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The Dehydration of *t*-Butyl Alcohol Catalyzed by Sulfonic Acid Resin

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Rates of *t*-butyl alcohol dehydration catalyzed by beads of sulfonic acid resin suspended in liquid reactant were measured at temperatures between 35 and 77°C. Catalytically active $-SO_3H$ groups were diluted by partial replacement with $-SO_3Na$, $-SO_3K$, and $-SO_3Rb$ groups. The order of reaction in $-SO_3H$ group concentration increased from 1 to about 4 as concentration increased 20-fold. The kinetics at low $-SO_3H$ group concentrations indicate a carbonium ion mechanism and at high concentrations a concerted mechanism with *t*-butyl alcohol hydrogen-bridged in a network of $-SO_3H$ groups. Rates of reaction catalyzed by variously crosslinked resins and by *p*-toluenesulfonic acid in solution are consistent with this interpretation.

INTRODUCTION

The potential value of ion-exchange resins for fundamental study of general acid catalysis in the absence of solvents was recognized twenty years ago by Bell (*1*). Attachment of acidic functional groups to an insoluble polymer matrix allows their exposure to reactants in an anhydrous, undissociated state with the possibility of at least partially avoiding the complication of competitive hydrogen bonding among the functional groups themselves. However most studies of catalysis by ion-exchange resins have involved specific acid (or base) catalysis in hydrated resins, which is best described as catalysis in aqueous solution within the confines of a polymer matrix (*2*). The few studies in aprotic solvent and with vapor-phase reactants suggest that ideal kinetics have some general validity in describing catalysis by functional groups in polymers. Haag (*3*) investigated the oligomerization of isobutylene in dry paraffin solvent catalyzed by crosslinked polystyrenesulfonic acid, clearly demonstrating Rideal kinetics. Johanson and coworkers (*4*, *5*) reported Langmuir–Hinshelwood kinetics of the dehydrations of methanol and ethanol vapors catalyzed by the sulfonic acid resin, inferring from reaction rate and adsorption equilibrium data that the acid groups are a nearly homogeneous array of catalytic sites. The kinetic data of Haag and Whitehurst (*6*), cited in (*7*), demonstrate identical activities of solution-phase and matrix-bound $[Pd(NH_3)_4]^{2+}$ groups in the carbonylation of allyl chloride. These results are basis for speculation that functional groups in organic polymers often lack the heterogeneity characteristic of catalytic centers on inorganic solid surfaces; differences in activities of fixed and soluble groups may often result only from differences in group interactions and mass transfer effects, while intrinsic activity of a group is unchanged.

The practical advantage of predictable properties in catalysts easily separated from reaction products has been realized in a few large scale applications of sulfonic acid resin catalysts (*8*). Potential applications were foreseen by Manassen and coworkers (*9*), who demonstrated a variety of polymer-catalyzed reactions analogous to reactions catalyzed in homogeneous solution by the same functional groups; the

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polymer catalysts may have stability at relatively high temperatures (~300°C).

The research described here extends studies (*10, 11*) of catalysis by resins of various $-SO_3H$ group concentrations; the present work involves an olefin-forming elimination reaction, the dehydration of *t*-butyl alcohol, first investigated with the resin catalyst by Frilette *et al.* (*12*). The mechanisms suggested for formic acid dehydration (*11*) and alcohol dehydration to ether (*10*) involve the concerted action of two or three sulfonic acid groups surrounding substrate molecules in the polymer matrix. The mechanisms are similar to the mechanism deduced by Pines and Manassen (*13*) for 1,2-*trans*-elimination in alcohol dehydration catalyzed by alumina; reaction is believed to occur preferentially in very small pores (as previously suggested by Schwab (*14*)) so that an alcohol molecule is exposed to a proton-donating site on one side and a proton-accepting site on the other. Some of the unique catalytic properties of zeolites may similarly be considered evidence of the solvent-like character of the small intracrystalline pores, which may be compared to the folded chains of enzymes, surrounding substrates and bonding to them at more than one position (*15*). The catalysis in these examples has characteristics traditionally attributed to both homogeneous and heterogeneous catalysis (*7*).

NOTATION

k_1	pseudo first-order rate constant, units of r
k_4	pseudo fourth-order rate constant, units of r
r	reaction rate, moles/sec equivalent total catalyst functional groups
R	gas constant, 1.987 cal/mole °K
T	temperature, °K
θ_{-SO_3H}	fraction of resin functional groups which are $-SO_3H$ groups

EXPERIMENTAL PROCEDURE

Catalyst Preparation

Beads of Amberlyst 15, a macroporous sulfonated copolymer of styrene and divinylbenzene, were obtained from Rohm and Haas. The resin was washed with methanol, then with water, and exchanged to the sodium form and back to the hydrogen form. Samples containing various concentrations of hydrogen and alkali metal exchange ions were prepared by equilibration with aqueous solutions containing appropriate amounts of HCl and the alkali metal chloride. Resins were washed with distilled water, dried in air, and weighed into vials which were placed in a vacuum oven at 120°C about 12 hr before a kinetics experiment. Original and reacidified air-dried samples were titrated with standard NaOH (*16*) to determine the concentration of acid groups and the exchange capacity.

Beads of Dowex 50W (200–400 mesh), gel-form sulfonated styrene–divinylbenzene resin, were supplied by Bio-Rad Laboratories. Samples containing nominally 2 and 8 mole % divinylbenzene crosslinking agent (DVB) were washed with distilled water and cycled between the hydrogen and sodium form. Hydrogen form resins to be used as catalysts were vacuum-dried 72 hr or more at either 65 or 105°C and stored over P_2O_5.

A soluble catalyst, *p*-toluenesulfonic acid monohydrate (mp 104–106°C), was obtained from Matheson, Coleman, and Bell. Anhydrous acid was obtained by vacuum drying for 48 hr at 90°C. Titration with standard NaOH indicated that essentially anhydrous acid was obtained; this showed little tendency to rehydrate (*17*, p. 129).

Reaction Rate Measurement

Catalyst beads were suspended in stirred liquid in a 500 ml flask held in a thermostat bath. In a typical experiment 150 g of *t*-butyl alcohol (Matheson, Coleman, and Bell, "Chromatoquality," containing either 0.011 or 0.068 wt % water by the manufacturer's Karl Fischer analysis) was weighed into the reactor and brought to temperature. A catalyst sample (containing 0.0005 to 0.03 equivalents of functional groups, depending on activity) was transferred directly from the vacuum oven to the reactor.

A port was opened periodically, and 0.5 ml samples of liquid were withdrawn with a sparger tube tipped with fritted glass. Samples were transferred to capped serum vials, from which syringe samples were taken for injection into a Hewlett–Packard Model 700 gas chromatograph to determine water, isobutylene, and *t*-butyl alcohol. The glc column, a 6-ft long, ⅛-in. diameter tube packed with 80–100 mesh beads of polystyrene (Porapak N), was held at 185°C. Helium carrier gas flow rate was 50 ml/min.

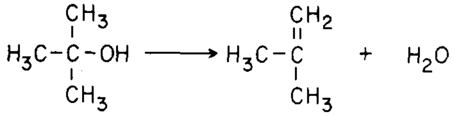
The reactor was held at 35, 55, or 70°C, and measured temperature variations were less than ±0.1°C. The number of samples drawn was usually 7 or 8; the frequency was chosen so conversion was at most roughly 1 mole/equivalent of total catalyst functional groups.

Since the glc column was subject to contamination by samples containing *p*-toluenesulfonic acid, some conversions were determined instead by measurement of isobutylene off-gas flow. Reactant was brought to a temperature of about 77°C (about 5°C below the boiling point), then nearly saturated with 1.2 wt % isobutylene before catalyst was charged. The volume of evolved isobutylene was measured at short intervals with a wet-test meter, providing differential conversion data. Reactant temperature varied within ±0.5°C of the set point. Details of this procedure are given in Ref. (*18*).

Results

Variations in stirring rate and in the ratio of reactant to resin catalyst mass did not affect reaction rates, indicating that liquid-phase mass transfer resistance was negligible. Intraparticle mass transfer resistance was negligible for the macroporous resin, but an induction period observed for the gel-form resin containing 8% DVB indicated an acceleration in reaction caused by the product water's swelling the gel matrix and reducing resistance to transport of reactant; the effect was negligible for the resin containing 2% DVB (*19*). Effects of catalyst drying time and temperature were negligible in the ranges investigated.

Product water analysis yielded precise conversion data only at conversions greater than those usually observed since the amount of impurity water in *t*-butyl alcohol was usually about equal to the amount produced in reaction. The glc data at higher conversions demonstrated the stoichiometry of the alcohol dehydration in the absence of side reactions.



$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH \longrightarrow H_3C-\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}} + H_2O$$

Representative conversion data determined from product isobutylene concentrations are shown in Fig. 1. Conversion data for the macroporous catalyst were fitted to straight lines passing through the origin, the slopes of which were initial reaction rates. Rates in repeated experiments at the higher temperatures typically agreed within ±10%; precision was less at 35°C. The rate data are shown in Fig. 2 for a series of the sulfonic acid resin catalysts with successively increasing fractions of the acid groups replaced by the salt of one of the alkali metals, Li, Na, K, or Rb. Catalyst activity at each temperature decreased strongly with increased replacement of $-SO_3H$ groups.

Resins contacted with large excesses of each of the alkali metal chlorides had activities at 70°C of the order of 10^{-5} moles/sec equivalent of catalyst functional groups. Activities were reduced at least tenfold when the sodium- and potassium-containing catalysts were further contacted with NaOH and KOH solutions, respectively, demonstrating that the small observed activities resided in remaining $-SO_3H$ groups, and that the salt-form resins have negligible catalytic activity.

The dependence of rate on the concentration of resin $-SO_3H$ groups is nearly first-order at the lowest concentrations and fourth- or fifth-order at the highest. The data at each temperature are represented by the following equation (Fig. 2):

$$r = k_1\theta_{-SO_3H} + k_4\theta^4_{-SO_3H} \tag{1}$$

The equation becomes increasingly inappropriate as temperature is reduced to 35°C, as a greater than fourth-order dependence

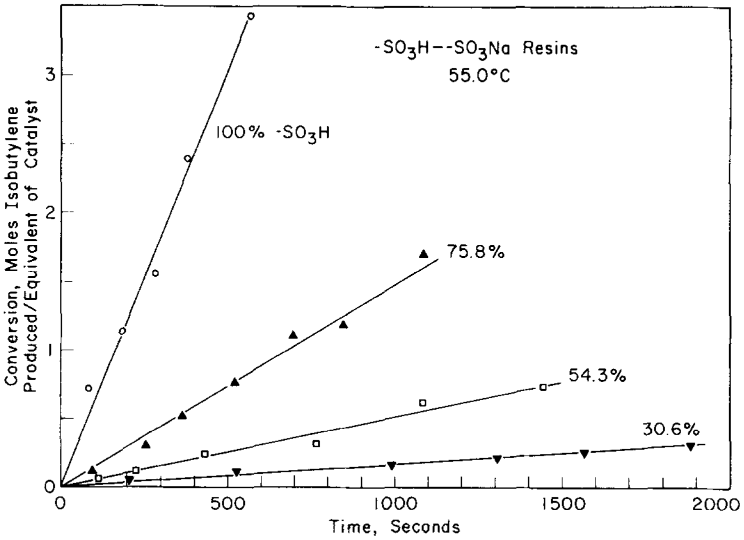


FIG. 1. Conversion of *t*-butyl alcohol catalyzed by macroporous resins.

of rate on $-SO_3H$ group concentration is observed at the higher concentrations.

The lines of Fig. 2 establish the values of k_1 and k_4 shown in Fig. 3. The following equations summarize the results:

$$k_1 = 7.78 \times 10^{11} e^{-23{,}000/RT} \tag{2}$$

$$k_4 = 3.65 \times 10^{11} e^{-20{,}800/RT} \tag{3}$$

The data of Fig. 4, obtained by metering off-gas evolution, provide a comparison of

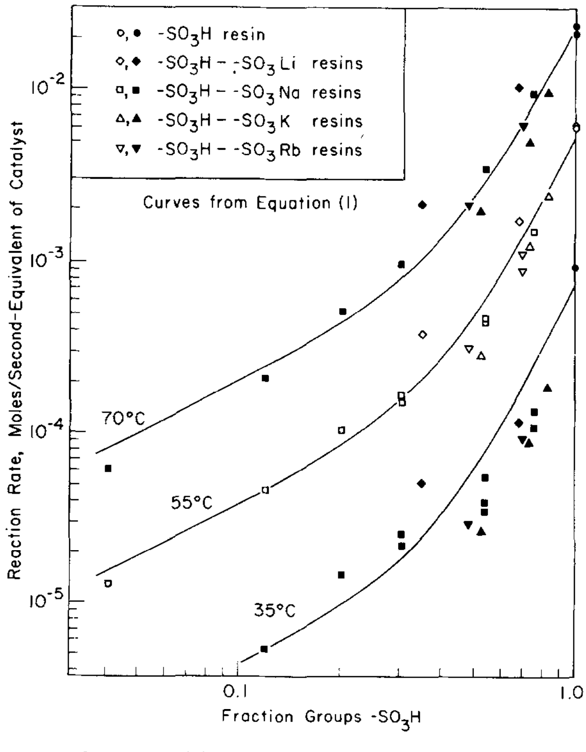


FIG. 2. Dependence of initial rate on temperature and resin composition.

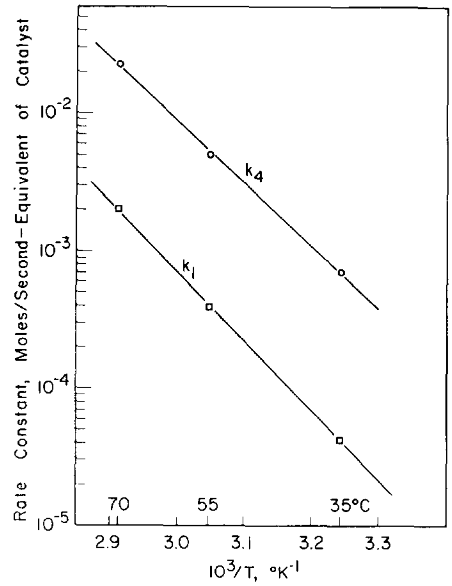


FIG. 3. Arrhenius plot: pseudo first- and fourth-order rate constants.

activities of several sulfonic acid resin catalysts and the soluble *p*-toluenesulfonic acid. Activities found by extrapolating rates to zero reactant water concentration, adjusted slightly to a standard temperature (77.5°C), are summarized in Table 1.* Data were reproducible with a precision of about ±15%.

The gel-form resin containing 8% DVB is roughly twice as active as the resin containing 2% DVB, consistent with the results of Frilette *et al.* (*12*). The result for the macroporous resin, which presumably contains about 20% DVB, confirms the pattern of higher activities for more highly crosslinked catalysts, which also show reduced inhibition by water. Comparison with the activity of *p*-toluenesulfonic acid is not entirely straightforward since rate was only approximately first-order in the concentration of catalyst. It is clear that the resins, with their high local concentrations of $-SO_3H$ groups, are much more effective than the soluble catalyst.

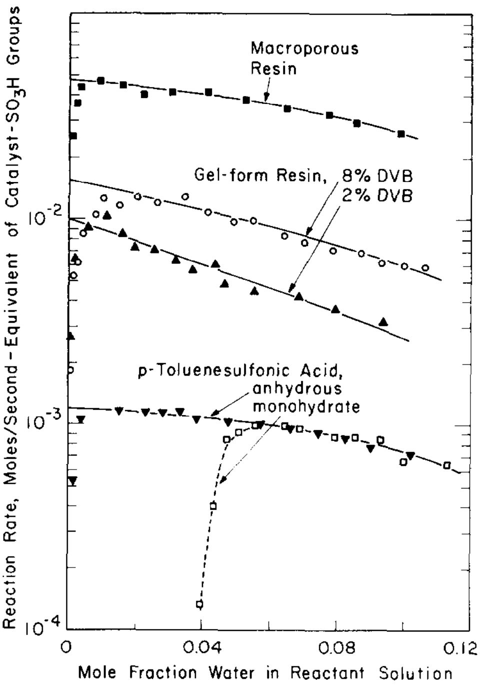


FIG. 4. Rate of *t*-butyl alcohol dehydration catalyzed by soluble and matrix-bound $-SO_3H$ groups. Resin catalysts at 75.5 ± 0.5°C; *p*-toluenesulfonic acid at 77.5 ± 0.5°C.

DISCUSSION

The lack of activity of the salt-form resins and the increase with increasing $-SO_3H$ group concentration demonstrate that $-SO_3H$ groups catalyze *t*-butyl alcohol dehydration, as was previously found for methanol, ethanol, and formic acid dehydrations (*10*, *11*). The catalytic activity of *p*-toluenesulfonic acid confirms the conclusion.

The lack of an effect of catalyst drying conditions suggests that anhydrous catalysts were generally obtained. The fact that rates decreased from initial values (on occasion observed when the number of water molecules present was small compared to the number of $-SO_3H$ groups) indicates that initial rates characterize catalysis by anhydrous $-SO_3H$ groups; activity declines with increased water concentration as water competes with alcohol for the groups.

The dependence of rate on concentration of resin $-SO_3Na$, $-SO_3K$, and $-SO_3Rb$ groups

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* Rates at short times were ignored in the extrapolation since the reactant solution was still not saturated with isobutylene. Intraparticle mass transfer also affected the early data for resin containing 8% DVB (*19*).

TABLE 1

CATALYST ACTIVITIES IN *t*-BUTYL ALCOHOL DEHYDRATION AT 77.5°C.

Catalyst	10^3 × equivalents of catalyst charged	Moles of alcohol charged	10^3 × initial rate, moles/sec equivalent	$10^3 \times k_1$ moles/sec equivalent	$10^3 \times k_4$ moles/sec equivalent
Macroporous sulfonic acid resin (Amberlyst 15, H^+ form)	2.0	3.16	$62^{a,b}$	3.0^c	42^c
Gel-form sulfonic acid resin					
Dowex 50W × 8, H^+ form	5.5	3.14	$20^{a,b}$	—	—
Dowex 50W × 2, H^+ form	6.2	3.14	$13^{a,b}$	—	—
p-toluenesulfonic acid	104^d	2.02	1.4	—	—
	83	2.02	1.2	—	—
	62	2.02	0.84	—	—
	42	2.02	0.80	—	—
	21	2.02	0.60	—	—
	10	2.02	0.67	—	—

[a] Value adjusted to 77.5°C from datum at 75.5°C.

[b] Initial rate independent of amount of catalyst charged.

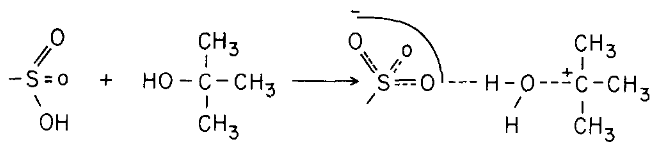
[c] From Fig. 3.

[d] About 0.5 *M* in reactant solution.

is nearly the same, from which it follows that these groups dilute the catalytically active $-SO_3H$ groups. The $-SO_3Li$ groups are exceptional; catalysts containing these groups are more active than the others of the same concentration of $-SO_3H$ groups.

The empirical representation of rate in terms of resin $-SO_3H$ group concentration supports the following interpretation, based on the assumption of a homogeneous array of $-SO_3H$ groups: The pseudo first- and fourth-order rate constants, k_1 and k_4, incorporate functions of alcohol concentration which are expected to be nearly the same for all experiments (saturated catalysts); the first-order term indicates a mechanism involving a single $-SO_3H$ group as the catalytic site, while the fourth-order term indicates a mechanism involving (approximately) four $-SO_3H$ groups acting in concert. The former term is of dominant importance at low $-SO_3H$ group concentrations ($\theta_{-SO_3H} \lesssim 0.2$), and the latter term is dominant at high concentrations.

The first-order reaction term is consistent with a carbonium ion mechanism, which according to Pines and Manassen (*13*) generally prevails in the dehydration of tertiary alcohols:



Suitable bases for abstraction of a proton from the *t*-butyl carbonium ion include the oxygens of sulfonate groups, water, and the alcohol.

The structures shown above are consistent with the results of ir studies of *p*-toluenesulfonic acid in methanol (*20*): At low acid concentrations the $-SO_3H$ groups dissociate and the excess protons tunnel between oxygen atoms of the solvent, producing a continuous absorption in the ir spectrum.

The fourth-order reaction term suggests

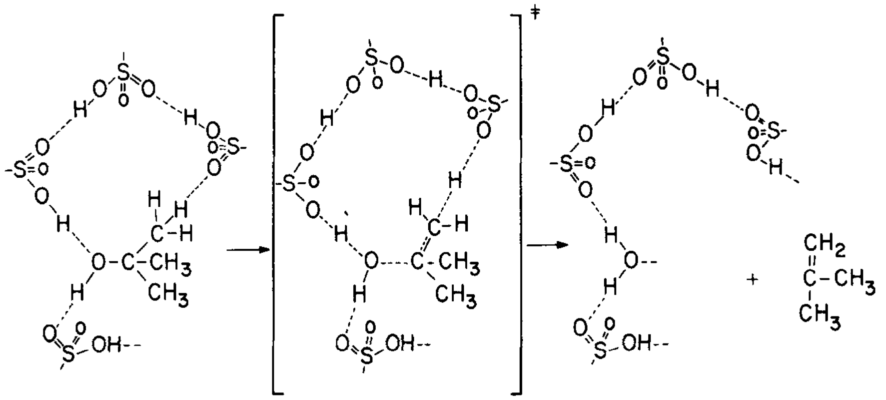


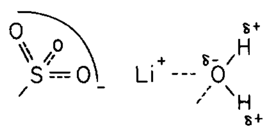
FIG. 5. Reaction mechanism involving four $-SO_3H$ groups.

a concerted mechanism* involving (approximately) four $-SO_3H$ groups. The detailed scheme of Fig. 5 is consistent with this interpretation, as are others involving three-dimensional hydrogen-bonded networks of $-SO_3H$ groups. This depiction of the network and the bonding of water (at low concentrations) are indicated by ir studies of Zundel demonstrating that $-SO_3H$ groups are strong proton acceptors as well as donors (*17*, pp. 116–231). The hydrogen bonds involving alcohol are indicated by Knözinger's ir study of methanol–resin combinations (*24*). Further, Kampschulte-Scheuing and Zundel's study of *p*-toluenesulfonic acid in methanol (*20*) demonstrates that at concentrations greater than about 2 *M* (occurring in resins at $\theta_{-SO_3H} \gtrsim 0.4$), $-SO_3H$ groups are increasingly associated in a network like that shown in Fig. 5: protons do not tunnel in this network, and the tautomeric shift requires a substantial activation energy.

The structures shown in Fig. 5 account for the observed inhibition by water and the strong depressive effect of replacement of $-SO_3H$ groups by metal sulfonate groups, one of which can interrupt the hydrogen-bonded network and suppress the synchronous proton transfer steps.

While the two rate constants are roughly equal, the concerted process is prevented from occurring at low $-SO_3H$ group concentrations because the rigid polymer matrix hinders network formation among the groups. The concerted mechanism is characterized by a slightly lower activation energy than the carbonium ion mechanism, which may reflect the advantage of the strong basic group ($-S{=}O$) in a rate-determining proton abstraction from a *β*-carbon.

The high activity of lithium-containing resins compared to the other metal-containing resins may be explained by a result of Zundel and Murr's ir studies (*25*): The last water of hydration in lithium-form resin is not removed by drying at conditions employed in this work. Hydrated $-SO_3Li$ groups may be proton donor–acceptors of sufficient strength to assist in the concerted reaction by their involvement in the hydrogen-bonded network:



The results show that hydrated $-SO_3Li$ groups are much less effective than $-SO_3H$ groups at equal concentrations, and acting alone they do not catalyze reaction by promoting carbonium ion formation.

The rate data of Table 1 may be interpreted in terms of the preceding model of $-SO_3H$ group catalysis. At low concentrations in *t*-butyl alcohol, *p*-toluenesulfonic acid catalyzes reaction predominantly

* A concerted mechanism for *t*-butyl alcohol dehydration catalyzed by alumina at temperatures less than 200°C has recently been elucidated by Knözinger and coworkers (*21–23*).

through the carbonium ion intermediate. However k_1 (the rate of carbonium ion reaction per equivalent of $-SO_3H$ groups present in the resin at low concentration) is as much as four times the rate of reaction per equivalent of *p*-toluenesulfonic acid, suggesting that some $-SO_3H$ groups in solution become inaccessible to the alcohol as a result of formation of hydrogen bonds among themselves. The greater than first-order dependence of rate on acid concentration suggests that reaction begins to occur by a concerted mechanism involving a network of hydrogen-bonded $-SO_3H$ groups.

The high activity of the resins compared to the soluble catalyst results from the predominance of the concerted mechanism at the high resin $-SO_3H$ group concentrations. The greater activity of the resins more highly crosslinked with DVB indicates the advantage of greater steric restriction of formation of the tight hydrogen-bond crosslinks, with a greater concentration of positions at which substrate can be bridged into the network. The increasing effect of water inhibition in resins of decreasing DVB content (Fig. 4) is explained by an increasingly strong tendency for a water molecule formed in the network (Fig. 5) to remain bound; the increasingly flexible network would adjust, forming as many as four hydrogen bonds between $-SO_3H$ groups and water, one to each hydrogen and one to each remaining electron pair of oxygen (*17*, p. 151).

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