

Benzene Propylation Catalyzed by Sulfonic Acid Resin

R. B. WESLEY* AND B. C. GATES

*Department of Chemical Engineering, University of Delaware,
Newark, Delaware 19711*

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Rideal kinetics have been observed for benzene propylation catalyzed by beads of sulfonic acid ion-exchange resin at 55°C and 1 atm. High catalytic activity (1.5×10^{-3} moles/equiv of acid groups sec) was found for macroporous but not for gel-form resins, demonstrating the practical advantage of high internal surface areas when reactants are almost incapable of swelling the polymer network. Reaction was inhibited by *n*-heptane, which weakly swelled the network, and this result implies that reaction took place not on the surface, but just within the underlying matrix. From the kinetics, the rate determining step has been identified as the combination of a *s*-propyl carbonium ion with a benzene molecule. The observed seventh-order dependence of rate on catalyst $-\text{SO}_3\text{H}$ group concentration suggests that the carbonium ion was stabilized by a surrounding solvent-like network of hydrogen-bonded acid groups sharing the proton deficiency.

INTRODUCTION

The development of macroporous resins has made practical the application of ion-exchange resin catalysis to reactions of non-polar molecules almost incapable of swelling the polymer network. The porous catalysts, offering a large number of $-\text{SO}_3\text{H}$ groups on roughly 40 m²/g of internal surface (1, 2), have been used for such reactions as phenol alkylation (1) and butene isomerization (3-5) and oligomerization (6). Since there has been little quantitative characterization of resin catalysts operating with nonpolar reactants, our objective was to determine kinetics of benzene propylation as a basis for comparing gel-form and macroporous resins and establishing the effects of water and acid group concentrations in the catalyst. Aromatic alkylation has been reported to follow Rideal kinetics (7), although no data are available in the literature.

* Present address: Dow Chemical Co., Midland, Michigan 48640.

NOMENCLATURE

<i>C</i>	Concentration in liquid phase, moles/liter
<i>k</i>	Reaction rate constant, moles/(equiv of catalyst functional groups sec)
<i>K</i>	Adsorption equilibrium constant, liters/mole
<i>K'</i>	Absorption (swelling) equilibrium constant, liters/mole
<i>r</i>	Reaction rate, moles/(equiv of catalyst functional groups sec)
θ	Fraction of catalytic sites occupied
θ'	Fraction of catalyst matrix swollen

Subscripts

B	Benzene
H	<i>n</i> -heptane
P	Propylene

EXPERIMENTAL PROCEDURE

The alkylation reaction was carried out at atmospheric pressure in a 500-ml round-bottomed flask held at $55.0 \pm 0.2^\circ\text{C}$ in a constant-temperature bath. A timer was started on addition of catalyst to the re-

actor, and 0.5-ml samples were removed periodically by syringe and analyzed by glc (8).

The stirred reactor typically contained 200 g of benzene, 4 g of suspended catalyst beads, and various amounts of dissolved propylene up to the saturation value of 0.2 moles/liter. Weighed amounts of *n*-heptane or water were occasionally included in the reaction mixture. The organic liquids were stored over molecular sieve desiccant, and the reactor was charged under a nitrogen blanket to exclude impurity water. Saturated reactant solutions were maintained by continuous sparging of propylene into the reactor through a bed of P_2O_5 desiccant, with the excess flowing out through a condenser. Alternatively, for unsaturated solutions, propylene was sparged only for a controlled period before the catalyst was charged.

The macroporous ion-exchange resin catalyst was H^+ -form Amberlyst 15 (Rohm and Haas), a sulfonated copolymer of styrene and divinylbenzene. Gel-form resins were also used, Dowex 50W-X2, -X4, and -X12 (Bio-Rad Laboratories), 200–400 mesh, containing 2, 4, and 12% divinylbenzene crosslinking agent, respectively. All resins were pretreated as usual (9), and each sample was transferred directly from a vacuum oven at 120°C to the reactor. In a series of Amberlyst resins, various fractions of the $-SO_3H$ groups were replaced by $-SO_3Na$ groups. For each weighed sample originally in the H^+ form, a fraction was weighed and converted to the Na^+ form by contacting with excess aqueous NaOH. The washed Na^+ -form and H^+ -form fractions were then recontacted in water and allowed to achieve an equilibrium distribution of exchange ions among the beads.

RESULTS

In the presence of the macroporous resin, benzene and propylene were converted to cumene, and conversions were normally so low that detectable amounts of dialkylate were not formed. In a single long run with a solution of benzene saturated with propylene, diisopropylbenzenes and triisopropylbenzene were observed as products. The se-

lectivity was roughly 0.03 moles of di- and tri-alkylate/mole of cumene at 2% conversion of benzene. A small peak, presumed to indicate propylene dimer, was also observed in the glc trace from this experiment.

From plots of conversion to cumene vs time, initial reaction rates were determined as the slopes of the straight lines through the origin. The rates per equivalent of catalyst functional groups were independent of the amount of catalyst charged, demonstrating the absence of a significant liquid-phase mass transport resistance.

Rates determined for a series of propylene concentrations in benzene (Fig. 1) suggest that reaction was first order at low propylene concentrations, becoming independent of propylene concentration at a value of about 0.05 moles/liter. For a series of solutions saturated with propylene, rate was found to increase more than linearly with increasing benzene concentration in *n*-heptane (Fig. 1). Strong inhibition of reaction by water is shown by data in Fig. 2, obtained for solutions of benzene saturated with propylene, to which small amounts ($\sim 1 \mu l$) of water were added.† Benzene solutions saturated with propylene were also used to determine the dependence of rate on acid group concentration: the logarithmic plot of Fig. 3 shows an approximately seventh-order dependence.

Each of the Dowex 50W gel-form resins was found to have negligible catalytic activity compared to the macroporous resin; the gel-form resins catalyzed no detectable reaction over periods of several hours.

DISCUSSION

The effect of propylene concentration on rate demonstrates a saturation of the catalytic sites, suggesting application of the Langmuir adsorption model to represent the kinetics. The dependence of rate on benzene concentration is qualitatively consistent with the Rideal mechanism found by Haag (7), whereby chemisorbed propyl-

† The data of Fig. 2 give only an upper limit to the solution concentrations of water, since a large fraction of the added water was combined with the catalyst and not present in solution.

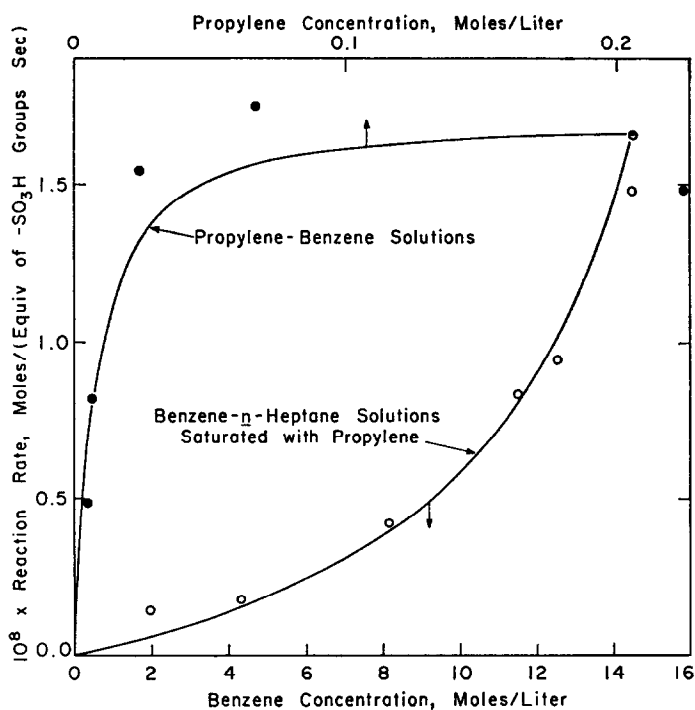


FIG. 1. Kinetics of benzene propylation catalyzed by macroporous sulfonic acid resin at 55°C and 1 atm; curves are given by Eq. (5).

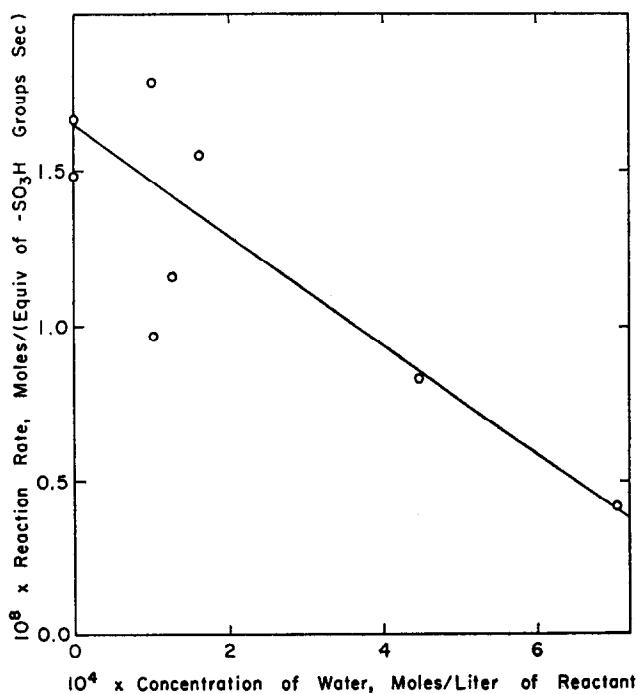


FIG. 2. Inhibition of the benzene propylation reaction by water at 55°C and 1 atm; reactant solution was saturated with propylene.

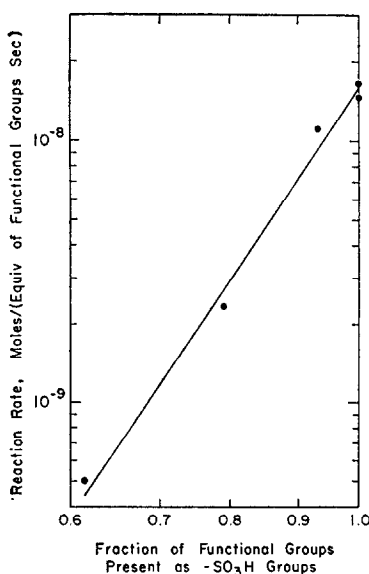


FIG. 3. Seventh-order dependence of benzene propylation rate on catalyst $-\text{SO}_3\text{H}$ group concentration at 55°C and 1 atm; reactant solution was benzene saturated with propylene.

ene reacts with benzene from the liquid phase. This simple interpretation is not sufficient, however, since the rate is not linearly dependent on benzene concentration. The curvature of the plot (Fig. 1) is consistent with the role of *n*-heptane as a reaction inhibitor. We postulate that the paraffin competed with benzene in swelling the resin matrix to a small degree. Such competitive swelling by a paraffin has been reported for 4% crosslinked gel-form resin catalyzing the phenol-acetone condensation reaction (10).‡

The foregoing interpretation leads to the following formulation of the kinetics. A Rideal mechanism is postulated, which accounts for the expected Friedel-Crafts chemistry: the rate determining step is the electrophilic attack on benzene in the resin matrix by propylene combined chemically with the sulfonic acid groups:

$$r = k\theta_P\theta'_B. \quad (1)$$

If the chemisorption of propylene is de-

scribed by the Langmuir isotherm, then

$$\theta_P = K_P C_P / (1 + K_P C_P). \quad (2)$$

Similarly, if a separate swelling equilibrium involving the nonpolar hydrocarbon matrix is approximated by the Langmuir isotherm, then

$$\theta'_B = \frac{K'_B C_B}{1 + K'_B C_B + K'_H C_H}. \quad (3)$$

Here the propylene swelling term is neglected because propylene concentration was always two orders of magnitude less than that of the other hydrocarbons.

Consequently, the rate equation is the following:

$$r = \frac{kK_P K'_B C_P C_B}{(1 + K_P C_P)(1 + K'_B C_B + K'_H C_H)}. \quad (4)$$

This equation and others similar in form have been compared to the data of Fig. 1, with values of the parameters determined by the nonlinear least-squares algorithm of Marquardt (12). The results indicate that the term $(K'_B C_B + K'_H C_H)$ is large compared to 1, and a good fit is given by the following simplified equation:

$$r = \frac{C_P C_B}{(1 + 136 C_P)(4.23 \times 10^6 C_B + 1.81 \times 10^6 C_H)}. \quad (5)$$

This equation is compared to the data in Fig. 1; the good agreement is interpreted as confirmation of the Rideal mechanism.

The absence of catalytic activity for the gel-form resins is evidence that swelling of the resins by the nonpolar reactants was so little that the tight polymer network prevented access of propylene to any $-\text{SO}_3\text{H}$ groups but the small fraction near the particle peripheries. This result is consistent with the observation that *t*-butyl alcohol did not penetrate the network until it was swollen by water (11) and agrees with the suggestion of Fang (13) that reactions of nonpolar molecules in the presence of the macroporous catalyst occur on the interior surface. The inhibition by *n*-heptane, however, implies that the reaction occurred within the matrix. We infer that reaction took place very near the surface, since the resin can be only slightly swollen by ben-

‡ These results suggest that the crosslinking of Amberlyst 15 may be considerably less than the previously surmised value of 20–25% (11).

zene or *n*-heptane. The strong inhibition by water confirms that only a small fraction of the catalyst $-\text{SO}_3\text{H}$ groups participated in the reaction: addition of only about 0.005 moles of water/equiv of total catalyst $-\text{SO}_3\text{H}$ groups halved the reaction rate.

The strong suppression of reaction by water is in agreement with Haag's results for isobutylene oligomerization catalyzed by the resin (6); the result is inferred to be general when weakly polar reactants compete with water in bonding to the $-\text{SO}_3\text{H}$ groups. The occurrence of a Rideal mechanism, also observed for isobutylene oligomerization, may also be quite general when the macroporous acid resin operates with weakly polar (hence weakly chemisorbed) reactants. Venuto (14) has reached a similar conclusion for reactions catalyzed by acidic zeolites.

The strong dependence of rate on catalyst $-\text{SO}_3\text{H}$ group concentration is suggestive of the qualitatively similar results which have been observed for alcohol (9, 15) and formic acid (16) dehydration reactions and butene isomerization (5). These results have been interpreted as evidence that the polar reactants bridge into the hydrogen-bonded network of acid groups in the catalyst (17). Extending this line of reasoning, we suggest that propylene was bonded into the network of $-\text{SO}_3\text{H}$ groups as shown in Fig. 4. The three-dimensional analog of this structure can be envisioned to involve as many as seven groups. Such a structure for a resin-solvated carbonium ion has been suggested previously (17); the ion-pair may be stabilized by the ability of the hydrogen-bonded network to main-

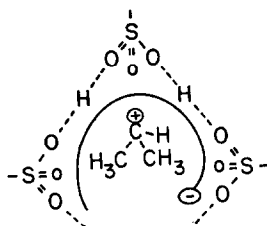


FIG. 4. Suggested ion-pair structure of adsorbed propylene involving a network of hydrogen-bonded acid groups.

tain its structure, with the proton deficiency shared among the interconnected groups. Insertion of $-\text{SO}_3\text{Na}$ groups or water molecules would cause a break-up of the network, prevent the sharing of the proton deficiency, and strongly reduce the proton-donating tendency of the groups (17), accounting for the observed dependence of rate on $-\text{SO}_3\text{Na}$ group and water concentrations. The suggested structure is speculative, but it is consistent with adsorption data for olefins, which indicate the presence of only very roughly 0.01 molecules/acid group (18, 19). The structure also appears to explain Haag's result (6) that diisobutylene is much more weakly chemisorbed than isobutylene: the larger molecule would be less easily accommodated, offering greater steric hindrance to formation of the proton-deficient network.

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