Bisphenol A Synthesis: Kinetics of the Phenol-Acetone Condensation Reaction Catalyzed by Sulfonic Acid Resin

The industrially important reaction of phenol and acetone to give bisphenol *A* and water was catalyzed by beads of ion-exchange resin (sulfonated styrene-divinylbenzene copolymer) suspended in a batch reactor containing liquid reactants. The data are summarized by a rate equation accounting for reaction in the resin competitively swollen by water, acetone, phenol, and methylcyclohexane.

The catalyst is modeled as two phases, each in equilibrium with the liquid: a polar phase consisting of sulfonic acid groups with hydrogen-bonded acetone and water and a nonpolar phase consisting of the hydrocarbon matrix swollen with organic components. The rate determining step is the electrophilic attack on phenol in the nonpolar phase by a carbonium ion intermediate in the polar phase.

Resin cross-linked with 4% divinylbenzene initially catalyzed acetone conversion at a rate of 5×10^{-4} (moles)/(equiv of acid groups s) at 364°K. An 8% cross-linked resin was much less active because the rigid polymer matrix was only slightly swollen by phenol, but a more highly cross-linked resin with macropores and accessible internal surface catalyzed reaction almost as rapidly as the 4% cross-linked catalyst.

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SCOPE

Sulfonic acid ion-exchange resins are industrial catalysts offering the advantages of an insoluble strong-acid phase—they are noncorrosive, easily separated from products, and resistant to degradation and the consequent pollution of effluent streams by dissolved acid.

The catalytic nature and accessibility of sulfonic acid groups in styrene-divinylbenzene (*DVB*) copolymers have been characterized by kinetic data obtained for resins of various degrees of cross-linking catalyzing reaction in the presence of molecules with a wide range of polarities and strongly different tendencies to swell the resin. The reaction of phenol and acetone to give bisphenol *A* and water was chosen because the reactants and products offer a wide range of polarities and because the reaction is industrially important.

Production of bisphenol *A* (an intermediate in synthesis of epoxy resins and polycarbonates) was 114 million kg in 1972. Since the patent literature suggests that sulfonic acid resins are the preferred industrial catalysts, an objective of this research was to provide kinetic data and yields of side products for preliminary process design estimates.

Initial reaction rate data were obtained at 364°K from a batch reactor containing beads of resin catalyst suspended in solutions of phenol and acetone, occasionally mixed with water or methylcyclohexane. Catalyst cross-linking was varied from 2 to 8% *DVB* in gel-form beads (Dowex 50W), and a series of resins was modified by replacement of the catalytically active —SO_3H groups with —SO_3Na groups or —$SO_2OCH_2CH_2SH$ groups. The modified resins were used to test the patent claim that the —$SO_2OCH_2CH_2SH$ groups are catalyst promoters. A highly cross-linked, macroporous sulfonic acid resin (Amberlyst 15), the form most commonly used as an industrial catalyst, was also tested.

CONCLUSIONS AND SIGNIFICANCE

An *empirical*, five-parameter rate equation has been found for the phenol-acetone reaction catalyzed by 4% cross-linked sulfonic acid resin at 364°K. It accounts for reaction in the swollen resin, with inhibition by water, acetone, phenol, and methylcyclohexane (listed in decreasing order of their effects). The rate equation and product selectivity data are recommended for preliminary process design estimates.

The kinetic results form the basis of a model in which the gel-form catalyst is represented as two separate, microscopically interwoven phases, each swollen in equilibrium with the surrounding liquid phase. One resin phase is polar (containing water, acetone, and sulfonic acid groups), and the other is nonpolar (containing phenol, acetone, methylcyclohexane, and the hydrocarbon matrix). The rate determining step is the attack of a highly polar intermediate (probably a tertiary carbonium ion) on phenol in the adjacent nonpolar phase. The model leads to a rate equation similar to the empirical equation, but having one more parameter and giving a slightly better fit to the data.

The model explains the effect of catalyst cross-linking. The observed reduction in reaction rate with increased cross-linking indicates a decreased tendency of the tighter resin network to be swollen by phenol; 8% cross-linked catalyst contained so little phenol that reaction was negligibly slow. The more highly crosslinked macroporous

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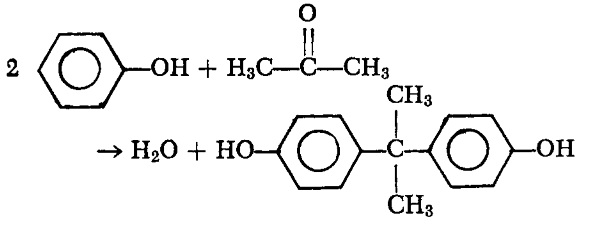
resin was much more effective because reaction occurred near its easily accessible internal surface.

Replacement of acid groups by —$SO_2OCH_2CH_2SH$ groups did not give a more active catalyst (in contrast to patent claims), but the ester groups reduced catalyst activity less than an equivalent number of —SO_3Na groups. The result suggests that the ester groups increased the tendency of the resin to be swollen by phenol.

Mineral acids in solution are among the least expensive and most widely used catalysts in the chemical process industries, and their solid analogs, ion-exchange resins, are finding increasing application for such reactions as olefin hydration (Neier and Woellner, 1972), esterification, and acylation (Kunin, 1970). Although the insoluble acids are roughly a thousand times as expensive as sulfuric acid per equivalent of acid groups, they offer the compensating advantages of being noncorrosive, easily separated from reaction products, and stable enough to prevent pollution of effluent streams by dissolved acid.

Catalysis within a swollen, hydrated matrix of an ion-exchange resin containing dissociated acid groups is similar to catalysis by hydrated protons in an aqueous solution (Helfferich, 1954), and reaction rates can probably be predicted well enough for many process design estimates on the basis of solution data. In contrast, catalysis by undissociated acid groups in an unhydrated matrix may be much more rapid (Gates and Rodriguez, 1973), involving more complex reaction chemistry and unique mass transfer phenomena. Alcohol dehydration in nearly anhydrous gel-form sulfonic acid resin, for example, has been interpreted as the reaction of alcohol molecules bridged within a network of hydrogen-bonded sulfonic acid groups (Thornton and Gates, in press). The catalytic groups in a particle are almost entirely inaccessible to reactant molecules in the absence of a strongly polar compound like water, which hydrates the acid groups, swells the resin network, and allows access of reactant molecules between the polymer strands to the particle interior (Heath and Gates, 1972). Since a number of the industrial reactions catalyzed by strong-acid resins involve weakly polar reactants nearly incapable of swelling the catalyst, a resin with modified physical properties has been developed (Bortnick, 1962). This resin is synthesized in the presence of a solvent having a strong affinity for the styrene and divinylbenzene (*DVB*) monomers but having only a weak tendency to swell the polymer. After polymerization, removal of the solvent leaves macropores and a solid with a surface area of about 4×10^4 m^2/kg (Kunin et al., 1962), which is accessible even to nonpolar reactants.

Since there are few data characterizing the sulfonic acid resin catalyst operating in the presence of only moderately polar reactants, and since the catalyst is of interest both from the standpoint of industrial application and fundamental catalytic chemistry, the present research was undertaken to provide a set of kinetic data illuminating the chemical nature of the catalyst. The reaction chosen for study was the condensation of phenol with acetone to give bisphenol *A*



(1)

A specific objective of the research was to determine the kinetics of this industrially important reaction, which is hardly described outside the patent literature. The recent patents (reviewed by Reinicker, 1973) point to the sulfonated styrene-*DVB* copolymer as the industrial catalyst of choice. The bisphenol *A* synthesis is inferred to be one of the most important applications of this catalyst; in 1972 the production of bisphenol *A* (used to produce polymers such as epoxy resins and polycarbonates) was 114 million kg and was increasing rapidly (Anderson, 1973).

The bisphenol *A* reaction is intriguing chemically because in solutions of acid catalyst it is promoted by sulfur-containing compounds like mercaptans (Apel et al., 1964) and the mechanism of the promotion is not understood. Several patents claim that the efficiency of the ion-exchange resin catalyst is analogously increased when sulfur-containing functional groups replace a fraction of the sulfonic acid groups (Apel et al., 1964; Wagner, 1965; Gammill et al., 1972). These claims point out the unique opportunities for tailoring the chemical as well as physical properties of the solid organic catalyst. A further objective of the research described here was to investigate the role of the sulfur-containing promoter groups.

EXPERIMENTAL PROCEDURE

Catalyst Preparation

The ion-exchange resin catalysts were sulfonated styrene-*DVB* copolymers, Dowex 50W and Amberlyst 15, obtained from Bio-Rad Laboratories and Rohm and Haas, respectively. The Dowex resins were obtained in batches containing approximately 2, 4, and 8% *DVB* cross-linking agent; the *DVB* content of Amberlyst 15 is perhaps as much as 20 to 25%, as inferred from its swelling characteristics and the effect of *DVB* on catalyst performance cited by Bortnick (1962).

Spherical resin beads obtained in several size ranges (Table 1) were thoroughly washed with distilled water before use. Catalysts subjected to several exchange cycles with 1 *M* NaOH and 1 *M* HNO_3 were found to be indistinguishable from samples simply washed in the pretreatment, although small amounts of amber-colored material (presumably low-molecular-weight polymer) were extracted during the ion-exchange cycles and washing. Ion-exchange capacities determined by titration against standard base ranged from 4.5 to 5.1 equiv/kg (Table 1). All resins were dried overnight in a vacuum oven at 393°K prior to use as catalysts.

Some samples of resin were modified by partial esterification of the sulfonic acid groups by 2-mercaptoethanol, which was added dropwise to a flask containing the resin suspended in *n*-heptane. The suspension was refluxed for two or three hours until the amount of product water indicative of complete uptake of alcohol in the esterification reaction had been collected in a trap. The resin was filtered and washed with *n*-heptane and ethanol. The fraction of esterified acid groups was determined by titration to determine the loss of acid groups. Another sample of resin was contacted with aqueous NaOH to convert a fraction of the —SO_3H groups to —SO_3Na groups. The degree of neutralization was measured by titration.

Measurement of Kinetics

Reaction kinetic data were determined with a batch reactor, a 250-ml round-bottomed flask immersed in a thermostated oil bath. The four necks of the flask were adapted for a stirrer, thermometer, condenser, and sampling port.

Premixed reactants (phenol and acetone, occasionally mixed with water or methylcyclohexane) were added to the flask and brought to reaction temperature (usually 363°K) before

Table 1. Sulfonic Acid Resin Catalysts

Resin type	DVB content, wt%	Mesh size range spherical beads △	Exchange capacity of H^+ form, equiv/kg	10^4 × initial rate of phenol-acetone condensation reaction at 364°K with solution of 12.5 ± 1.0 mole% acetone in phenol, (moles acetone converted)/(equiv s)
Dowex 50W	2*	100-200	4.88	9.55
Dowex 50W	4*	20-50	5.12	3.87
Dowex 50W	4*	50-100	4.83	3.12
Dowex 50W	4*	100-200	4.99	6.43, 5.49
Dowex 50W	4*	200-400	4.54	2.26
Dowex 50W	8*	50-100	5.01	—**
Amberlyst 15	20 to 25†	16-50	4.32	1.63

* Approximate value of DVB content from manufacturer's specification.
† Estimated roughly from resin physical properties and comparison with patent data (Bortnick, 1962).
△ Mesh size range of hydrated beads from manufacturer's specifications.
** No conversion was detected after 10^4 s.

catalyst beads were added. Reaction proceeded at atmospheric pressure, and product samples were drawn periodically at typical intervals of five minutes. Each 0.4-ml sample, often containing a few catalyst beads, was transferred to a sealed vial, and the reaction was immediately quenched by immersion of the vial in an ice-water bath.

Each product sample was analyzed with a Hewlett-Packard model 700 gas-liquid chromatograph (GLC) having a thermal conductivity detector. Since there was a wide range of component boiling points, it was convenient to analyze each sample twice, once at a low column temperature (383°K) to determine the ratio of the reactants, and again at a higher temperature (498°K) to determine the full product composition. The GLC column was 1.2 m of 3.2-mm stainless steel tubing packed with 3% SE-30 (a silicone rubber compound) on high performance Chromosorb W (80 to 100 mesh). The helium carrier gas flow rate was 0.50 ml/s, and sample volumes were one microliter. A few samples were also analyzed with a Hewlett-Packard GLC-mass spectrometer system to provide qualitative identification of the reaction products, including some formed in addition to water and bisphenol *A*.

A complete description of apparatus and procedures is given by Reinicker (1973).

RESULTS

The reaction of phenol with acetone was too slow to detect in the absence of catalyst, but in the presence of sulfonic acid resin, it proceeded with the formation of bisphenol *A*; conversions of the limiting reactant (usually acetone) as high as 60% were observed. At higher conversions, crystallization of products would have hindered operation. Catalyst washed and reused after runs demonstrated that activity loss was negligible during operating periods of several hours.

Product Distribution

Bisphenol *A* was the predominant product of the phenol-acetone reaction, but chromatographic analysis of samples taken after long run times, especially when initial acetone concentrations were high, showed eight products besides bisphenol *A* and water. Of the GLC peaks observed for the organic products, that for bisphenol *A* was always the largest. Two others, representing the ortho, para′ isomer of bisphenol *A* and 4,4′-hydroxyphenyl-2,2,4-trimethylchroman (Dianin's compound), were identified by their mass spectra. The peak indicating Dianin's compound was usually coincident with that for bisphenol *A*, being observed separately only for samples taken at low conversion. Bisphenol *A*, the ortho, para′ isomer, Dianin's compound, and water were the only reaction products present in greater than trace amounts.

Of the six trace products, four have been tentatively identified as mesityl oxide and phorone (the dimer and trimer of acetone), the ortho, ortho′ isomer of bisphenol A, and 2,4-bis(α,α-dimethyl-4-hydroxybenzyl)phenol, a polycondensation product. These identifications are generally consistent with patent reports (Reinicker, 1973).

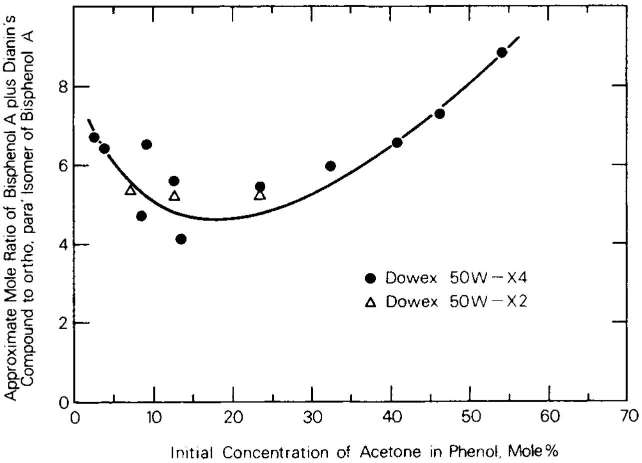


Fig. 1. Selectivity of the phenol-acetone condensation reaction at 364°K.

Quantitative results are shown in Figure 1, where the selectivity at 363°K, defined as the number of moles of bisphenol *A* plus Dianin's compound divided by the number of moles of the ortho, para′ isomer of bisphenol *A*, is plotted as a function of the initial reactant concentration. The data are only approximate because the relative GLC response factors of these compounds were unknown and assumed to be the same. The selectivity values are averages over individual runs carried out to conversions of typically 20% of the limiting reactant. There was considerable scatter during each run, and no pattern was observed with increasing conversion. There was no change in selectivity observed for variations in concentration of added water or methylcyclohexane or for variations in catalyst particle size, *DVB* content, or degree of esterification.

The selectivity at an initial acetone concentration of 12 mole% in phenol varied from 8 to about 4 as the reaction temperature was increased from 323 to 383°K.

The mole ratio of the bisphenol *A* to Dianin's compound was seldom measurable. At low initial concentrations of acetone in phenol (about 3 mole%), this product ratio was about 20. It decreased to 2 or 3 as initial acetone concentration was increased to 12 mole%, and then it increased to 15 when the initial acetone concentration was raised to 46 mole%.

Reaction Kinetics

Conversion data from a typical run are shown in Figure 2. The thermostat was set at 364°K, but the reactor temperature varied about 1°K during a run, falling initially as cooler catalyst was added, then rising in about 100 s because of the exothermic solvation of the resin.

Data obtained at low conversions, illustrated by the first five points of Figure 2, were fitted with straight lines, the slopes of which were initial reaction rates in units of (moles of acetone converted)/(sec equiv of catalyst functional groups). With the 4% cross-linked gel-form catalyst, initial rate data were determined in this manner for a series of reactant solutions containing acetone and phenol in various proportions (Figure 3) and for a series of solutions having fixed acetone to phenol mole ratios and various concentrations of added water or methylcyclohexane (Figure 4). The initial rate data have a precision of about ± 10%.

The data of Figure 3 show that the reaction rate increased to a sharp maximum as the acetone-to-phenol ratio increased to 12:88, a value well below the stoichiometric ratio of 1:2. The data of Figure 4 demonstrate strong inhibition of reaction by water and a much smaller effect of methylcyclohexane.

The reaction rates per equivalent of catalyst functional groups were found to be independent of stirring rate and the ratio of reactant to catalyst mass, demonstrating the absence of a significant liquid-phase mass transfer resistance. Variation of particle size of the gel-form catalyst containing 4% *DVB* had no effect on reaction rate (Table 1), demonstrating the absence of a significant intraparticle mass transfer resistance.[*] The thorough kinetic data were determined for 100 to 200 mesh beads of this catalyst, and the foregoing conclusions therefore demonstrate that the data represent intrinsic kinetics of the phenol-acetone condensation reaction.

Effect of Temperature

Thorough kinetic results were obtained only for the 4% cross-linked catalyst at 364 ± 1°K, but initial reaction rates were measured with this catalyst for a 12 mole% acetone in phenol solution at several temperatures between 325 and 384°K. The nonlinearity of the Arrhenius plot (Figure 5) is not surprising since, as is shown later, rates are dependent on several parameters, each expected to have an exponential dependence on temperature.

Effects of Catalyst Composition

The effect of partial esterification of the acid groups in the 4% cross-linked catalyst is shown in Figure 6. Introduction of the —SH groups reduced the activity of the catalyst, but not as much as introduction of an equivalent concentration of $—SO_3Na$ groups. This result appears to contradict the results of Apel et al. (1964), who claimed a promotion of the catalyst by attached —SH groups. A series of related experiments was performed to clarify the discrepancy. A reactant solution having an acetone-to-phenol mole ratio of 1:9 was modified by addition of 3.5 mole% mercaptoethanol. In the presence of unesterified catalyst at 364°K, this solution reacted about 1.2 times as fast as when the mercaptoethanol was absent, con-

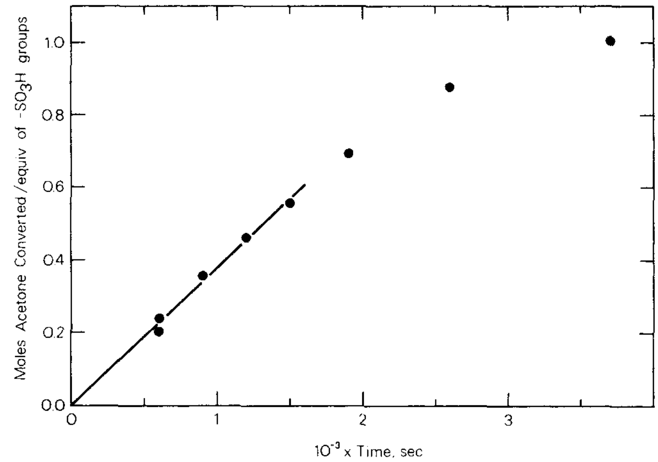


Fig. 2. Determination of initial rate of phenol-acetone condensation reaction at 364°K catalyzed by 9.25 × 10^{-3}kg of Dowex 50W-X4 (20-50 mesh). Initial solution was 100 ml 12.3 mole% acetone in phenol.

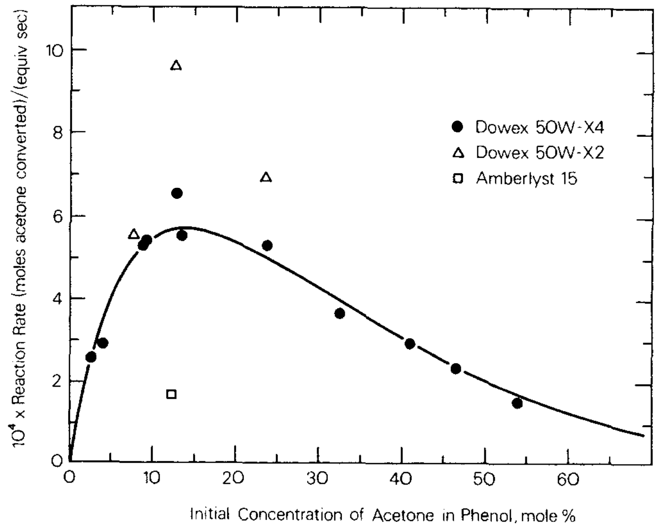


Fig. 3. Dependence of initial rate of phenol-acetone condensation reaction on composition of reactant solution. For reaction at 364°K catalyzed by Dowex 50W-X4, the curve was calculated from Equation (3) with the parameter values of Table 2.

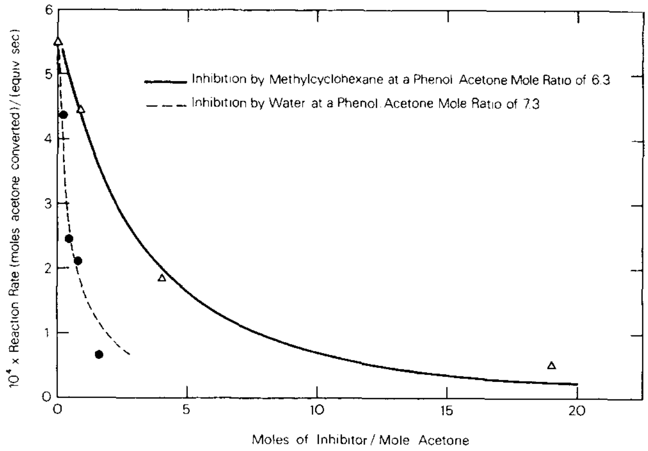


Fig. 4. Inhibition of phenol-acetone condensation reaction by water and by methylcyclohexane. Reaction at 364°K was catalyzed by Dowex 50W-X4. The curves were calculated from Equation (3) with the parameter values of Table 2.

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[*] The rates for the catalysts containing 4% DVB show no trend with particle size. The scatter is inferred to be an indication of variations in DVB content from batch to batch. These variations are expected for commercial resins, and the data of Table 1 confirm that rate is sensitive to catalyst DVB content.

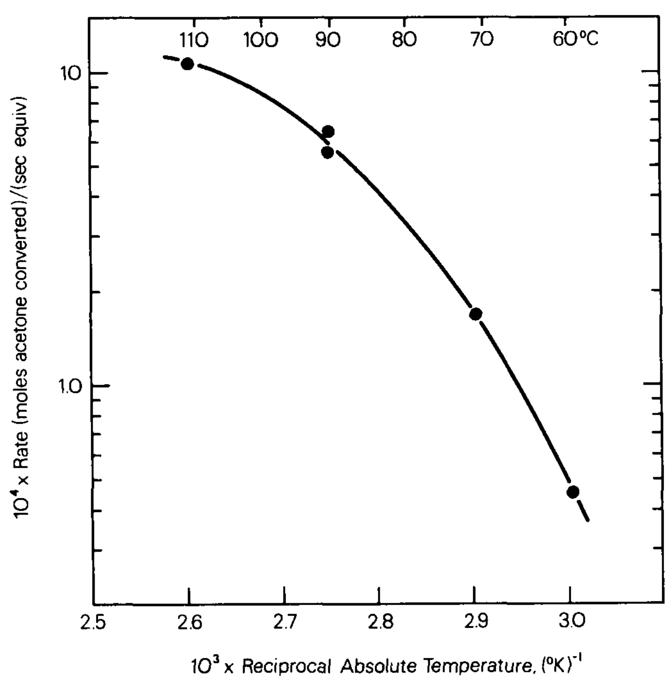

Fig. 5. Arrhenius plot: temperature dependence of rate of phenol-acetone condensation reaction catalyzed by Dowex 50W-X4.

firming the identification of dissolved mercaptoethanol as a promoter. A further experiment was performed with the unesterified catalyst and a modified start-up procedure, the one used by Apel. The 4% cross-linked catalyst was now presoaked in phenol before being charged to the reactor containing acetone and phenol at a mole ratio of 12:88. With this procedure, the initial rate was about twice as great as that observed when the catalyst was not presoaked in phenol. These results suggest that the apparent promotion effect observed by Apel was associated with the initially high resin phenol concentration, which might have been affected by the concentration of attached —SH groups.

DISCUSSION

Reaction Kinetics

The data of Figures 3 and 4 suggest a rate equation of the following form, which is consistent with a competition for catalytic sites among the reactants, water, and methylcyclohexane:

$$r = \frac{k\, C_A^{\alpha_1}\, C_P^{\alpha_2}}{(1 + [K_A C_A]^{\alpha_3} + [K_P C_P]^{\alpha_4} + [K_W C_W]^{\alpha_5} + [K_{MCH} C_{MCH}]^{\alpha_6})^{\alpha_7}} \quad (2)$$

Special cases of this equation can be derived under the assumption of competitive Langmuir adsorption on a homogeneous set of catalytic sites.

The data have been used to establish the goodness of fit with the best values of the parameters k and K_i for various assumed integral values of the α_i parameters between 0 and 3. The least squares criterion was applied according to the method of Marquardt (1963). Equations were initially screened by comparison with only the data of Figure 3, and many were rejected because of poor fit or the indication of negative values for one or more of the K_i parameters. The remaining equations were compared to the full set of data, those of Figures 3 and 4. The equation best representing the data is the following:

$$r = \frac{k\, C_A\, C_P^2}{(1 + K_A C_A + K_P C_P + K_W C_W + K_{MCH}\, C_{MCH})^2} \quad (3)$$

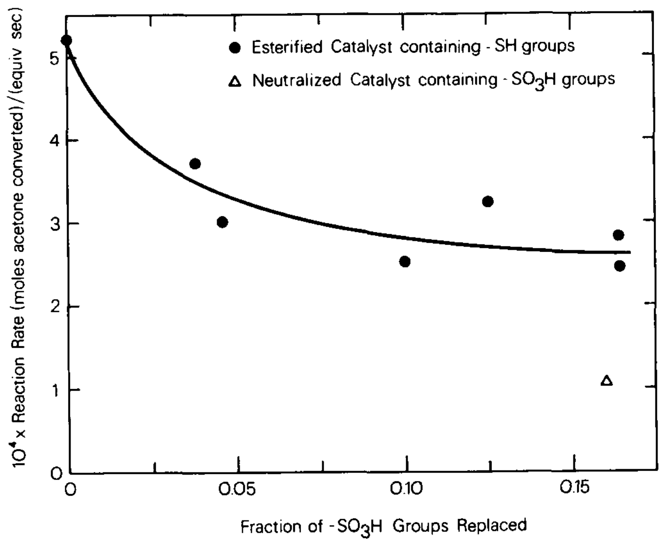

Fig. 6. Dependence of reaction rate on catalyst composition. Reaction of solution of 23 mole% acetone in phenol was catalyzed by Dowex 50W-X4.

This equation, with the parameter values of Table 2, is compared to the experimental points in Figures 3 and 4.

Several conclusions follow from the form and parameter values of the empirical rate equation. There is a significant inhibition term associated with each component, even methylcyclohexane, which at first might be expected to act only as a diluent.* The magnitude of the inhibition parameter K_i decreases with decreasing polarity of the compound, from 26 l/mole for water to 1.4 l/mole for methylcyclohexane. This pattern parallels the tendency of the compounds to swell the polar resin (Bodamer and Kunin, 1953; Davies and Owen, 1956; Reinicker, 1973).

The strong inhibition by water is not surprising since water inhibits many reactions catalyzed by resin-bound sulfonic acid groups (Gates and Rodriguez, 1973). The effect is explained by a competition between reactants and water, which strongly hydrates the acid groups (Zundel, 1969). The inhibition by methylcyclohexane cannot be explained in the same way, however, since the paraffin has no affinity for the polar acid groups. Yet methylcyclohexane, like phenol and acetone, is capable of swelling the nonpolar polystyrene matrix, experiencing hydrophobic bonding; the kinetic results therefore suggest that there was competition among the organic species for positions in the hydrocarbon matrix holding the acid groups. These positions are roughly comparable to the hydrophobic pockets in enzymes.

The foregoing conclusions are combined in the following paragraphs with the known chemistry of acid-catalyzed condensation reactions to give a quantitative representation of the reaction process in the swollen resin.

Reaction Model: The Two-Phase Swollen Catalyst

Carbonium ion mechanisms account for many acid-catalyzed condensation reactions, as illustrated, for example, by Venuto and Landis (1966) for the zeolite-catalyzed phenol-acetone condensation reaction. The mechanism proposed in Figure 7 incorporates the essential char-

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* *It is probable that the equation could be improved by addition of an inhibition term for bisphenol A; the K value is expected to be somewhat greater than that for phenol.*

TABLE 2. RATE EQUATIONS

Equation	Parameter values							Sum of squares of deviations of predicted from observed rates[c]
	$10^3 \times k^a$	$\underline{K}_A'^b$	$\underline{K}_W'^b$	K_A or $\underline{K}_A^b$	K_P or $\underline{K}_P^b$	K_W or $\underline{K}_W^b$	K_{MCH} or $\underline{K}^b_{MCH}$	
$r = \dfrac{k\, C_A C_P^2}{(1 + K_A C_A + K_P C_P + K_W C_W + K_{MCH} C_{MCH})^2}$	5.86	—	—	10.8	2.14	26.0	1.40	1.77
$r = \dfrac{k\, C_A C_P^2}{(1 + \underline{K}_A' C_A + \underline{K}_W' C_W)\,(1 + \underline{K}_A C_A + \underline{K}_P C_P + \underline{K}_{MCH} C_{MCH})^2}$	11.6	1.95	2.42	11.5	3.76	—	2.96	1.65
$r = \dfrac{k\, C_A C_P^2}{(1 + \underline{K}_W' C_W)\,(1 + \underline{K}_A C_A + \underline{K}_P C_P + \underline{K}_{MCH} C_{MCH})^2}$	16.0	—	1.86	15.2	3.04	—	2.03	2.02

[a] (moles of acetone converted)/(equiv s)
[b] liters/mole
[c] [(moles of acetone converted)/(equiv s)]^2

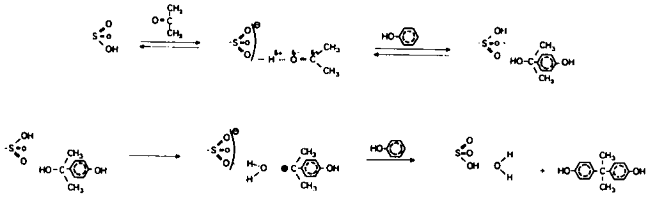

Fig. 7. Proposed reaction mechanism for phenol-acetone condensation reaction in sulfonic acid resin.

acteristics of the known chemistry: electrophilic attack on the aromatic ring by polar reaction intermediates, which may be carbonium ions.* The first step depicted in Figure 7 is hydrogen bonding of the carbonyl group of acetone to a resin —SO_3H group. The occurrence of hydrogen bonding has been established by the infrared spectra of Knözinger and Noller (1967), indicating less than complete removal of the proton from the —SO_3H group, hence the ion-pair-like structure shown, rather than a carbonium ion. This intermediate, to be referred to as chemisorbed acetone, is envisioned to react readily with phenol from the surrounding nonpolar matrix, as shown in the second step. The product is a tertiary alcohol, which can readily form a carbonium ion and is expected to react with phenol from the swollen gel phase as shown on the second line of Figure 7. Although the carbonium ion intermediate is relatively stable and likely to occur, the final step might actually take place via a nonionic, hydrogen-bonded structure, as has been suggested on the basis of infrared and kinetic data for dehydration reactions of butyl alcohols (Gates et al., 1972; Thornton and Gates, in press).

The reaction mechanism of Figure 7 can be written as the following sequence of elementary steps, where the Ads refers to chemisorbed species (hydrogen bonded to acid groups) and Abs refers to absorbed species (swelling the nonpolar part of the polymer matrix):

$$A_{Abs} + \text{—}SO_3H \overset{\underline{K}_1}{\rightleftarrows} A_{Ads} \qquad \text{(a)}$$

$$A_{Ads} + P_{Abs} \overset{\underline{K}_2}{\rightleftarrows} I_{Ads} \qquad \text{(b)}$$

$$I_{Ads} + P_{Abs} \overset{k_3}{\rightarrow} H_2O_{Ads} + BPA_{Abs} \qquad \text{(c)}$$

If adsorbed species I, the tertiary alcohol shown in Figure 7, is present in low concentration, then a plausible assumption is that step (c) is rate determining. Corresponding to this assumption, the rate equation can be written as

$$r = k_3\, C_{I_{Ads}}\, C_{P_{Abs}} = k_3\, \underline{K}_2\, C_{A_{Ads}}\, C^2_{P_{Abs}} \qquad (4)$$

If the assumed adsorption equilibrium of acetone on acid groups is described by a Langmuir isotherm, then, in the absence of other components,

$$C_{A_{Ads}} = \frac{\underline{K}_A'\, C_A}{1 + \underline{K}_A'\, C_A + \underline{K}_P'\, C_P} \qquad (5)$$

If acetone and phenol are combined with only a small fraction of the acid groups, then

$$C_{A_{Ads}} \cong \underline{K}_A'\, C_A \qquad (6)$$

Further, if the assumed absorption (swelling) equilibrium is also described by a Langmuir isotherm, (which is the simplest equation accounting for competitive absorption in a matrix which can be saturated), then

$$C_{P_{Abs}} = \frac{\underline{K}_P\, C_P}{1 + \underline{K}_A\, C_A + \underline{K}_P\, C_P} \qquad (7)$$

When Equations (6) and (7) are substituted into Equation (4), the resulting rate equation in terms of measured solution concentrations is

$$r = \frac{k_3\, \underline{K}_2\, \underline{K}_A'\, \underline{K}_P^2\, C_A\, C_P^2}{(1 + \underline{K}_A\, C_A + \underline{K}_P\, C_P)^2} \qquad (8)$$

This equation has just the form of the empirical rate equation in the special case for which only phenol and acetone are present in the reaction mixture (Figure 3).

To summarize, the subset of results shown in Figure 3 is consistent with the representation of the ion-exchange resin as two separate but microscopically interwoven phases—one polar and therefore expected to contain the sulfonic acid groups, water, and acetone, and the other only slightly polar and therefore expected to contain methylcyclohexane, phenol, acetone, and the hydrocarbon strands of the polymer. Reaction is perceived to occur by a process consistent with this model and with the expected chemical mechanism of acid-catalyzed condensation reactions. The close agreement between the data of Figure 3 and the model equation supports the interpretation.

If this physical picture is in essence correct, however,

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* Similar mechanisms account for the formation of the significant side products, the ortho, pará isomer of bisphenol A and Dianin's compound (Reinicker, 1973).

then it is not expected that the polar reactant, acetone, would be chemisorbed on only a small fraction of the acid groups, as was assumed in the development leading to equation (8). A better representation of the data would be expected with a more complex equation accounting for the presence of acetone in significant amount in each of the two resin phases. The revised equation is the following:

$$r = \frac{k_3 \underline{K}_2 \underline{K}_A' \underline{K}_P^2 C_A C_P^2}{(1 + \underline{K}_A' C_A + \underline{K}_W' C_W)(1 + \underline{K}_A C_A + \underline{K}_P C_P + \underline{K}_{MCH} C_{MCH})^2} \qquad (9)$$

The results of Table 2 show that this equation gives a slightly better fit to the data than Equation (3), which is not surprising since an adjustable parameter has been added. Nonetheless, the parameter values appear to be physically meaningful and give added support to the model. The value of $\underline{K}_A'$ is only slightly less than the value of $\underline{K}_W'$, confirming the inappropriateness of its neglect in the development of Equation (8) (see the third equation in Table 2). The result indicates stronger bonding of water than of acetone to the acid groups, which is roughly consistent with the swelling data of Davies and Owen (1956). The value of $\underline{K}_A$ is several times greater than the values of $\underline{K}_P$ and $\underline{K}_{MCH}$, suggesting that acetone is more easily accommodated in the nonpolar matrix than the larger cyclic compounds, which are similar to one another in size and have approximately equal $\underline{K}$ values.

The two-phase resin model now provides a basis for explaining the remaining results. The data of Figure 3 and Table 1 show a sharp decrease in reaction rate with an increase in catalyst *DVB* content from 2 to 8%. The decreasing rate is explained by a decrease in K_P with increased resin cross-linking. The literature (Helfferich, 1962) shows that resin swellability is decreased with increasing tightness of the network. The lack of catalytic activity of Dowex 50W-X8 is then explained by its inability to accommodate phenol.

This conclusion is in accord with results for 4% cross-linked resins presoaked in phenol—the application of initially high phenol concentrations could be a processing advantage for batch reactor operation, but would have no effect on steady state conversion in a flow reactor.

The foregoing conclusions lead to a speculative interpretation of the effect of —SH groups incorporated in the resin matrix: they may simply increase the affinity of the resin for phenol. This suggestion is consistent with the results of Figure 6, which show that replacement of acid groups by their salts reduced catalytic activity more than replacement by —SH groups; in terms of the model, the decrease in concentration of I_{Ads} was partly compensated in the esterified resin by an increase in the concentration of P_{Abs}.*

The result that the resin's tendency to be swollen by phenol decreases strongly with increased cross-linking implies that the highly cross-linked macroporous resin was only weakly swollen by phenol. Since reaction in the presence of this catalyst was rapid, it is inferred that reaction occurred near the interior surface. The same conclusion has been drawn for the benzene propylation reaction catalyzed by the macroporous resin (Wesley and Gates, in press).

Since it is clear that not all acid groups were utilized in the macroporous resin (which had an exchange capacity about the same as that of the gel-form resins), we infer that it might be advantageous in the catalyst synthesis to include a rapid sulfonation step designed to limit the sulfonic acid groups to a region near the surface, where they are effective.

PROCESS DESIGN RECOMMENDATIONS

Although Equation (9) is based on a realistic model of the catalytic process, Equation (3) is less complex, represents the data as well, and is more appropriate for preliminary process design estimates. The kinetics and available patent information point to the following design recommendations: a tubular flow reactor should be chosen to operate with a feed composition of less than about 12 mole% acetone in phenol. The acetone concentration should be less than that for the maximum rate since that value corresponds to the maximum yield of side products, and bisphenol A must meet strict color requirements for its end use in polymers. Similarly, the choice of reaction temperature would reflect the tradeoff between increased rate and poorer selectivity at higher temperatures. A temperature higher than about 330°K would be necessary to prevent crystallization of products and plugging of the catalyst bed. Solvent should not be added to prevent crystallization since it would inhibit reaction. The strong inhibition of reaction by product water suggests that the optimum conversion per pass would not be high.

The catalyst would be chosen on the basis of its selectivity, activity, and stability. The highly cross-linked macroporous catalyst is not much less active than the gel-form catalysts, and it is expected to be more stable and have less tendency to contaminate the product by sloughing of material produced by polymer degradation.

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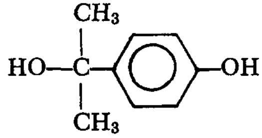
NOTATION

A = acetone
BPA = bisphenol *A*
C = concentration
DVB = divinylbenzene
I = reaction intermediate postulated to be the tertiary alcohol



k = reaction rate constant, variable dimensions
K = concentration equilibrium constant, l/mole
$\tilde{K}$ = inhibition parameter in empirical rate equation, l/mole
$\underline{K}'$ = Langmuir adsorption equilibrium constant for chemisorption on (hydrogen bonding to) —SO$_3$H groups
$\underline{K}$ = Langmuir absorption equilibrium constant for swelling of hydrocarbon matrix
P = phenol
r = reaction rate, (moles of acetone converted)/(equivalent of catalyst functional groups sec)
α_i = integer; $0 \leqq \alpha_i \leqq 3$

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* This interpretation fails to account for the true promotion by mercaptans in acid solution.

Subscripts

A = acetone
Abs = absorption (swelling)
Ads = adsorption (chemisorption or hydrogen bonding)
MCH = methylcyclohexane
P = phenol
W = water

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Synthesis of Distillation Systems with Energy Integration

A formal method is described for the synthesis of multicomponent distillation systems when energy integration is considered between streams both within the separation sequence and in other parts of the process. The pressure in each column is considered as an optimization variable for both the energy integration and column sizing computations. Four rules are used to enumerate all feasible energy matches between the streams associated with the distillation columns. A bounding strategy which uses both upper and lower bounds is combined with dynamic programming to synthesize the optimal distillation sequence with energy integration. A five-component separation problem demonstrates the effectiveness of the methods.

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SCOPE

Distillation systems are widely used in the manufacture of petroleum and petrochemical products. These systems consume large amounts of energy to achieve separation. In view of increasing energy costs, it is important to design distillation systems which consume less energy.

Several authors have described intuitive schemes for minimizing energy consumption in multicomponent distillation processes, for example, King (1971), Petlyuk et al.

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