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Kinetics of Dehydration of *ter* -Butyl Alcohol Catalyzed by Ion Exchange Resins

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The dehydration of *tert*-butanol catalyzed by 2% and 8% cross-linked Dowex 50 W is studied. Assuming the reactions to be heterogeneous, the data are found to agree with a simple Langmuir-Hinshelwood model in which the competitive chemisorption of alcohol and water is postulated. The most likely catalytic sites are the anhydrous, un-ionized sulfonic acid groups, or their monohydrates.

Increased cross-linking affects the energetics of the sulfonic acid groups. This is reflected in changes in the chemisorption constants, increased rates of conversion, and perhaps an alteration of the activation energy of the reaction.

INTRODUCTION

The catalytic properties of ion exchange resins have received considerable attention (*1*). These materials are of practical interest since they are readily available and easily separated from the reaction mixture. Other features of these materials have evoked academic interest. This has ranged from studies of the effect of the polymeric moiety on the activity of simple catalytic centers (*2*) to the simulation of enzyme behavior by the introduction of complex prosthetic groups (*3*).

The purpose of the present study is to examine in some detail the resin-catalyzed dehydration of 2-methyl-2-propanol (*tert*-butyl alcohol). The cross-linked polystyrene sulfonic acids used in this investigation are known to be efficient acid catalysts (*4*, *5*). We shall attempt to treat the decomposition as a surface-catalyzed reaction rather than one which proceeds in a homogeneous acid phase. In this treatment, the resin is conceived as a porous solid with catalytic sites distributed over the internal surfaces. The kinetic approach used has been outlined by Hinshelwood, and is sometimes referred to as "Langmuir-Hinshelwood" kinetics (*6*).

tert-Butyl alcohol is well-suited to the present study. Although thermally stable at high temperatures, it is catalytically decomposed at its boiling point in the presence of the resin catalyst, thus permitting studies to be made with simple equipment at atmospheric pressure. Also, the decomposition products are restricted to 2-methylpropene (isobutene) and water, since for this alcohol the formation of di-*tert*-butyl ether does not occur under the conditions of the experiments (*7*).

EXPERIMENTAL METHODS

Dehydration apparatus. The equipment shown in Fig. 1 was used throughout the present study. The resin catalyst, prepared as described below, was charged to the boiling flask which contained about 100 ml of dry *tert*-butanol at room temperature. The mixture was brought to rapid reflux with constant stirring. The heat input was then adjusted so that the reflux zone extended about 3 inches into the glass bead packing shown in the drawing. This packing was inserted to damp erratic convection currents in the vicinity of the vapor front.

Under the conditions described, the isobutene formed by the dehydration reaction was rapidly expelled from the boiling alcohol at a steady rate. Rate measurements were made periodically by utilizing the rising

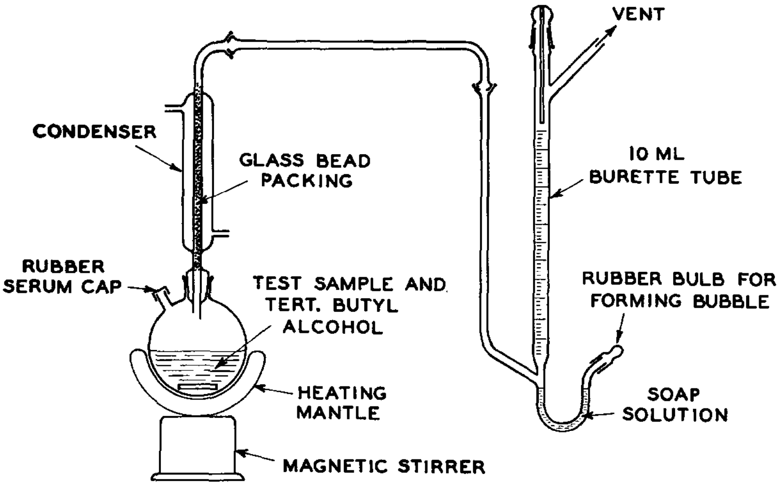

FIG. 1. Dehydration apparatus.

film flow meter shown in the drawing. Simultaneously with each rate measurement, a small amount of vapor was withdrawn through the serum cap and condensed directly into a Hamilton microsyringe to provide a 3-μl sample. This was analyzed as described in a subsequent paragraph.

The observed rates of decomposition showed a marked dependence on the concentration of water in the system, especially at very low concentrations. Suitable small changes in the water content at the lower levels were provided by the accumulation of water resulting from the dehydration reaction alone. As conversion progressed, there was a marked decrease in the rate of accumulation and the rate itself became less sensitive to additional water. Therefore, in order to study an extended range of water concentration within a reasonable period of time, increments of water beyond the first six or seven were provided mostly by injections through the serum cap. After an injection, 15 min was allowed to re-establish equilibrium before making measurements. Analyses of the samples of vapor phase provided data on water activities corresponding to the respective observed rates of isobutylene evolution.

Analysis of vapor. The samples of vapor phase were analyzed by use of a Perkin-Elmer Model 154 Vapor Fractometer fitted with a 15-ft by 1/4-inch O.D. copper column containing Carbowax 1000 (10%) on Haloport F. The column was operated at 125°C with a helium carrier stream flowing at 70 cc/min. This system effectively resolved isobutylene, *tert*-butyl alcohol, and water. Study of samples of *tert*-butyl alcohol which contained from 0 to 20 wt % of water showed peak height linearly related to wt % water with a relative error of less than 1% for 3-μl sample size. Thus, samples of vapor phase were analyzed for water content directly from peak height. The samples were found to contain about 3.2 wt % isobutene throughout, so this quantity will be neglected in the data to be presented.

Temperature control. The characteristics of the alcohol-water system are such that thermostatting or other means to control temperature was not necessary. The boiling point of *tert*-butyl alcohol is 82.5°C, and its azeotrope, containing 35.4 mole % water, boils at 79.9°C (*8*). The compositions encountered in the present studies were at most only slightly richer in water than the azeotrope, and the temperatures of the refluxing mixtures were found by actual observation to span an interval of less than 2°C.

Preparation of catalysts. The catalysts used were prepared from commercially available bead resins, viz., Dowex 50 W X-2 and X-8. These are manufactured by sulfonation of copolymers of styrene with 2 and 8% divinylbenzene, respectively.

Both samples of resin were purchased as

50–100 mesh particles. Finer particles were prepared by grinding and sieving the ground material.

The resins, purchased in the H+ form, were washed with distilled water to remove any extraneous material and were conditioned by converting to the sodium and reconverting to the hydrogen form. Samples were dried under vacuum at 100°C in a drying pistol for 2 hr prior to use.

An approximate amount of sample was introduced initially, and the exact amount was determined by titration at the end of the experiment.

RESULTS AND KINETICS ANALYSIS

Dowex 50 W X-2

Three series of measurements with different amounts of catalyst and different particle sizes were made with the low cross-linked resin. Data from these experiments are collected in Table 1. The first two series were made with 100-micron particles, using 1.14 meq (~0.2 g) catalyst in the first case, and 4.44 meq (~0.8 g) in the second. The smaller charge of catalyst allowed precise measurements of the isobutene evolution rates in the low water region where the rates would otherwise be relatively fast. Data from the larger charge overlap those from the first experiment over a considerable range, and extend further into the region of the more aqueous alcohol compositions. Data from the two series appear to be in good agreement, as shown in Fig. 2. This agreement is of considerable significance and will be discussed in the following paragraphs.

TABLE 1
RATE OF ISOBUTENE FORMATION WITH DOWEX 50 W X-2

1.14 Meq catalyst, 75–125 micron particles		4.44 Meq catalyst, 75–125 micron particles		2.82 Meq catalyst, 150–300 micron particles	
Rate[a]	[W][b]	Rate	[W]	Rate	[W]
44.6	.017	30.4	.039	30.8	.025
39.1	.024	23.0	.061	27.0	.045
35.1	.040	13.6	.150	24.0	.065
34.0	.050	12.2	.160	22.6	.071
29.2	.058	6.78	.254	19.5	.088
19.9	.103	5.68	.303	13.2	.164
18.8	.109	5.47	.305	9.22	.218
15.5	.139	4.77	.355	6.56	.280
14.4	.151	4.19	.369	4.57	.355
10.6	.211	4.21	.376	3.22	.416
10.3	.211	4.01	.382		
6.66	.299	3.92	.392		
6.10	.303	3.78	.375		
		3.58	.352		

[a] Rate of isobutene formation in cc/sec/meq × 10^2.

[b] Mole fraction of water in the vapor phase determined by chromatographic analysis.

Differential Character of Reactor

For heterogeneous catalysts, it is well known that the observed kinetics may be very different from the relations in the immediate vicinity of the catalytic site. These differences originate from concentration gradients of various types. Although the complete elimination of such gradients is not possible, it is very desirable to reduce them to the extent that they are no longer of consequence. A reactor system in which this is achieved is called a "differential reactor." The reader is referred to an excellent treatment of this subject given by Weisz and Prater (*9*).

The system used in the present study includes a solid (catalyst), liquid, vapor, and gas phase. Furthermore, during the course of a series of measurements there is a gradual change in the compositions of these phases as water produced by the dehydration accumulates. It becomes pertinent, therefore, to ask if the measurements made with this system truly reflect the intrinsic behavior of the catalyst.

If we neglect, for the moment, the problem of gradients within the catalyst particle itself, we may consider the catalyst simply as an emitter of isobutene and water. These are distributed uniformly through the liquid phase by agitation, and in the course of refluxing the isobutene is expelled from the system to form a gas phase while the water tends to equilibrate with the vapor phase. High local concentrations of isobutene even in the immediate vicinity of the catalyst particle are not likely to persist since they would be removed by bubble formation due to lowering of the boiling point. A qualitative examination of Fig. 2 shows that the

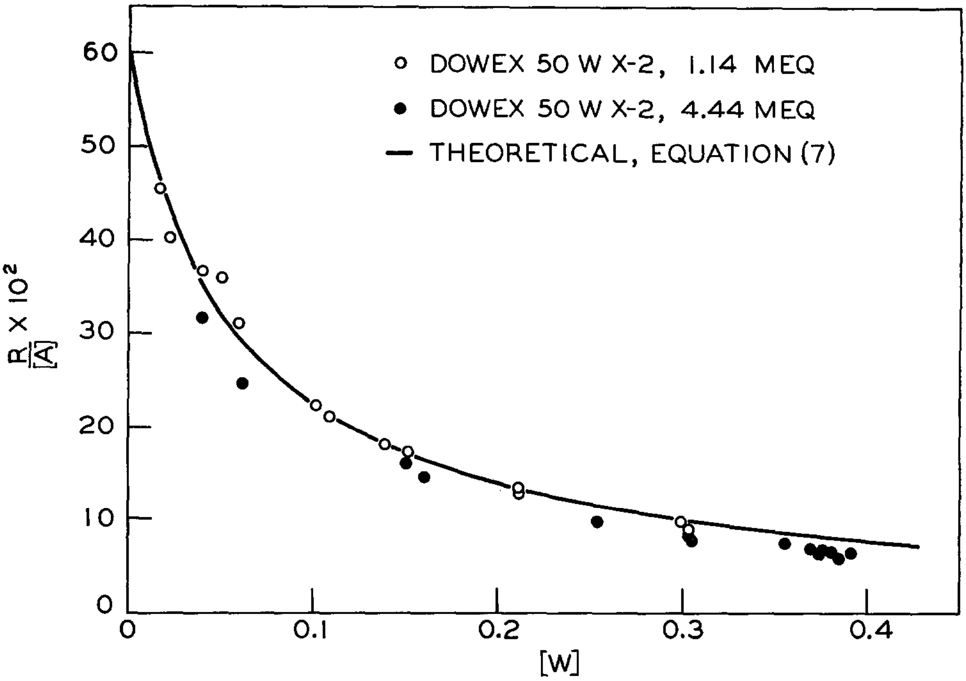

FIG. 2. Behavior of low cross-linked resin.

initial rate of evolution of isobutene is high but falls rapidly as water accumulates. Measurements made at one instant will reflect the behavior of the emitter at some prior instant, i.e., we can expect that the isobutene rate measurements will contain a positive error, while the water vapor pressure measurements will contain a negative error. These errors will become smaller in a system operating at constant reflux rate as the amount of emitter in the system is reduced, and in the limit they will vanish. As shown in Fig. 2, a drastic reduction in the amount of catalyst produces little change in the data; and we may assume that the measured rates and concentrations adequately reflect the instantaneous situation at the catalyst boundary.

A third series of measurements made with particles twice as large as in the other two series (Table 1) showed no marked effect of particle size. The absence of significant gradients within the smaller particles may be assumed. Thus, considered together, the three series of measurements establish the *differential* character of the reactor as used in this study.

Kinetic Analysis

Consideration of Fig. 2 shows that a model based only on an isotherm for sorption of alcohol on catalytic sites is inadequate since the reaction is of apparent order much greater than one. The model suggested by the data is one in which the product water depresses the catalytic rate by competitive sorption on active catalytic sites. The kinetic equation for the most simple form of this model may be generated as follows:

The productive reaction sequence, representing the chemisorption of alcohol on the catalytic sites, followed by desorption of products, is given by:

$$[A] + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AS \xrightarrow{k_3} \text{Olefin} + [W] + S \quad (1)$$

The reverse reaction may be ignored in the present study since the equilibrium for the system corresponds to essentially complete decomposition (*10*). The chemisorption of water may be written:

$$[W] + S \underset{k_5}{\overset{k_4}{\rightleftharpoons}} WS \quad (2)$$

In these expressions,

[A] and [W] = activities of alcohol and water, respectively, the standard state being chosen as pure vapor at 1 atm and 80°C;

S = number of free sites in the system at any time;

AS and WS = number of sites occupied by chemisorbed alcohol or inactivated by chemisorbed water at any time.

At any instant, the rate of isobutene formation dn/dt, is represented by:

$$dn/dt = k_3 \times AS \qquad (3)$$

For the steady state, we may write:

$$K_A[A] \times S = AS \text{ and} \qquad (4)$$
$$K_W[W] \times S = WS$$

where

$$K_A \cong \frac{k_1}{k_2 + k_3}, \quad K_W = \frac{k_4}{k_5}$$

The total number of sites, N, is given by:

$$N = S + AS + WS \qquad (5)$$

Substitution of (4) and (5) into (3) gives:

$$\frac{dn}{dt} = N\frac{k_3 K_A[A] \times S}{S + AS + WS} \qquad (6)$$

Eliminating S,

$$R = \frac{dn/dt}{N} = \frac{k_3[A]}{[A] + (1/K_A) + (K_W/K_A)[W]} \qquad (7)$$

where

R = the specific rate of isobutene evolution and

N = titrable acidity measured in milliequivalents.

In the experiments as performed, the partial pressure of the olefin is always quite small, so that we may write $[A] + [W] \approx 1$. Based on this approximation, a useful and very sensitive linearized form of (7) is:

$$\frac{R}{[A]} = \frac{k_3}{1 + (1/K_A)} - \frac{(K_W/K_A) - 1}{1 + (1/K_A)} \cdot \frac{R}{[A]}[W] \qquad (8)$$

Figure 3 shows such a plot for the data in Table 1.

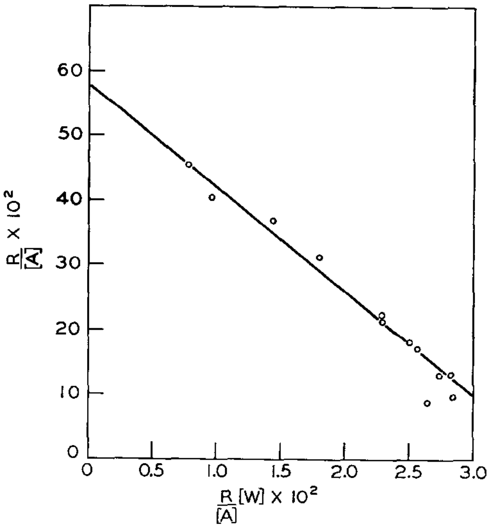

FIG. 3. Dowex 50 W X-2.

Effect of Cross Linking

A series of measurements was made with the 8% cross-linked Dowex 50 W. It was found necessary with this resin to use considerably smaller particle size (<50 microns) to avoid effects of particle diffusion limita-

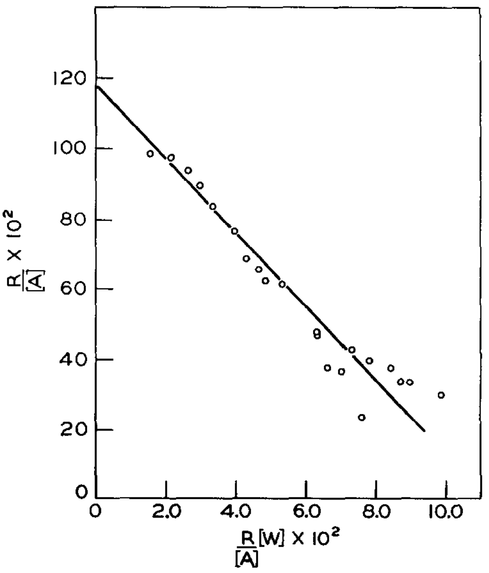

FIG. 4. Dowex 50 W X-8.

tions. This is understandable in view of the expected lower diffusivity of the more highly cross-linked material.

The general characteristics of the kinetics for the higher cross-linked material are similar to those for the other sample, as shown in Fig. 4. However, the value at the intercept is much larger and the slope somewhat less, revealing a strong dependence of the characteristic constants on the level of cross linking.

DISCUSSION

Mechanistic interpretations of acid-catalyzed transformations usually are based on a set of stoichiometric reactions, i.e., reactions in which well-defined ions, molecules, and functional groups participate, presumably on a statistical basis. However, the kinetics of certain of these reactions appears to require a definition of "acidity" which has no obvious relation to stoichiometry. Since the hydration of isobutene is just such a case (*11*), it is surprising to find the observed rates in the present study in agreement with an unsophisticated model based on stoichiometry. The extent of this agreement is shown most clearly by Fig. 2, in which a theoretical curve is superimposed on observed data. Certainly, an apparent agreement of this kind might arise even though the actual catalysis were considerably more complex than assumed in the model, in which case the agreement would become trivial. It seems more probable, however, that a basic simplicity truly exists, and that the catalysis may be understood in terms of an element of structure together with valid kinetic and mass action constants. Assuming the agreement to be significant, it is of some interest to discuss the inferences that may be drawn concerning the nature of S, the active sites.

There is little doubt that the catalytic intermediates in the present instance involve the hydrogen form of the anhydrous sulfonic acid group or its hydrates. For, catalysis is exhibited by simple as well as polymeric arylsulfonic acids, and it is virtually absent when only the salts of these acids are present.

We may now consider which of the *stoichiometric* hydrates is compatible with the model. In the construction of this model we have assumed the existence of an invariant number of sites which are noninteracting. We have also assumed that the monohydrate of the site S, viz. WS, is catalytically inactive. This does not necessarily mean that S itself is anhydrous, but only that the addition of one *more* molecule of water renders it inactive. Water sorption isotherms determined in the *absence* of alcohol suggest that the resinous sulfonic acids form tri- and tetrahydrates quite readily, i.e., in the range of water vapor pressures encountered in the present study (*12*). To reconcile this behavior with the relatively simple sorption isotherm assumed for the kinetic model is difficult. For, the assumption of an invariant number of sites distributed among S, AS, and WS does not allow for substantial removal of these as higher hydrates such as W_2S. However, recent studies made on the sorption of water from alcohol solution suggest that the hydration number of the proton is abnormally low, probably because of substitution of alcohol for water in the primary solvation shell (*13*). In the light of these results it seems reasonable to assume that only one, or at most two, water molecules may combine with the anhydrous sulfonic acid group in the presence of high concentrations of *tert*-butyl alcohol. Should the hydration number be one, the kinetic equations as written would be exact and S would represent the un-ionized, anhydrous sulfonic acid group. Should the hydration number be two, the monohydrated site S would correspond to the hydronium ion. In this instance S would be in equilibrium with the anhydrous sulfonic acid group. If we characterize this equilibrium by the constant K'_W, and the equilibrium with the second water molecule by K_W, a modification of Eq. (8) is obtained which has the same intercept term but the following slope term

$$\left[\frac{(1/K_A K'_W[W]^2) + (K_W/K_A) - 1}{1 + (1/K_A)}\right]$$

With sufficiently large values of K'_W and K_A, this term reduces to the slope term of Eq. (8) except for very small values of W. Since no marked curvature is shown by the plots of Figs. 3 and 4, we may conclude either that the active site is the anhydrous sulfonic acid group, or that it is the monohydrate, for which case the values of K'_W and K_A are large. We cannot distinguish between these alternatives with the information at hand.

As to the effect of cross linking, we note that the 8% cross-linked resin has about twice the catalytic activity of the 2% resin at zero water. One may infer from this finding that resins prepared in the ordinary fashion are likely to be heterogeneous to the extent that the cross-linking agent is nonuniformly incorporated in the structure. Thus, the heterogeneity postulated by students of ion exchange behavior has a demonstrable counterpart in catalysis.

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