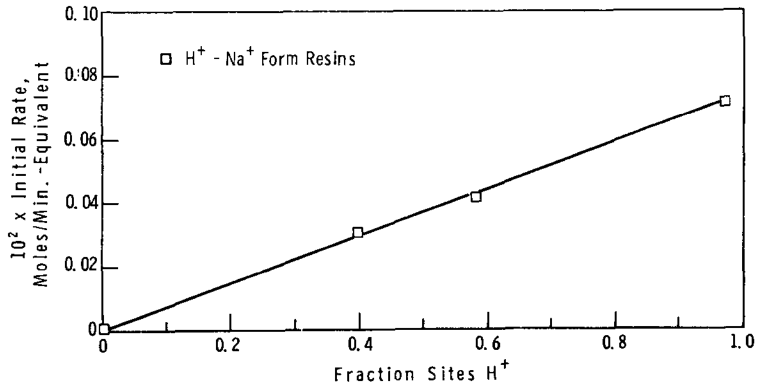


FIG. 11. Dependence of ethanol initial rate on resin composition at 85.0°C.

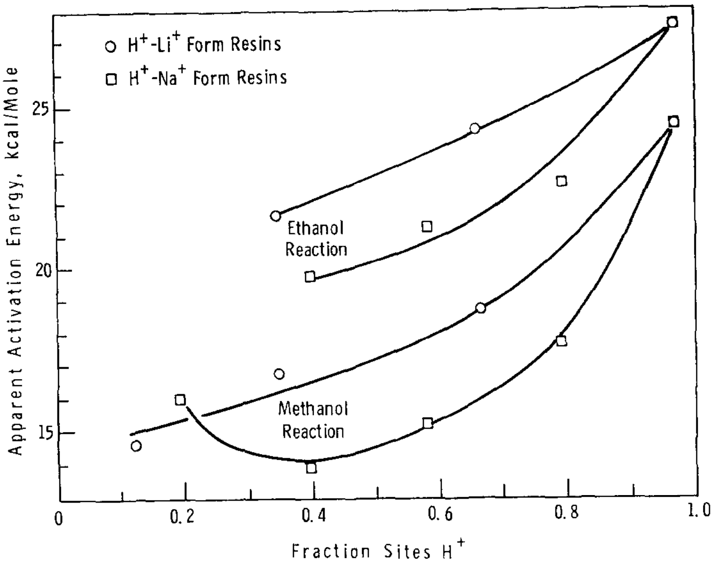


Fig. 12. Dependence of apparent activation energy on resin composition.

ium and sodium ions suggests strongly that these ions, while alone lacking catalytic activity, somehow interact with the catalytically active hydrogen sites and do not simply dilute them. Water, like alcohol, is strongly bound by polar interactions to exchange ions. Glueckauf and Kitt (*11*) report the following values for the number of water molecules associated with each exchange ion at 25°C and infinite dilution of the resin exchange ions: 3.9 for hydrogen, 3.3 for lithium, and 1.5 for sodium. Since both water and ethanol are strongly chemisorbed on the hydrogen form resin at reaction conditions (*2*, *13*), it may be inferred that considerable amounts of methanol and ethanol are combined with lithium and sodium sites and that the alcohols are

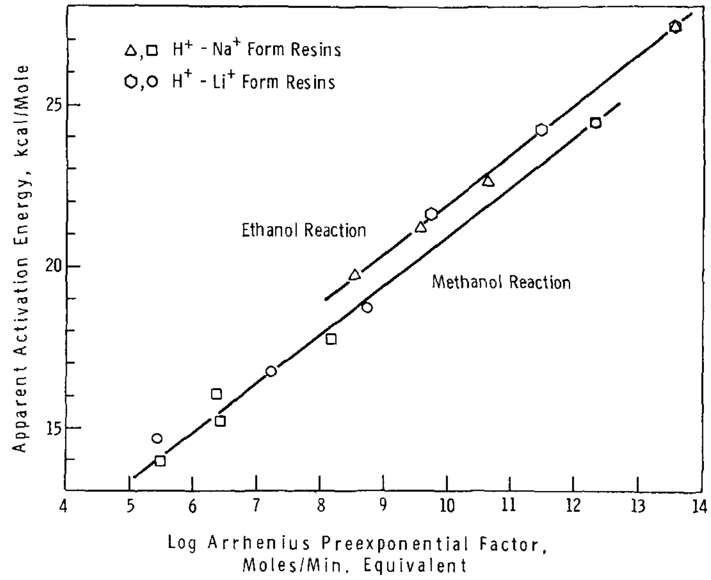
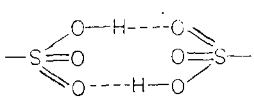


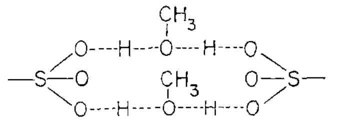
Fig. 13. Compensation effect.

more strongly combined with lithium than with sodium sites at reaction conditions. If a reaction step is postulated which involves the combination of two alcohol molecules, one combined with a hydrogen exchange site, the other with an adjacent exchange site, not necessarily hydrogen, then the observed higher activity is expected for the lithium-hydrogen form resins corresponding to their higher alcohol concentrations.

The infrared measurements of Zundel *et al.* (*12*) indicated a pairing of functional groups in the dehydrated resin by formation of hydrogen bonds:



A pairing of sulfonic acid groups was also postulated by Ulbricht (*5*) and by Knözinger (*6*) for the methanol–functional group combinations, with two methanol molecules doubly hydrogen-bonded and two singly hydrogen-bonded per pair of sulfonic acid groups. Since adsorption experiments of Herlihy (*13*) indicate that 0.85 molecules of ethanol are bound per functional group at 120°C and 1 atm, it may be supposed that formation of only the more strongly combined doubly hydrogen-bonded form is necessary for catalysis:



A similar structure is envisioned as a reaction intermediate for ethanol and also when one of the hydrogen exchange ions is replaced with lithium or sodium, with correspondingly weaker polar bonding to the oxygen of the alcohol.

In the proposed reaction scheme a proton would be donated by a sulfonic acid group to an alcohol molecule, with a compensating proton transfer occurring from the adjacent alcohol. Presumably the evolution of ether would leave water bound to sulfonic acid groups.

The observed differences in effect of sodium and lithium might be explained not by their participation in the reactions, but by a heterogeneity in the resin. Heterogeneity for ion-exchange processes is well known (ref. 4, p. 121), and has been suggested for catalysis by Frilette *et al.* (*3*), who observed the influence of resin cross-linking on the rate of dehydration of *tert*-butanol to isobutene. Replacement of hydrogen ions by sodium ions might remove more active hydrogen sites than the corresponding replacement by lithium ions. This is consistent with the lower Arrhenius pre-exponential factors observed for the sodium-containing catalysts. Alternatively, replacement of hydrogen ions by sodium ions might lead to a lesser degree of segregation of uniformly active hydrogen sites. If this were so, the results would suggest a dual-site mechanism consistent with that which has been proposed.

ACKNOWLEDGMENT

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