

Catalysis by Matrix-Bound Sulfonic Acid Groups: Olefin and Paraffin Formation from Butyl Alcohols

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Catalysis by a poly(styrene-divinylbenzene) matrix containing $-SO_3H$ groups was characterized by reaction rates and product distributions for reactions of isopropyl, isobutyl, and *s*-butyl alcohols at about 100°C. Infrared spectra of functioning catalyst membranes established the presence of a network of hydrogen-bonded $-SO_3H$ groups at low alcohol concentrations and dissociated groups at high concentrations. When partial pressures of alcohol contacting the catalyst exceeded about 0.1 atm, the alcohols (like water) were reaction inhibitors, and the catalyst approached the character of an acid solution. In contrast, as substrate concentration approached zero, *s*-butyl alcohol gave predominantly *trans*-2-butene without 1-butene; and isobutyl alcohol gave not only butenes, but isobutane and tar. The high catalytic activity and unusual selectivity of the network incorporating small amounts of alcohols demonstrate that the proton donor-acceptor tendencies of the network are significantly stronger than those of the solvated acid groups. The dehydration reaction mechanisms are suggested to involve concerted proton transfers within cyclic hydrogen-bonded networks incorporating $-SO_3H$ groups which surround and conform to alcohol molecules.

INTRODUCTION

Catalysis by acid groups in solution is complicated by interactions of the groups with one another and with solvents, and catalysis by acid groups on surfaces is complicated by the heterogeneity of the groups. An intermediate class of acid catalysts, which is in some ways more amenable to study, is formed by solid matrices with pendant functional groups. The sulfonic acid ion-exchange resin (an industrial catalyst offering the practical advantages of strong acidity with insolubility) offers advantages to researchers because the matrix-bound groups evidently constitute a nearly homogeneous array of catalytic sites; these can be studied over a wide range of substrate concentrations (in the absence of solvents) and can be characterized by spectroscopic methods not much more difficult than the ones used for solutions (1, 2).

Almost all the reported investigations of catalysis by acid groups in organic matrices

have involved dissociated groups in hydrated resins. Yet there is a marked change in the nature of the catalyst as water is removed: At high concentrations, water is a diluent in the dehydration of *t*-butyl alcohol, but at the lowest concentrations, water is a strong inhibitor, and the catalyst is much more efficient (3). These results point to a transition from catalysis in a hydrated matrix, strongly resembling an aqueous solution, to catalysis by anhydrous acid groups, which are known to form a strongly hydrogen-bonded network among themselves (1, 2).

The research described below was intended to characterize catalysis by sulfonic acid groups in a flexible polymer matrix, with emphasis on the little-studied phenomena involving the acid groups in the presence of very low concentrations of water and substrates. The substrates chosen were butyl alcohols, since bonding of alcohols and sulfonic acid groups is easily

studied by infrared spectroscopy (2, 4) and since the product distributions from butyl alcohols are useful indicators of reaction intermediates (5, 6).

EXPERIMENTAL METHODS

Catalyst Preparation

Membranes of styrene-divinylbenzene copolymer were synthesized from the monomers and sulfonated according to a procedure similar to that of Zundel (1). The styrene (Eastman Chemicals) and divinylbenzene (DVB) (Matheson, Coleman, and Bell) were vacuum distilled at 22°C to remove stabilizers and polymeric impurities. Solutions of about 8 mole% DVB in styrene were prepared, containing about 0.1 wt% benzoyl peroxide to initiate the copolymerization reaction. The solution of monomers was introduced into a space between two glass plates held apart by a tantalum foil window with a thickness of 5 μ m. The polymerization reaction proceeded for 5 days at 70°C and then for 2 days at 90°C.

Each resulting membrane was carefully removed under water and dried at 50°C; it was then cut to give a disc about 5 cm in diameter and placed in a covered petri dish with several milliliters of chlorosulfonic acid; care was taken to ensure that the membrane was uniformly and rapidly wetted by the acid. The chlorosulfonation reaction was allowed to proceed at 45°C for 3 days, then excess acid was removed, and the membrane was exposed to moist air, and the chlorosulfonic acid groups were hydrolyzed. When no further evolution of hydrogen chloride was observed, the membrane was washed with distilled water and stored in a warm oven. A typical membrane weighed about 0.04 g in an air-dried state (containing about 20 wt% water) and contained about 0.2 mEq of $-\text{SO}_3\text{H}$ groups as measured by titration against standard base.

Apparatus

The flow system shown schematically in Ref. (2) was used for simultaneous mea-

surement of reaction rates and infrared spectra of single functioning catalyst membranes. The apparatus was constructed of stainless steel and glass. The metal transfer lines, superheater, and vaporizer were heated electrically. Liquid was fed at a constant rate from a syringe pump (Sage Model 249), flowing to a vaporizing column packed with glass beads, where it was mixed with a steadily flowing stream of nitrogen carrier gas. The vapor stream was heated to the reaction temperature *en route* to the reactor, which was a heated infrared gas cell containing a single catalyst membrane. The cell was mounted in a Perkin-Elmer Model 247 infrared spectrophotometer. Products flowed from the reactor to a reference cell, and since the conversions were always low, the compositions of the vapors in the two cells were nearly the same, and the resulting infrared absorption spectra were characteristic of the catalyst membrane and the chemically combined reactants. Products flowed from the reference cell to the heated gas sampling valve of a Hewlett-Packard Model 5750 gas chromatograph.

The construction of the reactor is shown in Fig. 1. The stainless steel cell body was wound with a resistance heater and insulated. Sodium chloride windows were clamped to the cell body and sealed with silicone rubber gaskets. The windows were electrically heated to prevent their dissolution by condensing vapors. Midway between the entrance and exit lines, the catalyst membrane was held perpendicular to the infrared beam. Temperature was monitored with a thermocouple located less than 2 mm from the membrane.

The gas chromatograph was equipped with flame ionization detectors, which were not responsive to water produced in the catalytic reactions. Products were analyzed at 140°C in a 1/8-in. o.d. column packed with 80 to 100 mesh particles of Porapak N. This column failed to separate the butene isomers, so supplementary analyses were performed for this purpose at 22°C with a column containing Chromosorb P loaded with a saturated solution of silver nitrate in benzyl cyanide.

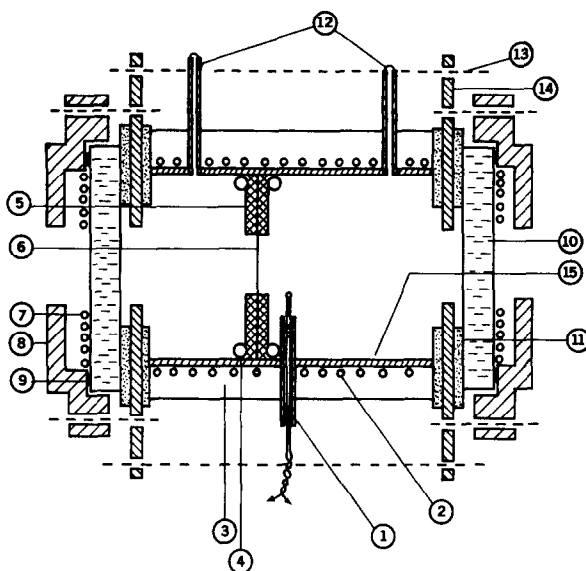


Fig. 1. Details of infrared cell-flow reactor construction: (1) thermocouple in thermowell; (2) cell body heater wires; (3) insulation; (4) spring rings; (5) Teflon gauze supports; (6) catalyst membrane; (7) window heater wires; (8) brass window clamps; (9) paper washer; (10) NaCl windows; (11) silicone rubber gaskets; (12) inlet and outlet tubes; (13) securing bolts with collars; (14) stainless steel end plates; (15) stainless steel cell body. Cell length and diameter were 5 cm.

Measurement of Rates and Spectra

The liquid feeds were alcohols: *s*-butyl, bp 98–100°C; isobutyl, bp 107.5–108.5°C (both from Matheson, Coleman, and Bell); or isopropyl (0.04% water, Baker): each was used without further purification. Water was added to some feeds, and all feeds contained 1 mole% diethyl ether, which served as an internal standard for the gas chromatographic analysis of products. The feeds also contained 0.005 mole% nitric acid, which had no measurable effect on spectra or reaction rates, yet prevented the slow loss of catalyst activity observed in its absence. It is presumed that the catalyst deactivation was caused by neutralization of acid groups by small amounts of basic impurity in the feeds—catalyst activity can be strongly reduced by neutralization of a small fraction of the groups (7).

Alcohol flow rates were in the range 1.4×10^{-6} to 1.1×10^{-5} moles/sec, and the partial pressures were varied from 0.01 to 0.35 atm. Reaction temperatures between 84 and 105°C were measured with a preci-

sion of $\pm 0.3^\circ\text{C}$. Pressure was 1.09 ± 0.04 atm.

In each run a steady state was achieved, as indicated by repeated product analyses by gas chromatography. The infrared beam was normally off during operation to prevent heating of the catalyst, but several scans of the catalyst spectrum were typically made between product analyses. Details of procedure and apparatus are given elsewhere (8).

RESULTS

Infrared absorption spectra of working catalysts in contact with *s*-butyl alcohol are compared with previously reported data for methyl alcohol (2) in Fig. 2. The spectra obtained for *s*-butyl, isobutyl, isopropyl, and methyl alcohols contacting the catalyst were essentially indistinguishable. Spectra at wave numbers greater than about 1400 cm^{-1} were obtained only with the lowest partial pressures of isopropyl and butyl alcohols because strong absorption by alco-

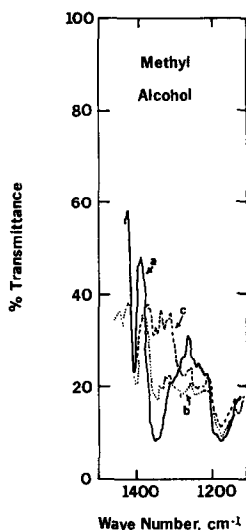


FIG. 2a. Infrared spectrum of functioning sulfonic acid resin catalyst in contact with methyl alcohol (2). (a) $P_{\text{MeOH}} = 0.026$ atm; (b) $P_{\text{MeOH}} = 0.36$ atm; (c) $P_{\text{MeOH}} = 0.60$ atm.

hol vapor in the cells obscured any signal originating in the catalyst.

Conversions of each alcohol were demonstrated to be in the differential range (typically 0.5–10%), which implies that reaction rates were determined directly and that inhibition by water produced in the reactions was negligible. It is inferred that when pure alcohol feeds were used, negligible

amounts of water were retained by the catalyst; this inference is confirmed by results showing that rate measurements were unaffected by conversion levels in preceding experiments.

Secondary butyl alcohol was found to undergo catalytic dehydration to give 1-butene, *cis*-2-butene, and *trans*-2-butene. Rate data obtained with alcohol and alcohol–water feeds are shown in Fig. 3. The data show first-order kinetics at the lowest partial pressures of alcohol and inhibition of reaction by water, as well as inhibition by the alcohol itself at the higher partial pressures. The rate of formation of each hydrocarbon product is shown in Fig. 4.

Isobutyl alcohol reacted to give a mixture of butenes (which were not resolved) and another product, isobutane, which was formed only at low substrate partial pressures (Fig. 5). Identification of the paraffin was confirmed in an analysis with a gas chromatograph–mass spectrometer system. The reaction of isobutyl alcohol was accompanied by a loss in catalyst activity, about a 20% decrease in rate over some tens of hours of operation. The catalyst in operation became covered with a dark, sticky tar; neither tar formation nor catalyst deactivation was observed with any of the other alcohols studied.

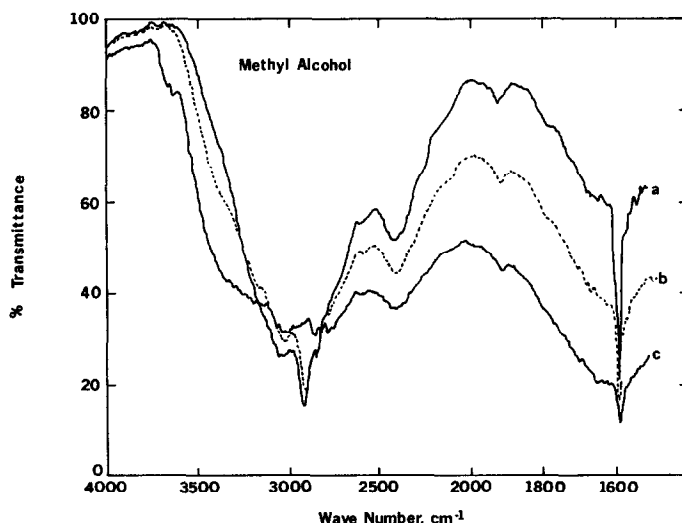


FIG. 2b. Infrared spectrum of functioning sulfonic acid resin catalyst in contact with methyl alcohol (2). (a) $P_{\text{MeOH}} = 0.026$ atm; (b) $P_{\text{MeOH}} = 0.12$ atm; (c) $P_{\text{MeOH}} = 0.60$ atm.

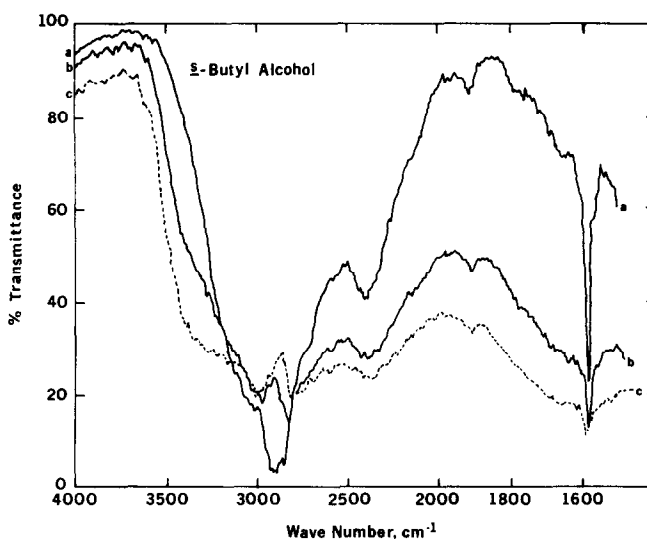


FIG. 2c. Infrared spectrum of functioning sulfonic acid resin catalyst in contact with *s*-butyl alcohol. (a) $P_{s\text{-BuOH}} = 0.014$ atm; (b) $P_{s\text{-BuOH}} = 0.11$ atm; (c) $P_{s\text{-BuOH}} = 0.33$ atm.

Rates of reaction of isopropyl alcohol are shown in Fig. 6. The principal dehydration product was propylene, but at the higher alcohol partial pressures, traces of isopropyl ether were also detected. Data are presented for a catalyst containing 5% DVB as well as the standard catalyst containing 8%

DVB, which was used for the other alcohols. The less highly crosslinked catalyst was several times more active at the low alcohol partial pressures, even at a temperature 9°C lower than that for the standard catalyst. The less highly crosslinked catalyst, however, approached an activity less than

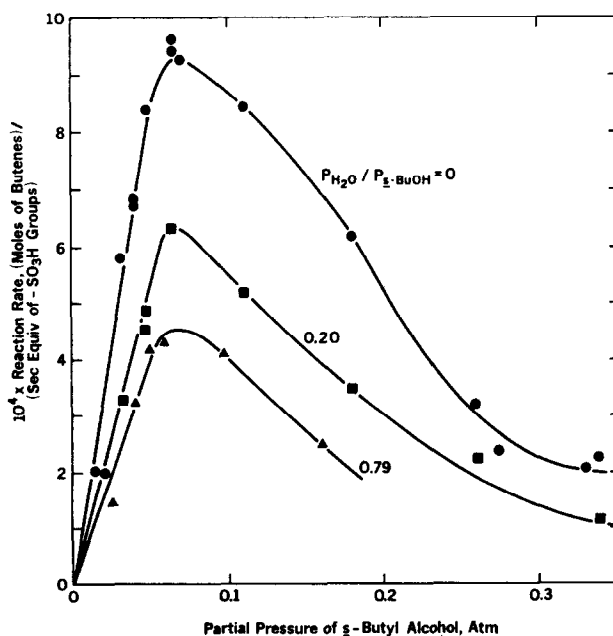


FIG. 3. Rate of dehydration of *s*-butyl alcohol catalyzed by sulfonic acid resin at 97°C .

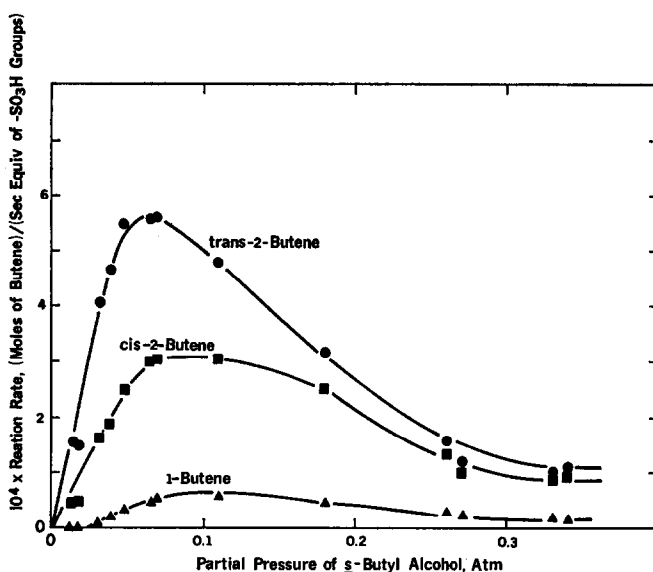


FIG. 4. Rates of formation of butenes from *s*-butyl alcohol catalyzed by sulfonic acid resin at 97°C.

that of the standard catalyst at the higher alcohol partial pressures.

The kinetic results for the three alcohols reacting in the membranes are free of mass transfer influence (8). The kinetics indicate primary product formation, which for dehydration of *s*-butyl alcohol is confirmed by calculations based on the data of Kalló and Preszler (9), demonstrating that butene

isomerization was an order of magnitude slower than butene formation from the alcohol. The kinetics demonstrate the following general pattern: The olefin-formation reactions are first order in substrate partial pressure up to a value of roughly 0.1 atm (Table 1). At substrate partial pressures increasing beyond this value, the rates decrease, demonstrating the role of each sub-

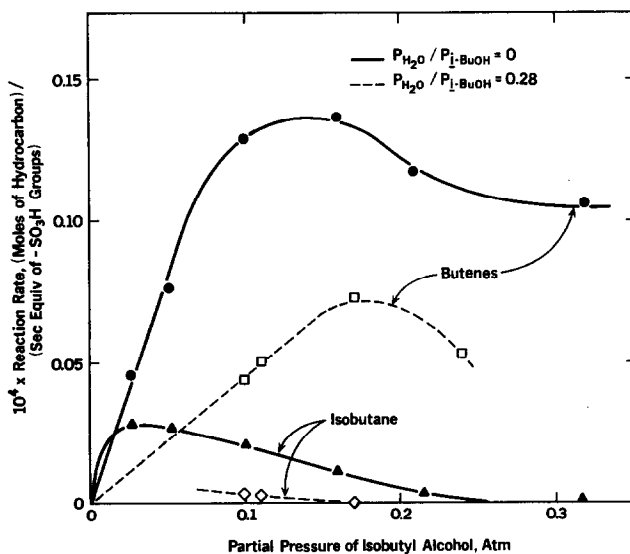


FIG. 5. Rates of formation of butenes and isobutane from isobutyl alcohol catalyzed by sulfonic acid resin at 105°C.

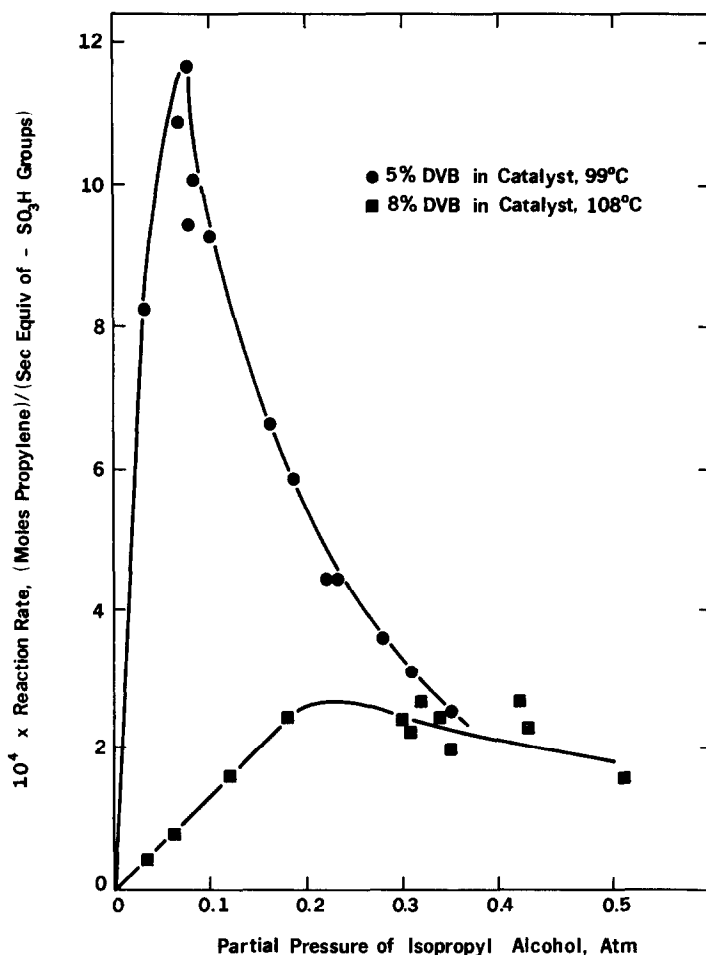


FIG. 6. Effect of catalyst crosslinking on the rate of dehydration of isopropyl alcohol.

 TABLE 1
 FIRST-ORDER RATE CONSTANTS FOR ALCOHOL DEHYDRATION^a

Substrate (alcohol)	Temp (°C)	Range of substrate partial pressure for first-order reaction (atm)	First-order rate constant for formation of the product ^b				
			Propylene	1-Butene	<i>cis</i> -2-Butene	<i>trans</i> -2-Butene	All butenes
Isopropyl	108	0-0.2	1.3×10^{-3}	—	—	—	—
Isobutyl	105	0-0.05	—	—	—	—	1.6×10^{-4}
<i>s</i> -Butyl	97	0-0.05	—	—	4.7×10^{-3}	1.2×10^{-2}	1.7×10^{-2}
<i>s</i> -Butyl	84	0-0.02	—	—	—	—	1.1×10^{-2}

^a Catalyst was 8% crosslinked sulfonic acid resin.

^b Rate constants have dimensions of [moles of product]/[(sec) (equiv of $-\text{SO}_3\text{H}$ groups) (atm)].

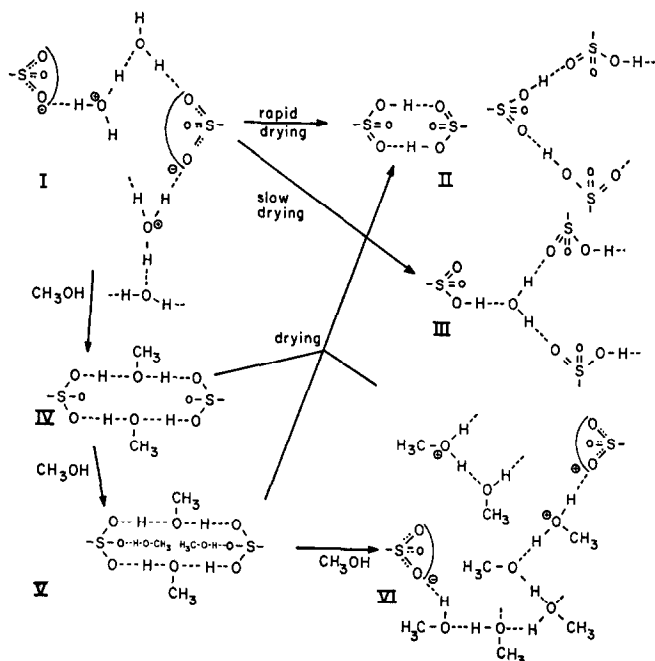


FIG. 7. Summary of structures of sulfonic acid resin with hydrogen-bonded water and methyl alcohol (2).

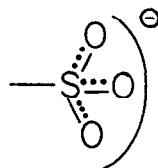
strate as a reaction inhibitor. Water is a strong inhibitor at all observed partial pressures. Product distribution changes in the same direction with increased substrate or water partial pressure.

DISCUSSION

The near equivalence of the spectra for the various alcohols contacting the functioning resin catalyst (Fig. 2) demonstrates that the same functional group chemistry describes the interactions of each of the alcohols with $-\text{SO}_3\text{H}$ groups of the catalyst. The conclusion is in agreement with the observations of Knözinger and Noller (4), who reported experiments with methyl, ethyl, and isopropyl alcohols at unspecified temperatures in the absence of reaction.

The previously deduced structures of the groups interacting with methanol and water are summarized in Fig. 7 (2). The data most conclusive in determination of these structures have been the infrared absorption bands of $-\text{SO}_2\text{OH}$ groups (1):* the 1350 and 1172 cm^{-1} bands identify the antisym-

metric and symmetric vibrations of the $\text{S}=\text{O}$ bonds, respectively, and the 907 cm^{-1} band identifies the stretching vibration of the $\text{S}-\text{O}$ bond. The spectra shown for methanol contacting the catalyst (Fig. 2a) demonstrate the disappearance of the $\text{S}=\text{O}$ bonds (hence the disappearance of the undissociated acid groups) with increasing partial pressure of methanol (2, 4). Correspondingly, the formation of



ions is demonstrated by the appearance of bands at 1200 and 1034 cm^{-1} , representing antisymmetric and symmetric stretching vibrations of the ion, respectively (2, 4).

Although these bands were obscured for propyl and butyl alcohols at all but the lowest partial pressures, the information available (exemplified by Fig. 2c) is sufficient to demonstrate the essential behavior of the acid groups. The peak at 2950 cm^{-1} [indicating the stretching vibration of an $-\text{OH}$ group in the network of hydrogen-

* The band assignments referred to here are based on the interpretations of Zundel (1) and are consistent with those cited previously (2).

bonded $-\text{SO}_3\text{H}$ groups (structure II of Fig. 7)] and the peak at 2405 cm^{-1} (indicating the first overtone of the $-\text{OH}$ bending vibration in this network) both decreased with increasing alcohol partial pressure [as observed for methanol (Fig. 2b)], demonstrating that addition of alcohol led to dissociation of the acid groups and break-up of the strongly hydrogen-bonded network. Correspondingly, a broad band appeared between about 3600 and 2000 cm^{-1} , as previously found and identified (2, 4) with $-\text{OH}$ groups in hydrogen bonds involving $-\text{SO}_3\text{H}$ groups and methanol (structures IV and V). The absence of a band indicating free $-\text{OH}$ groups {expected at about 3525 cm^{-1} [Ref. (1), p. 129]} demonstrates that almost all the $-\text{OH}$ groups of methanol and the catalyst were involved in hydrogen bonds.

The spectra of Fig. 2c, showing that the network structure II was broken up by addition of *s*-butyl alcohol, also show that the break-up was almost complete at roughly 0.1 atm partial pressure of the alcohol. Since this is the partial pressure corresponding to the maximum rate of the dehydration reaction, it is concluded that the network structure corresponds to the most active form of the catalyst. The conclusion is valid for all the olefin-forming alcohols studied.

The rate data shown in Figs. 3 and 5 demonstrate that water inhibited the reactions. This conclusion has been drawn for other alcohols (2, 3) and is explained by a competition for acid groups between alcohol and water, as exemplified by the structures of Fig. 7. The new and surprising result shown in Figs. 3-6 is the inhibition of reaction by the alcohols themselves at partial pressures greater than about 0.1 atm . This result, with the infrared spectra, demonstrates that the network of acid groups solvated by hydrogen-bonded alcohol (structures IV, V, and VI†) is markedly less effective catalytically than the network of acid groups themselves (structure II). We infer that at alcohol partial pressures less than about 0.1 atm , the rate of reac-

tion increased linearly with increased substrate partial pressure as the substrate occupied a proportionately increasing fraction of the bonding sites formed by its breaking into the network of $-\text{SO}_3\text{H}$ groups. At higher partial pressures, bonding sites of this type no longer existed, and added substrate found positions only among the dissociated acid groups already hydrogen bonded to alcohol molecules.

The structural determinations of resins in various degrees of hydration (1) demonstrate that the anhydrous network has very strong hydrogen-bond donor-acceptor properties. For example, in structure III, water is bonded to three acid groups (or possibly even four, as an acid group interacts with each of the two remaining lone pairs of electrons of the oxygen); this water is so tightly held that it cannot be removed even at severe drying conditions. Yet when the acid groups are strongly hydrated and dissociated (structure I), the proton acceptor strength of the resin is reduced so much that the resin can be dried completely, providing the process is fast and the last water molecules do not have sufficient opportunity to form bonds with more than one $-\text{SO}_2\text{OH}$ group before leaving the matrix. We are led to the conclusion that the catalytic efficiency of the network of $-\text{SO}_3\text{H}$ groups (structure II) is a consequence of its strong proton-donating and proton-accepting tendencies. The catalyst becomes markedly less efficient as compounds like water or alcohol are added, because the polar compounds break into the network, cause the protons of the acid groups to be dissociated, and reduce the proton donor-acceptor strength of the network.

When the preceding results are compared to results in the literature for strongly hydrated resins [e.g., Ref. (3)], they lead to the following rough classification of regimes of catalysis by the sulfonic acid resin:‡

1. Strongly hydrated resins containing dissociated acid groups and hydrated protons strongly resemble aqueous solutions of strong acid (3, 13).

‡ In this classification, we have overlooked the interesting complications occurring when non-polar compounds are also present to swell the resin (11, 12).

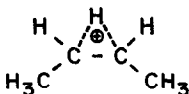
† Structure VI is inferred from infrared data for *p*-toluenesulfonic acid in methanol solution (10).

2. Resins swollen by an excess of polar compounds like alcohols contain dissociated acid groups and solvated protons, as found, for example, in solutions of *p*-toluenesulfonic acid in methanol (10).

3. Resins in the presence of only small amounts of polar compounds contain a hydrogen-bonded network of $-SO_3H$ groups with strong proton donor-acceptor properties. Consequently, these resins are distinct from acid solutions and can be much more efficient catalytically.

The selectivity data for *s*-butyl alcohol (Fig. 4) lend support to this classification. At substrate partial pressures greater than about 0.2 atm, all three straight-chain butene isomers were formed in roughly the same proportion. The *cis* to *trans* ratio was 0.8, exceeding the equilibrium value of 0.45 (14). This result is similar to those reported by Manassen and Klein (15) for dehydration of *s*-butyl alcohol in an aqueous solution of 0.55 *N* perchloric acid at about 100°C; they found *cis* to *trans* ratios between 1 and 2, which are greater than the values observed here. Yet when 0.3 moles of water/mole of *s*-butyl alcohol were added to the feed (at about 0.15 atm alcohol partial pressure), the *cis* to *trans* ratio produced in the resin increased from 0.8 to 1.0, approaching the aqueous solution values. We infer that reaction in the solution involved hydrated species and that reaction in the resin involved alcohol-solvated species and (when water was present) hydrated species. The small difference in selectivity between the resin and an aqueous acid solution is then attributed to the small differences in solvation of the ionic species, including the transition state.

Manassen and Klein explained the preference for formation of the *cis* over the *trans* product by the greater stability of the *cis* π -complex formed from a proton and an olefin:



Pines and Haag (16) similarly accounted for the *cis* preference in the reaction cat-

alyzed by alumina at 350°C. Whatever the explanation for the *cis* preference, the important result here is the similarity between reaction in solution and reaction in the resin containing alcohol-solvated protons. A solvated carbonium ion intermediate in some form is clearly indicated.

The selectivity of the catalyst in contact with *s*-butyl alcohol changed substantially as the substrate partial pressure approached zero (Fig. 4). The *cis* to *trans* ratio decreased from 0.8 to 0.25, and the rate of 1-butene formation approached zero. These results point to a significantly changing character of the catalyst with decreasing substrate concentration; in particular, they point to the absence of a carbonium ion intermediate, which would be expected to yield all three of the butenes. The data for isopropyl alcohol (Fig. 6) also suggest a changing mechanism with decreased substrate concentration—the less highly cross-linked catalyst was the less active at high concentrations, but became the more active at low substrate concentrations, as catalysis by the network of acid groups became predominant.

The data for isobutyl alcohol (Fig. 5) confirm the pattern: At the lowest substrate partial pressures, isobutane was produced about as rapidly as butenes, but the data show that the paraffin formation was hindered more than olefin formation by increased alcohol or water concentration. The rate data of Fig. 5 and the infrared spectra (not shown) strongly suggest that the formation of isobutane took place in the network of acid groups, but not in the presence of solvated, dissociated groups, although the olefin formation was catalyzed by both. The tar formation was associated with isobutane formation, which implies that a strongly polar reaction intermediate abstracted a hydride ion, giving isobutane and a carbonium ion. The hydride donor could have been the polymer backbone, isobutyl alcohol, or even a hydrocarbon product (17). The carbonium ion thus formed could have reacted with the alcohol or butene, beginning a polymerization reaction and ultimately giving the observed tar. Whatever the species abstracting the hy-

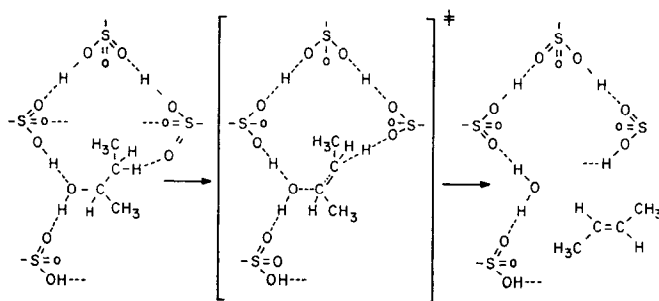


FIG. 8. Mechanism of dehydration of *s*-butyl alcohol hydrogen bridged in a network of $-\text{SO}_3\text{H}$ groups.

dride ion, it could be formed only from substrate bridged into the network of acid groups and influenced by its strong proton donor-acceptor properties.

These results point to a surprising similarity between the network of $-\text{SO}_3\text{H}$ groups and the concentrated sulfuric acid used in alkylation processes. With this evidence of the unique catalytic character of the hydrogen-bonded network of acid groups, we are faced with the question of its interpretation in terms of the reaction intermediates existing within it. A cyclic intermediate has been suggested for the dehydration of

t-butyl alcohol bridged into the network (7), and the analogous suggestion for the dehydration of *s*-butyl alcohol is depicted in Fig. 8. In this process there is a coupled transfer of protons in the network, with the abstraction of a β -proton by the strongly basic, doubly bonded oxygen of an acid group; this bond breaking is expected to be rate determining.

The evidence in favor of such a cyclic nonionic intermediate is the following: (a) The bonding within the network is consistent with the infrared spectra; (b) The dependence of rate on acid group concentra-

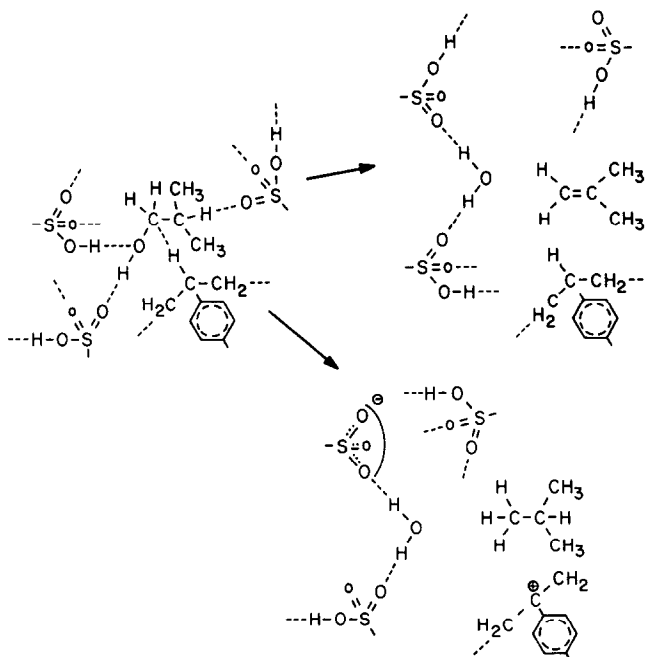


FIG. 9. Mechanisms of formation of isobutane and isobutene from isobutyl alcohol hydrogen bridged in a network of $-\text{SO}_3\text{H}$ groups.

tion (for *t*-butyl alcohol) indicates the participation of several groups (7); (c) Such an intermediate would be formed only at low substrate concentrations, when the catalyst is most efficient, and, correspondingly, at these concentrations the proton donor-acceptor properties of the groups are greatest.

The dehydration of isobutyl and isopropyl alcohols can be interpreted in the same way, as shown for the former in Fig. 9. The primary alcohol reacts roughly 100 times more slowly than *s*-butyl alcohol (Table 1), corresponding to the greater difficulty of removing a proton from its β -carbon atom. Since this process is relatively slow, we speculate that isobutyl alcohol gives an opportunity (lacking for secondary and tertiary alcohols) for the α -carbon atom to abstract a hydride ion and form isobutane, as shown in Fig. 9. This process might be especially favored in a network with very few substrate molecules, since all the acid groups shown would be available to substrate; furthermore, an acid group in addition to the ones depicted could form another hydrogen bond, this one to the remaining lone pair of electrons of the oxygen of the alcohol (corresponding to the analogous structure previously cited for water in the network).**

This suggestion of the involvement of a number of proton-donating groups leads to a speculative interpretation of the role of the flexibility of the network, as influenced by the crosslinking. The less highly crosslinked matrices would be the ones best able to conform to isolated substrate molecules, bonding to them at the maximum number of positions and having the greatest tendency to donate and abstract protons. The effect of crosslinking on the rate of iso-

** The adsorption equilibrium study of Komers, Tomanová and Beránek (18) may be interpreted as confirmation of the suggestion; their results indicate the bonding of an acid group to each of the two remaining lone pairs of the oxygens of ethers. (Their data were obtained at 150°C; adsorption of diethyl ether at 120°C has been found to be negligible, however, confirming the validity of its use as an unreactive internal standard in this work (19).)

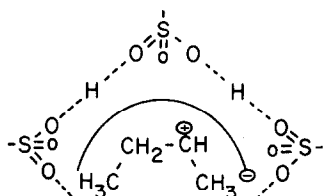
propyl alcohol dehydration at the lowest partial pressures shown in Fig. 6 can therefore be explained as an indication of the stronger proton donor-acceptor properties of the more flexible, conformable matrix. On the other hand, the greater efficiency of the more rigid matrix at high substrate concentrations [also observed for *t*-butyl alcohol (7)] may indicate a higher concentration of neighboring acid groups held apart from one another, offering substrate molecules positions remaining in the network of acid groups and still not broken up and solvated (7).

The cyclic intermediates in the network of $-\text{SO}_3\text{H}$ groups may occur with some generality. Any polar molecule could be bridged into the network, where it would experience strong polarizing forces which could lead to proton transfers. The acid groups in a flexible matrix are unique in their ability to conform to a reactant.†† Groups restricted on surfaces can hardly conform at all, whereas groups in solution (e.g., those of *p*-toluenesulfonic acid in CCl_4) may be restricted too little: The hydrogen bonding of the acid groups to one another might be associated with so little steric hindrance that a substrate molecule could break in only with difficulty. The data for *t*-butyl alcohol dehydration catalyzed by resins and by the soluble acid (7) confirm this interpretation. It is evident that for many catalytic applications, resin physical properties can be tailored to give optimum conformability.

Although alcohol dehydration reactions taking place in the flexible network of $-\text{SO}_3\text{H}$ groups evidently do not proceed *via* carbonium ion intermediates, there is evidence that butene isomerization reactions catalyzed by the resin (9, 20, 21) and by solid *p*-toluenesulfonic acid (22) do involve the *s*-butyl carbonium ion. Uematsu (21) has observed that all three butene isomers were formed and that the rate of butene isomerization was strongly dependent on the

†† The conformability, susceptibility to substrate inhibition, and diversity of multisite interactions are properties which the resin catalyst has in common with natural polymeric catalysts, the enzymes.

resin $-\text{SO}_3\text{H}$ group concentration, a result which suggests that catalysis involved a number of groups within the hydrogen-bonded network, even when the intermediate species was ionic. These results suggest that a carbonium ion solvated by the acid groups was formed:



In this ion-pair structure, the intact network of hydrogen-bonded $-\text{SO}_3\text{H}$ groups is envisioned as sharing a proton deficiency and enveloping the carbonium ion. Since the dehydration of *s*-butyl alcohol is fast compared to the butene isomerizations, the concerted dehydration process of Fig. 8 is inferred to be more efficient than one proceeding via the *s*-butyl carbonium ion.

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