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General and Specific Acid Catalysis in Sulfonic Acid Resin

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Kinetics of dehydration of *t*-butyl alcohol at 80°C were determined from rates of evolution of product isobutene from almost-constant-boiling alcohol–water and alcohol–methylcyclohexane mixtures containing suspended beads of sulfonated styrene–divinylbenzene resin. Reaction in the absence of water was catalyzed by the matrix-bound $-SO_3H$ groups; the turnover number was about 0.2 sec^{-1}. Water added to the reactant competed for $-SO_3H$ groups, strongly inhibiting the reaction up to a concentration of about 0.7 *M*. The inhibiting effect decreased on further addition of water, and at concentrations exceeding about 11 *M*, water became only a diluent; then the reaction was catalyzed by hydrated protons in the resin matrix and was first-order in alcohol concentration. The kinetics are represented by an equation summing the limiting rates at high and low water concentrations.

INTRODUCTION

Acid–base catalysis in solution by H_3O^+, OH^-, and undissociated acid and base is often described by kinetics of the following form (*1*):

$$r = k_{H_3O^+}C_{H_3O^+}C_S + k_{OH^-}C_{OH^-}C_S + k_{HA}C_{HA}C_S + k_BC_BC_S \quad (1)$$

A single term in the equation may predominate for an aqueous solution at a certain pH value.

Acid–base catalysis by functional groups attached to a solid is sometimes analogous to the extent that it can be described by a special case of the same equation. For example, sulfonic acid ion-exchange resin in the presence of high concentrations of water can be modeled as a homogeneous phase containing H_3O^+, with *r*, the rate of reaction per unit volume of resin, represented by the first term on the right-hand-side of Eq. (1) (*2*, *3*). When used in the presence of low water concentrations, sulfonic acid resin catalyst is best represented as a fixed array of undissociated acid groups; since the groups have a strong tendency to be hydrated, water is usually a reaction inhibitor (*4*–*9*). In the special case of low coverage of the groups by substrate, the rate may be represented by the third term on the right-hand-side of Eq. (1). More than one term is required when both dissociated and undissociated groups are present simultaneously.

In the experiments reported here we have measured kinetics of the dehydration of *t*-butyl alcohol catalyzed by beads of sulfonic acid resin suspended in liquid reactant. The data demonstrate a pattern analogous to that in solution acid–base catalysis: on addition of water there is a transition from catalysis by bound $-SO_3H$ groups to catalysis by hydrated protons in the matrix.

NOMENCLATURE

C	Concentration, moles/liter
k	Reaction rate constant, liter/(mole sec)
κ	Reaction rate constant, moles/(equiv of acid groups sec)
κ'	Pseudo-first-order reaction rate constant, liter/(equiv of acid groups sec)

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K	Adsorption parameter in empirical rate equation, liter/mole
r	Homogeneous reaction rate, moles/(liter sec)
R	Heterogeneous reaction rate, moles/(equiv of acid groups sec)
$\alpha, \beta, \gamma, \delta$	Integral or half-integral powers in empirical rate equation

Subscripts

A	Alcohol
B	Base
HA	Acid
W	Water
S	Substrate

EXPERIMENTAL

The method was extended from that of Frilette *et al.* (*4*). A mixture of about 200 ml of *t*-butyl alcohol and water or of *t*-butyl alcohol and methylcyclohexane was charged to an electrically heated, stirred, three-neck reaction flask and brought to a boil. A weighed sample of Amberlyst 15 (macroporous sulfonated styrene–divinylbenzene copolymer, 3.0×10^{-3} equiv/air-dried g; preconditioned as usual (*10*)) was dried under vacuum at 120°C and charged immediately to the reactor. Isobutene produced in the alcohol dehydration reaction flowed as off-gas through a condenser to a soap-film flow meter. Flow rate was measured periodically, typically for half an hour after the start of reaction. For any of the boiling reaction mixtures, the observed reactor temperature was initially 80 ± 2°C since the alcohol–water and alcohol–methylcyclohexane mixtures form minimum boiling-point azeotropes within this range. Since the normal boiling point of *t*-butyl alcohol (82.5°C) is only slightly higher than those of the azeotropes, data obtained for the pure reactant were not seriously in error.

RESULTS

Typical off-gas flow rate data are shown in Fig. 1. The results for each run were extrapolated to zero time, giving an estimate of reaction rate for the solution composition charged to the reactor. Rates were initially

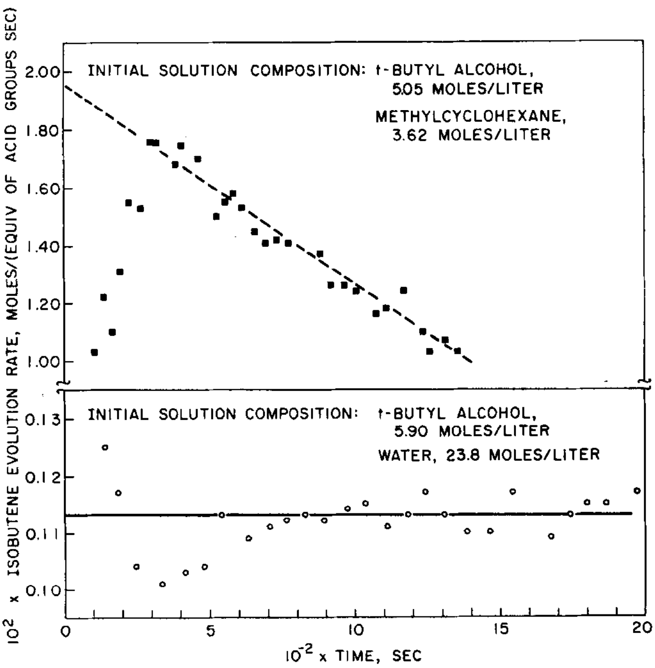

FIG. 1. Determination of reaction rates for initial solution compositions by extrapolation of isobutene evolution rates.

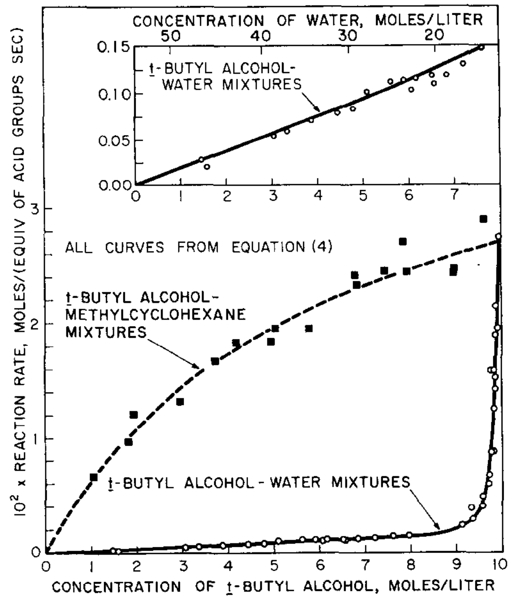

FIG. 2. Kinetics of *t*-butyl alcohol dehydration catalyzed by sulfonic acid resin at 80°C.

less than the extrapolated values because isobutene was accumulating in the still unsaturated solution. Rate decreased markedly after saturation of each alcohol–methylcyclohexane solution because water accumulated, lowering the temperature and inhibiting the reaction.

The rate data found by extrapolation are collected in Fig. 2. They demonstrate strong inhibition by water present at the lowest concentrations. The extrapolated rates for these solutions are relatively imprecise because the rate was sensitive to accumulation of small amounts of water and because deviations from the desired reactor temperature were relatively large. The data of Fig. 2 show that at the higher water concentrations the competitive inhibition no longer occurred; rate was proportional to the concentration of alcohol, with water acting only as a diluent.

DISCUSSION

The absence of mass transport influence on reaction rate has been demonstrated previously (*11*), and therefore we conclude that the data represent intrinsic kinetics of the dehydration of *t*-butyl alcohol.

The results of Fig. 2, showing a strong inhibition by water at the lowest concentrations and a transition from first-order toward zero-order reaction with decreasing diluent concentration, point to the applicability of a rate equation accounting for competition between alcohol and water for catalytic sites. Langmuir–Hinshelwood kinetics have been found repeatedly to represent data for reactions catalyzed by matrix-bound $-SO_3H$ groups (*4–9*). The present data were therefore compared to equations of the following form (which implies the assumption that methylcyclohexane is an inert diluent):

$$\text{R} = \frac{\text{K}(K_AC_A)^\alpha}{[1 + (K_AC_A)^\beta + (K_WC_W)^\gamma]^\delta}. \qquad (2)$$

Machine computations with a least-squares parameter estimation program (*12*) were performed to determine the goodness of fit with the best values of K, K_A, and K_W for integral and half-integral values of the exponents ranging from zero to three. Although several equations gave good representations of the data for low water concentrations, none adequately represented those for high water concentrations since water was no longer an inhibitor.

The data of Fig. 2 (inset) show that for alcohol–water mixtures the kinetics became first-order in the limit as C_A approached zero:

$$\text{R} = \text{K}'C_A. \qquad (3)$$

The value of K' determined from data for $C_A < 8\,M (C_W > 12\,M)$ is 1.84×10^{-3} liter/(equiv of acid groups sec). We infer that at high water concentrations reaction was catalyzed by hydrated protons in a resin medium strongly resembling a water–alcohol solution.

We have two limiting cases in Eqs. (2) and (3). Since catalysis by the $-SO_3H$ groups is much more rapid than catalysis by hydronium ions, little error results from our approximating the complete set of rate data by the sum of the limiting cases. A number of equations have been compared to the data, and the best few are collected in Table 1. The most precise representation is given by the following equation, which is compared to the data in Fig. 2:

TABLE 1
EMPIRICAL RATE EQUATIONS

Equation	Parameters: k moles/(equiv of acid groups sec)	Parameters: K_A liter/mole	Parameters: K_W liter/mole	Parameters: k' liter/(equiv of acid groups sec)	Sum of squares of deviations of predicted from observed rates moles/(equiv of acid groups sec)
$\mathrm{R} = \dfrac{\mathrm{k} K_A C_A}{1 + K_A C_A + K_W C_W} + \mathrm{k}' C_A$	0.0425	0.158	3.55	0.000184	0.0205
$\mathrm{R} = \dfrac{\mathrm{k} K_A C_A}{1 + K_A C_A + (K_W C_W)^2} + \mathrm{k}' C_A$	0.0386	0.188	1.89	0.000184	0.0158
$\mathrm{R} = \dfrac{\mathrm{k} K_A C_A}{1 + K_A C_A + (K_W C_W)^3} + \mathrm{k}' C_A$	0.0355	0.220	1.58	0.000184	0.0225

$$\mathrm{R} = \frac{\mathrm{k} K_A C_A}{1 + K_A C_A + (K_W C_W)^2} + \mathrm{k}' C_A. \quad (4)$$

The parameter values determined by the nonlinear estimation procedure (with k' fixed) are summarized in Table 1. At values of $C_W > 11\ M$ ($C_A < 8\ M$) the first term on the right-hand-side of Eq. (4) is less than about 10% of the rate, corresponding to catalysis predominantly by hydrated protons (specific acid catalysis). At values of $C_W < 0.7\ M$ the second term on the right-hand-side is less than about 10% of the rate, corresponding to catalysis predominantly by undissociated $-SO_3H$ groups (general acid catalysis).

The kinetics of general acid catalysis of *t*-butyl alcohol dehydration found here differ slightly in form from those reported by Frilette *et al.* (*4*) and by Jeřábek *et al.* (*13*), whose equations were based on more restricted sets of data. In view of the imprecision of the data, especially at low water concentrations, we regard the discrimination among possible rate equations as less than a sufficient basis for determining the number of $-SO_3H$ groups constituting a catalytic site. The question is discussed elsewhere on the basis of infrared spectra and data indicating the dependence of rate on $-SO_3H$ group concentration (*10, 14*).

The values of the kinetic parameters imply that the first-order rate constant for reaction catalyzed by $-SO_3H$ groups at very low coverage by alcohol (when $\mathrm{R} = \mathrm{k} K_A C_A$) is about 40 times the first-order rate constant for reaction catalyzed by hydrated protons at low alcohol concentrations (when $\mathrm{R} = \mathrm{k}' C_A$). The reaction rate when the $-SO_3H$ groups are saturated with substrate (when $\mathrm{R} = \mathrm{k}$) is 0.0386 mole/(equiv of acid groups sec); if a catalytic site consists of four $-SO_3H$ groups (*10*), then the turnover number is 0.15 sec^{-1}.*

In summary, the present results demonstrate the transition from general to specific acid catalysis as water is added to matrix-bound $-SO_3H$ groups. This transition may account for the often complex kinetics of reactions catalyzed by ion-exchange resins in various degrees of hydration.

For example, Metzner *et al.* (*15*) determined kinetics of isobutene hydration catalyzed by sulfonic acid resin, observing reaction rates proportional to the amount of water sorbed by the resin up to a concentration of about 3 mole/equiv of acid groups. At higher values the rate was independent of water concentration. Since infrared studies of resin hydration (*16*) show that $-SO_3H$ groups are dissociated on addition of two molecules of water per group (a

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[*] The kinetic results of Jeřábek *et al.* (*13*), obtained for reaction of *t*-butyl alcohol at 95°C, suggest that the more weakly acidic $-P(OH)_2$ and $-PO(OH)_2$ groups have about 0.04% and 0.3% of the activity of the $-SO_3H$ groups, respectively.

value corresponding approximately to the transition in the olefin hydration kinetics), we infer that at the higher water concentrations reaction was catalyzed by hydrated protons, and that at the lower concentrations reaction involved hydrogen-bonded water molecules in the network of $-SO_3H$ groups.

Kinetic data for the dehydration of isopropyl alcohol at 90–110°C (*7*) are consistent with this interpretation. At low water partial pressures ($\lesssim 20\%$ of the vapor pressure) the reaction was inhibited by water and described by Langmuir–Hinshelwood kinetics. Data for higher water partial pressures could not be represented by extrapolation of the equation. We infer that beyond the range of applicability of the equation, there were more than about two water molecules present per acid group, with catalysis by hydrated protons. The inference is confirmed by data of Herlihy (*17*) for equilibrium adsorption of water on sulfonic acid resin—when the partial pressure of water was equal to 20% of the vapor pressure at 100°C (or at 118°C), the amount of water adsorbed was about two molecules per acid group.

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