

EXPERIMENTS IN HETEROGENEOUS CATALYSIS:

Kinetics of Alcohol Dehydration Reactions

B. C. GATES

*University of Delaware
Newark, Delaware 19711*

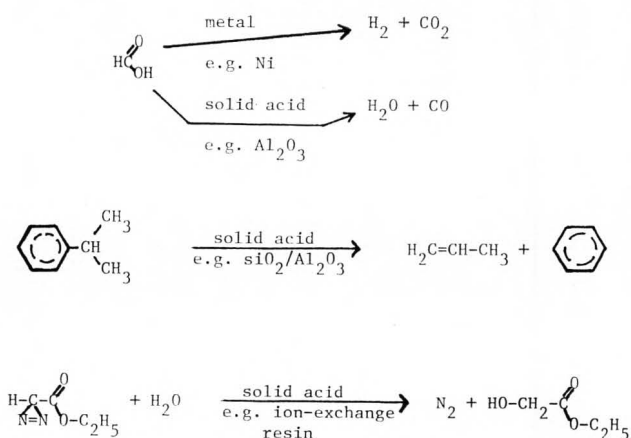
J. D. SHERMAN

*Union Carbide Corporation
Tarrytown, New York 10591*

IN MANY INDUSTRIAL chemical processes, the reactions are catalytic, taking place on internal surfaces of high-area porous solids. The chemical nature of surface catalytic sites is difficult to determine, and consequently an industrial catalyst is chosen not from understanding of reaction mechanism, but from results of trial-and-error experiments designed to determine the solid having the best combination of catalytic activity (measured by reaction rate), selectivity (measured by product distribution), and stability (measured by rate of decay of activity and selectivity during operation). Potential catalysts are often evaluated in continuous flow reactors at conditions approximating those of industrial operation. Products flowing from test reactors can be analyzed efficiently by such methods as gas chromatography or mass spectrometry, and tests may be designed to establish from product analyses the influence of temperature, pressure, and reactant composition on catalyst activity, selectivity, and stability.

Before the development of analytical methods like gas chromatography allowed efficient evaluation of catalyst performance, there was little quantitative data available. Early researchers in catalysis recognized the advantages of experiments that could be interpreted without the need for frequent product analyses, and consequently some of the most thorough investigations concerned reactions of model compounds which give gaseous products and allow rates of reaction to be measured as rates of gas evolution. For example, the following decomposition reactions have been

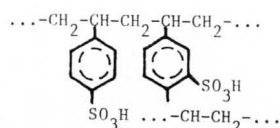
studied extensively to characterize catalysis by solid acids and by metals [1, 2, 3]:



Reactions in this class are no longer objects of much research, but they retain their value as easily accessible means for study of heterogeneous catalysis, a practically important subject which is usually neglected in undergraduate laboratories. Our objective is to point out a heterogeneously catalyzed reaction, the dehydration of *t*-butyl alcohol to give isobutene, which can be investigated in a simple, inexpensive, and safe experiment; yielding thorough kinetic data in a short time. One of the recommended catalysts is an ion-exchange resin, which is applied industrially to catalyze the hydration of propylene to give isopropyl alcohol [4].

EXPERIMENTAL METHODS

TERTIARY-BUTYL ALCOHOL at its boiling point (82.5°C) undergoes no decomposition reaction, but in the presence of an acid such as a sulfonated copolymer of styrene and divinylbenzene (an ion-exchange resin),



a decomposition reaction proceeds rapidly, giving water and isobutene gas [5]. The rate of isobutene evolution can be measured easily with a soap-film flow meter or a wet-test flow meter. When this rate is measured with the equipment shown in Figure 1, the reaction rate can be measured as a function of alcohol concentration in solution with methylcyclohexane (expected to be an inert diluent) and as a function of alcohol concentration in solution with water (a reaction inhibitor). Methylcyclohexane and water have been chosen because each forms an azeotrope with *t*-butyl alcohol at about 78°C; a range of solution compositions, all boiling at nearly the same temperature, can therefore be studied—and the reactants themselves provide a thermostat.

In the suggested experiment, a series of methylcyclohexane-*t*-butyl alcohol solutions is prepared, and each is stored over particles of activated Linde 4A Molecular Sieve to remove impurity water. In a kinetics experiment, 200 ml of solution are charged to the reaction flask and brought to a boil. A weighed sample of ion-exchange resin catalyst beads (Amberlyst 15, Rohm and Haas) is transferred rapidly to the reactor from a vacuum oven at 120°C, where it has been

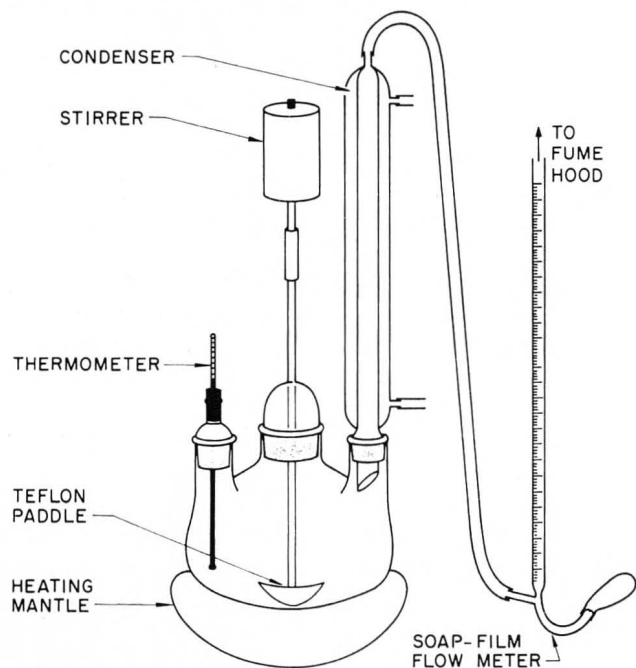


FIGURE 1. Apparatus for Measurement of *t*-Butyl Alcohol Dehydration Kinetics.

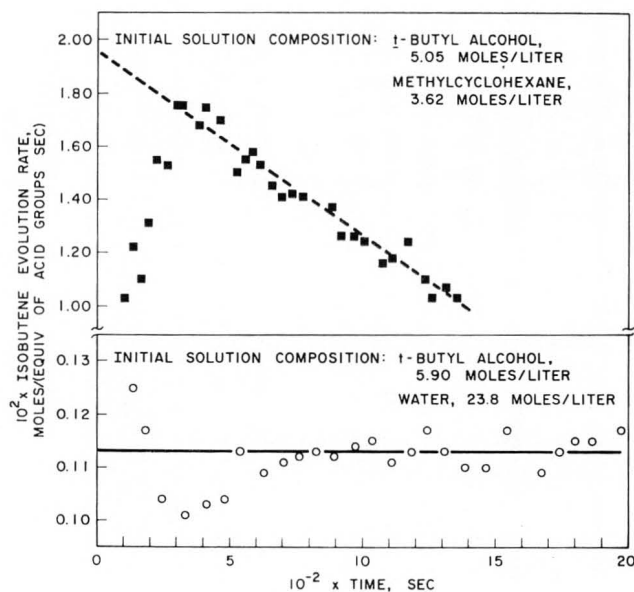


FIGURE 2. Rates of *t*-Butyl Alcohol Dehydration (8).

dried overnight. The rate of evolution of isobutene is then measured periodically, about once per minute, for half an hour. Typical results (Figure 2) indicate a rapidly increasing rate of evolution as the solution becomes saturated with isobutene. After saturation, the rate of evolution becomes equal to the rate of reaction, which decreases with time as water accumulates in the reactor and inhibits reaction. The reaction rate characteristic of the initial solution composition is determined by extrapolation of the reaction rate data to zero time (Figure 2). Rate is determined for various stirring speeds and amounts of catalyst in the reactor, and when there is no effect of either variable on rate per equivalent of catalyst $-\text{SO}_3$ groups, determined by titration (ref. 6, pp. 91-92), the reaction is free of the influence of mass transfer in the liquid phase, and intrinsic chemical kinetics are determined [7].

Data for water-alcohol solutions are obtained in a similar way; the procedure is simpler when the water concentration is high. Then as illustrated by the data of Figure 2, the solution becomes saturated rapidly with isobutene, and after data are collected for a few minutes, a known amount of water is added to the reactor and the procedure is repeated for the new solution composition.

RESULTS

A SET OF RATE DATA is shown in Figure 3 [8]. These results demonstrate kinetics common to many reactions catalyzed by surfaces and

enzymes: The data represented by the dashed line show that the reaction is approximately first order in reactant concentration at the lowest values, approaching zero order at high values as the catalytic sites (sulfonic acid groups) become saturated with reactant. The data represented by the solid line show that water present at the lowest concentrations is a strong inhibitor, competing with alcohol for the catalytic sites. When water is present in high concentrations, it is no longer an inhibitor (inset, Figure 3); the resin becomes strongly hydrated and similar to an aqueous solution of dissociated acid; the reaction is catalyzed by hydronium ions and is first order in reactant concentration.

An interpretation of the catalyst structure and reaction mechanism is given elsewhere with an empirical rate equation [8]. Determination of a non-linear rate equation to fit the data is easily accomplished with the least-squares algorithm of Marquardt [9], which is a standard program available at many computer centers.

EXTENSIONS OF THE EXPERIMENT

THE ADVANTAGES OF THIS experiment are the ease of production of kinetic data and the many possibilities for modification and extension. Most of the modifications suggested in the following paragraphs have been investigated by students in freshman research seminars at the University of Delaware and Massachusetts Institute of Technology.

Catalysts—The resin catalyst can be modified easily by ion exchange, as sulfonic acid groups are replaced by their salts.* Replacement of acid groups markedly reduces catalytic activity [10]. The reaction is also catalyzed by many other insoluble acids, including commercial zeolite crack-

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*The process of ion exchange is widely applied in water purification, and this application of the resins is industrially much more important than catalytic applications [9].

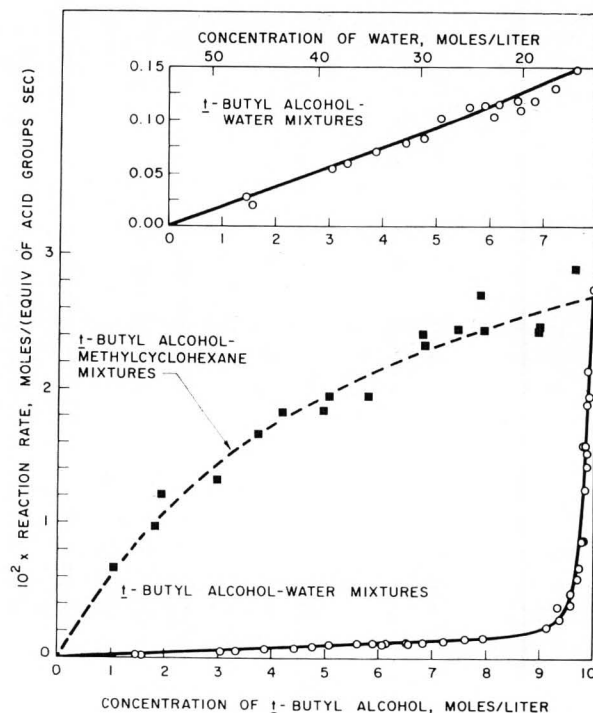


FIGURE 3. Kinetics of *t*-Butyl Alcohol Dehydration Catalyzed by Sulfonic Acid Ion-Exchange Resin at $80 \pm 2^\circ\text{C}$ (8).

ing catalysts (used in gasoline manufacture) and the zeolite H-mordenite [11]. The zeolites have only about 1% of the activity of the sulfonic acid resin per unit mass of catalyst. Soluble acids such as *p*-toluenesulfonic acid** and polystyrenesulfonic acid (analogs of the resin) can also be used.

Reactions—Other alcohols, e.g. *s*-butyl alcohol, undergo dehydration reactions to give olefins in the presence of the resin catalyst. Reaction of *s*-butyl alcohol at its normal boiling point (99.5°C) proceeds at only about 0.2% of the rate observed for *t*-butyl alcohol at its normal boiling point.

Decomposition reactions giving carbon monoxide from formic acid and from methyl and ethyl formates have also been investigated with the resin catalyst [13].

Reactor Design—A modified glass reactor shown in Figure 4 (a Schwab reactor) has been used for determining rates of reaction occurring as vapor-phase reactants flow at steady state through a bed of catalyst particles. Analysis of the reactor performance has been described by

**The anhydrous acid can be prepared from the commercially available monohydrate by drying under high vacuum at 40°C for 130 hours [12].

Weisz and Prater [2]. This reactor has a separately heated catalyst section, allowing study of reaction at various temperatures.

The reactor is suited to all the reactants and catalysts mentioned in the preceding paragraphs. If *s*-butyl alcohol is used as the reactant, then the gas produced in the resin-catalyzed reaction is butene-1 plus *cis*- and *trans*-2-butenes; the selectivity can therefore be studied as a function of temperature and alcohol and water partial pressures [14], provided an instrument such as a gas chromatograph is available for product analysis.

Since the resin catalyst undergoes desulfonation and loss of catalytic activity during operation at temperatures higher than about 130°C, this reactor also provides an opportunity for evaluation of catalyst stability.

Mass Transfer—Mass transfer effects in catalyst particles have been observed with ion-exchange resins like Dowex 50W-X12. This is a nonporous gel-form resin distinct from Amberlyst 15, which is a porous solid with a high internal surface area, and the interior acid groups of the gel are inaccessible to reactant alcohol

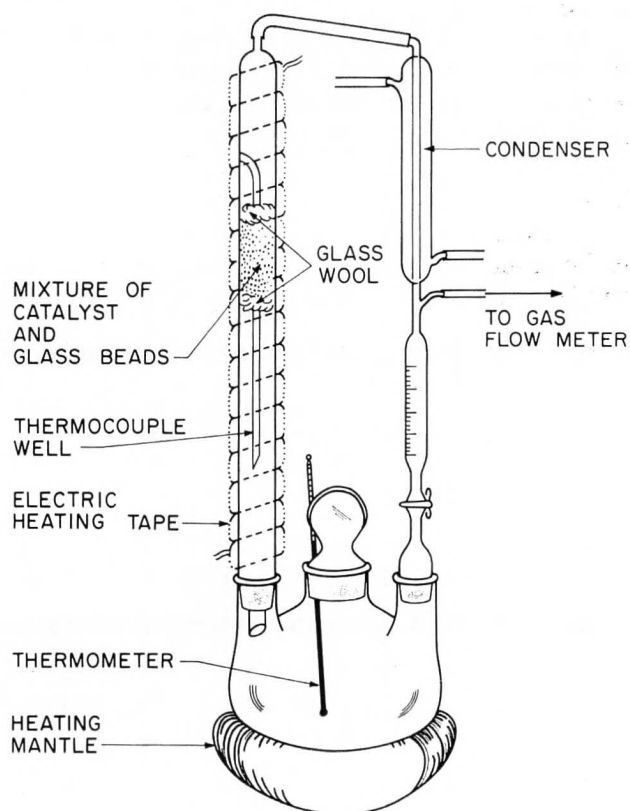


FIGURE 4. Schwab Reactor for Measurement of Reaction Rates with Vapor-Phase Reactants flowing through a Bed of Solid Catalyst Particles.

Bruce Gates has degrees in ChE from Berkeley and the University of Washington. He worked on petroleum process development at Chevron Research Company, and since 1969 he has been at the University of Delaware. His research in applied catalysis is focused on hydroprocessing of fossil fuels and on the design and characterization of polymeric catalysts incorporating acidic, basic, and metal groups.

John Sherman studied ChE at RPI and MIT and was a member of the MIT faculty from 1962 until 1966. He later worked on development of catalyst carriers and zeolites for the Norton Company in Worcester, Massachusetts. Since 1969 he has been with the Linde Division of Union Carbide in Tarrytown, New York, where, as a supervisor in the Molecular Sieve Department, he is involved in developing new products for adsorption and ion exchange.

until water is present to hydrate and swell the resin and allow passage of alcohol molecules between the polymer strands. The performance of gel-form catalysts depends strongly on particle size, crosslinking (divinylbenzene content), and water content, and the effects can be measured with the apparatus shown in Figure 1 [6].

The operation of each reactor can also be modified by inclusion of a desiccant such as Linde 4A Molecular Sieve, which selectively adsorbs water produced in reaction and reduces the product inhibition as reaction proceeds. □

REFERENCES

1. Mars, P., Scholten, J. J. F., and Zwietering, P., *Advan. Catal.* 14, 35 (1963).
2. Weisz, P. B., and Prater, C. D., *Advan. Catal.* 6, 143 (1954).
3. Gruber, P. E., and Noller, H., *Z. Phys. Chem. (Frankfurt)*, 41, 353 (1964).
4. Neier, W., and Woellner, J., *Chem. Technol.*, 95, February, 1973.
5. Frilette, V. J., Mower, E. B., and Rubin, M. K., *J. Catal.* 3, 25 (1964).
6. Helfferich, F., "Ion Exchange," McGraw-Hill, New York, 1962.
7. Heath, H. W., Jr., and Gates, B. C., *Amer. Inst. Chem. Eng. J.* 18, 321 (1972).
8. Gates, B. C., and Rodriguez, W., *J. Catal.* 31, 27 (1973).
9. Marquardt, D. W., *J. Soc. Ind. Appl. Math.* 11, 431 (1963).
10. Gates, B. C., Wisnouskas, J. S., and Heath, H. W., Jr., *J. Catal.* 24, 320 (1972).
11. Ignace, J. W., and Gates, B. C., *J. Catal.* 29, 292 (1973).
12. Zundel, G., "Hydration and Intermolecular Interaction. Infrared Investigations with Polyelectrolyte Membranes," p. 129, Academic Press, New York, 1969.
13. Knözinger, E., and Noller, H., *Z. Phys. Chem. (Frankfurt)*, 79, 66 (1972).
14. Thornton, R., and Gates, B. C., *J. Catal.*, in press.