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The Dehydration of Formic Acid Catalyzed by Polystyrene Sulfonic Acid

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Rates of formic acid dehydration in a flow reactor were measured at atmospheric pressure and temperatures between 110 and 157°C. Catalyst was a cation exchange resin (cross-linked polystyrene sulfonate) in the hydrogen form and the 49% hydrogen, 51% sodium form. Sulfonic acid groups are the catalytic sites, and the reaction intermediate involves two or three such groups. Structures of a hydrogen-bonded intermediate complex are proposed with reaction mechanisms.

INTRODUCTION

Cross-linked polystyrene sulfonic acid, a cation exchange resin, is an active catalyst for such acid-catalyzed reactions as the dehydration of alcohols (*1–4*). For the reactions of methanol and ethanol the resin has identifiable catalytic sites, the sulfonic acid groups (*1*). These groups in the dehydrated state may constitute a nearly homogeneous array of sites, as suggested by Kabel and Johanson (*2*). They observed Langmuir-Hinshelwood kinetics for the dehydration of ethanol to diethyl ether and evaluated kinetic parameters approximately equal to independently determined Langmuir adsorption equilibrium constants for ethanol, ether, and water.

The resin-catalyzed formic acid dehydration was investigated by Andrianova and Bruns (*5, 6*), who measured kinetics at temperatures between 130 and 175°C. At 150°C the reaction is roughly first-order in formic acid partial pressure for pressures less than 1 atm. The order decreases with increasing pressure, suggesting the catalytic sites are nearly saturated with formic acid at 1 atm. The formic acid dehydration is inhibited by water, as are the alcohol dehydrations. With increase in degree of sulfonation of the resin from 1.9 to 4.8 meq/g, the rate of reaction per sulfonic acid group at 175°C increased from 0.31 to 1.6 g/sec, suggesting that the reaction intermediates involves two or three sulfonic acid groups. The present experiments were undertaken to provide further evidence concerning the dependence of reaction rate on resin sulfonic acid group concentration.

EXPERIMENTAL METHODS

Equipment

The reactor system (Fig. 1) was constructed of glass. The reactor was a tube 3 cm in diameter and 10 cm long. It was connected to a vaporizing coil and built into a vessel for boiling organic liquids to provide constant temperature operation. The reactor ends were plugged with glass wool and packed with 3 mm diameter glass beads. The center section of the reactor was packed for a length of about 5 cm with a mixture of 3 mm diameter glass beads and 2 to 8 g of catalyst beads. Liquid formic acid flowed from two constant-head tanks, one of which was a modified buret; volumetric flow rate was measured with a stopwatch. Reactant flowed from the buret through the vaporizing coil, upward through the reactor, and through a heated exit tube to the vapor-sampling valve of a Perkin-Elmer 116E gas chromatograph.

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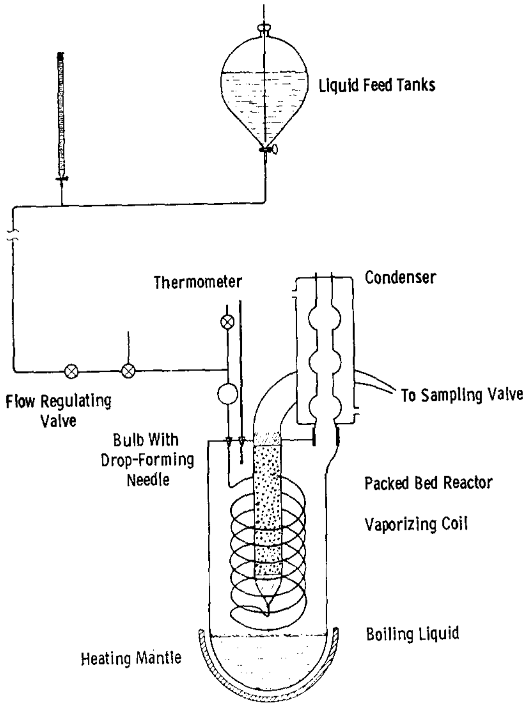


FIG. 1. Reactor system.

The valve was enclosed in a box, heated with a hot air stream, and thermostated at 105°C to prevent condensation of the product vapors. The Perkin-Elmer "BA" column was used for analysis of carbon monoxide and formic acid. Analysis of water was not precise with this method and was omitted. The column was maintained at 150°C, and helium carrier gas flow rate was 55 ml/min.

Materials

Reagent grade formic acid (98–100%) was obtained from Riedel-de-Haen and distilled from anhydrous copper sulfate to remove water. Helium was supplied by Linde, 99.98% pure. Catalyst was the ion exchange resin Dowex 50W X-8 (a sulfonated copolymer of styrene and 8% divinylbenzene), manufactured by the Dow Chemical Company and supplied in the hydrogen form as 50- to 100-mesh (150–300 μ) particles.

Procedure

The complete batch of catalyst was preconditioned by twice converting it to the sodium form and then again to the hydrogen form. Lithium, sodium, and potassium form resins were prepared by contacting the hydrogen form with excesses of the metal hydroxides in aqueous solution. The resin containing 51 mole % sodium and 49 mole % hydrogen was prepared by repeated contacting with an aqueous solution of the appropriate equilibrium composition. The resins were washed with distilled water and dried in air. Compositions and capacities were found by titration to determine exchangeable hydrogen ion in the original and completely acidified samples.

Conversion data were obtained for reaction at atmospheric pressure. Each datum is an average of at least three and usually more separate analyses of reactor products with the corresponding flow rate measurements. Each result was obtained in an apparent steady state indicated by the absence of a trend in the analyses.

Precision

Conversion data are precise within ±6%, flow rates within ±3%, and reaction rates within ±9%. Differential conversion was assumed. All but two conversions were less than 0.06 moles reacted per mole fed. The data of Andrianova and Bruns (*5*), indicating a moderate inhibition by product water, suggest the reported conversions are slightly beyond the differential range, affecting the accuracy of rates by a few percent. Thermostat temperatures are correct within ±2°C.

RESULTS

Preliminary experiments were conducted with qualitative gas chromatographic analysis. With the hydrogen form catalyst the decomposition of formic acid to carbon monoxide and water was demonstrated. No carbon dioxide was found. The lithium, sodium, and potassium form resins had no measurable catalytic activity at 120°C.

Results for the hydrogen form and the 49% hydrogen form resin are shown in Fig. 2 for temperatures from 110–157°C. Considerable variation in activity was observed for individual catalyst samples as well as various samples of one composition. The

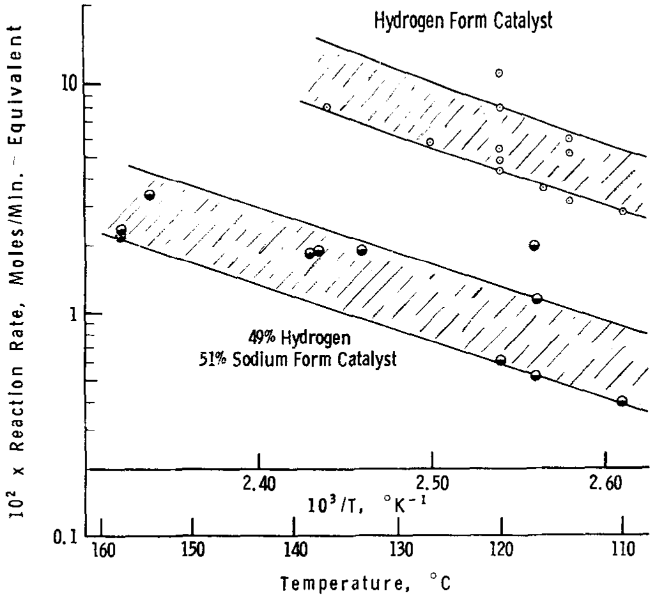


Fig. 2. Rate of formic acid dehydration.

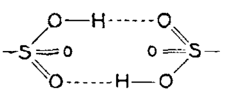
scatter is not resolved, though it may be the result of inconsistent reactor start-up procedures. Air-dried catalyst containing about 30% water was contacted with liquid formic acid in various amounts as the thermostat was brought to operating temperatures; this was done to avoid rapid catalyst drying and the irreversible loss of activity which had been observed for the esterification of acetic acid with ethanol (*7*) and the dehydration of methanol and ethanol (*8*).*

The results of Fig. 2 are consistent with those of Andrianova (*6*) in showing a second- or third-order dependence of reaction rate on catalyst sulfonic acid group concentration. An apparent activation energy of 12 kcal/mole is estimated for each catalyst, nearly equal to the value of 13 kcal/mole reported by Andrianova.

Discussion

The strong temperature dependence of reaction rates is evidence that diffusion in the vapor phase external to the catalyst particles did not significantly affect rates. The lack of a considerable intraparticle diffusion resistance is indicated by Andrianova (*6*), who varied particle size in the range pertinent to this work and observed no influence on rate for values somewhat greater than those reported here.

The absence of catalytic activity for the salt forms of the resin demonstrates that the ion exchange resin's catalytic activity resides in the sulfonic acid groups. The dependence of activity on sulfonic acid group concentration indicates that the reaction intermediate includes two or three groups. The nature of the chemical bonds may be inferred from the results of several infrared investigations which indicate the formation of strong hydrogen bonds with resin sulfonic acid groups acting as both proton acceptors and donors. Zundel *et al.* (*9*) found that sulfonic acid groups in the dehydrated resin are paired by formation of a doubly hydrogen-bonded structure:



Zundel and Metzger (*10*) summarized results for dehydrated resins. At low concentrations water is strongly bonded to three sulfonic acid groups:

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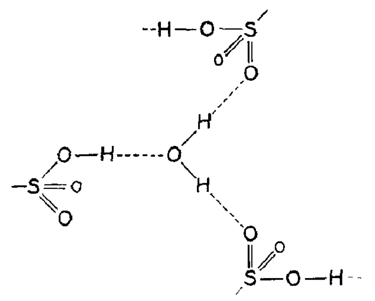
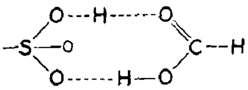
* Andrianova (*6*) reports without elaboration that steady-state activities are generally less than initial activities.



A fourth sulfonic acid group may be similarly bonded to the remaining electron pair of the oxygen in water.

Infrared spectra of formic acid combined with the ion exchange resin at room temperature were observed by Knözinger and Noller (*11*). They proposed that formic acid is bound by hydrogen bonds similar to those in formic acid dimers and in the dehydrated resin:



Their analysis defined the chemical bonds without excluding the possibility that formic acid is combined with more than one sulfonic acid group.

A reaction intermediate involving formic acid bridged between two sulfonic acid groups is proposed in Fig. 3. No free hydroxyl groups are shown as their absence is indicated for both formic acid (*11*) and water (*10*) combined with the resin. Two hydrogen bonds to the carbonyl oxygen are shown, analogous to the structure suggested for water. According to Knözinger and Noller motion of a proton bonded to carbonyl oxygen is described by a potential curve with two minima, and the position farther from the carbonyl group is the more probable. In the suggested transition state the protons are depicted nearer to the carbonyl oxygen as the C=O and the C–H bonds break with formation of a hydrogen bond to the sulfonate group.

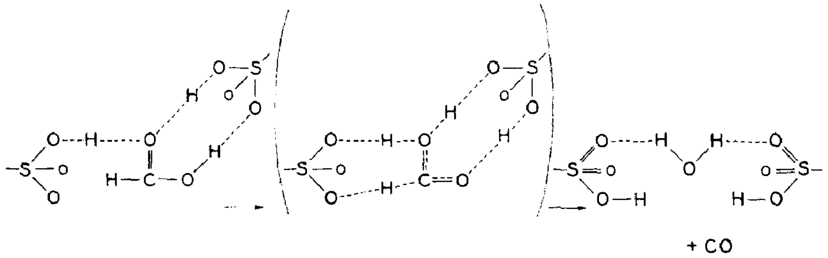


FIG. 3. Reaction mechanism involving two sulfonic acid groups.

The second reaction scheme (Fig. 4) is similar to the first but involves three sulfonic acid groups. The proton transfers required in the proposed mechanisms exclude the possibility of reaction when one of the several sulfonic acid groups is re-

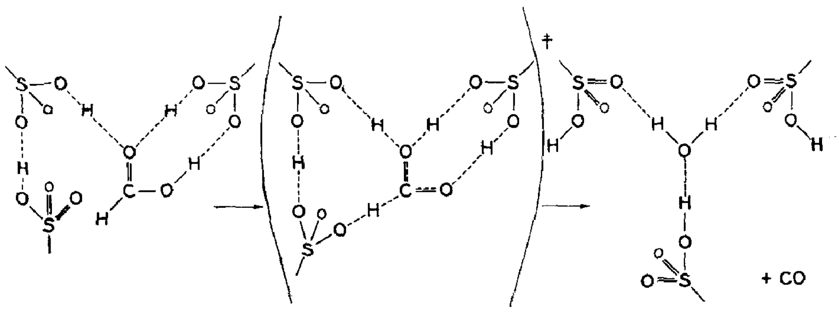


FIG. 4. Reaction mechanism involving three sulfonic acid groups.

placed by its salt, corresponding to the results. Likewise the reaction of acetic acid in the hydrogen form resin is excluded, corresponding to Knözinger's observation (*12*). The structures of the reaction intermediate are similar to those suggested for the methanol and ethanol dehydrations, which proceed at approximately the same rate (*1*).

Water in the catalyst is expected to suppress the formic acid reaction by binding to sulfonic acid groups in competition with reactant. Zundel and Metzger (*10*) found that resin structure depends on the severity of drying conditions. When hydrated resin is rapidly dried at 150°C all of the water is removed, but when drying is slow the structure shown above is formed, and the remaining strongly-bound water is not removed even at the severe conditions. It is suggested that the variations observed in formic acid dehydration rates correspond to various residual water concentrations in the resin.

ACKNOWLEDGMENT

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