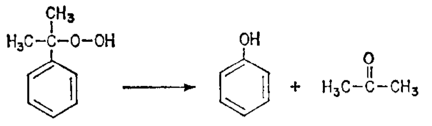
JOURNAL OF CATALYSIS 54, 442–445 (1978)

Decomposition of Cumene Hydroperoxide Catalyzed by Soluble and Polymer-Bound Sulfonic Acid Groups

Most reactions catalyzed in strongly acidic solutions are also catalyzed by polymeric solids containing $-SO_3H$ groups, and high concentrations of reactants within the swellable polymer matrix and cooperative effects among anhydrous $-SO_3H$ groups often contribute to a high catalytic activity (*1*, *2*). The decomposition reaction of cumene hydroperoxide giving phenol and acetone


(1)

is catalyzed both in acid solution (*3–5*) and in the presence of sulfonated poly(styrene–divinylbenzene) (*6*). The reaction is of interest because of its industrial application and because it can be carried out under anhydrous conditions, allowing the study of general acid catalysis. The experiments reported here were designed to characterize a macroporous sulfonated poly(styrene–divinylbenzene) catalyst for this reaction and to compare its performance with that of a soluble analog, *p*-toluenesulfonic acid (PTSA).[1]

Cumene hydroperoxide of 99.98% purity was obtained from a technical grade sample (Krackeler and Campbell) by purification of the sodium salt (*7*); the purity was checked by iodometry (*8*) and infrared spectroscopy. Reagent-grade acetone solvent was redistilled over anhydrous K_2CO_3. Anhydrous *p*-toluenesulfonic acid was obtained by dehydrating the monohydrate (Matheson, Coleman, and Bell) at 35°C and 6 Torr in the presence of P_2O_5 (*9*). Titration with standard NaOH confirmed that the product was anhydrous, and as expected (*9*), it had little tendency to rehydrate.

The solid catalyst was 30- to 50-mesh beads of Amberlyst 15, a macroporous, sulfonated copolymer of styrene and divinylbenzene supplied by the Rohm and Haas Co. The sample was pretreated in the standard way (*10*). Catalyst samples having various ratios of $-SO_3H$ to $-SO_3M$ groups were obtained by equilibrating $-SO_3H$ form beads with aqueous solutions containing appropriate amounts of HCl and MCl, where M was Li, Na, K, or Rb. Thoroughly washed samples were dried at 120°C and 10 Torr in the presence of P_2O_5. Samples were transferred directly from the vacuum oven to the reactor for catalysis experiments. Acid-group concentrations in the polymers were determined by titration against standard base (*11*), and the $-SO_3M$ content of each was calculated by difference from the initial and final acidities.

Kinetics experiments were performed with a thermostated stirred batch reactor

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[1] Notation: C, concentration (molar); k_i, pseudo $(i + 1)$th-order rate constant for solution reaction (seconds^{-1}·[liters per mole]^i); $\mathbf{k}_i$, pseudo $(i + 1)$th-order rate constant for resin-phase reaction (moles per liter per equivalent of functional groups ·seconds); M, metal; PTSA, *p*-toluenesulfonic acid; R, gas constant (calories per mole·degrees Kelvin); **r**, rate of cumene hydroperoxide decomposition catalyzed by the polymer (moles per liter per equivalent of functional groups·seconds); T, temperature (degrees Kelvin); θ_{-SO_3H}, fraction of functional groups in polymer which are $-SO_3H$ groups.

0021-9517/78/0543-0442$02.00/0

(*6*). The reaction was followed by determination of cumene hydroperoxide in periodically drawn samples using cyclic voltammetry (*7*) or iodometry (*12*). The reaction products were identified by gas chromatography; only phenol and acetone were found.

Determination of the distribution of cumene hydroperoxide between the polymeric catalyst and the surrounding liquid was made in the same device, using various concentrations of the reactant in the range 0.06 to 0.14 mol/kg of acetone as well as variable amounts of polymer. Amberlyst 15 in the $-SO_3Li$ form was used, since rapid reaction in the presence of the acid form would have interfered with the experiment. Typically, 50 ml of acetone and an appropriate amount of cumene hydroperoxide were transferred into the reactor, brought to 40°C, and analyzed for cumene hydroperoxide. Then the resin (swollen in acetone) was weighed into the reactor. The mixture was allowed to equilibrate (requiring $\gtrsim 10$ min), and the solution was analyzed for cumene hydroperoxide. From this analysis, the cumene hydroperoxide concentration in the polymer phase was calculated.

The polymer catalyst was generally more active than the soluble *p*-toluenesulfonic acid when equal numbers of equivalents of acid were compared. For example, when 0.017 equiv of $-SO_3H$ groups were present per liter of solution (containing acetone and cumene hydroperoxide), the apparent first-order rate constant was 2.7×10^{-3} s^{-1} for the polymer and 2.6×10^{-4} s^{-1} for the soluble analog; the ratio of these two rate constants decreased with an increasing amount of catalyst in the reactor.

Helfferich (*13*) has shown that for aqueous solutions of acid and strongly hydrated sulfonic acid resin catalysts the higher efficiency of the resin is often a consequence of the favorable distribution of the organic reactants between the resin and external solution. To test this possibility for our anhydrous reaction system, the distribution coefficient of cumene hydroperoxide between the phases was estimated from the equilibrium swelling experiments. The experiments with the $-SO_3Li$ form resin gave a result which suggests that the resin-phase concentration of reactant was about the same as that in the external solution; over the entire range of concentrations tested, the distribution coefficient was 0.94 (mol of cumene hydroperoxide/kg of resin)/(mol of cumene hydroperoxide/kg of solvent). If we assume that the swelling in the acid-form resin was similar to that in the $-SO_3Li$ form, as seems likely (*9*), then we are led to the suggestion that the concentration of reactant in the resin was about the same as that in the external solution during reaction; nonetheless, the environment surrounding the catalytic groups in the swollen resin was significantly different from that in the solution of *p*-toluenesulfonic acid in the reactants.

The kinetics experiments gave conversion-time plots for reaction with *p*-toluenesulfonic acid catalyst in solution which had a slight "S" shape indicating a small autocatalytic effect; this might be attributed to the product phenol (*6, 14–17*). Therefore, to simplify matters, the data were used to determine initial rates, eliminating the influence of the reaction products. Reaction times were at most 20% of the half-time for cumene hydroperoxide conversion.

The reaction was approximately first-order in reactant, and the data of Fig. 1 show the dependence of the pseudo-first-order rate constant on the concentration of *p*-toluenesulfonic acid. At the lowest catalyst concentrations, the reaction order with respect to the catalyst was about 1, and as concentration increased roughly tenfold, the order increased to about 1.6.

These results are consistent with the complicated nature of general acid catalysis in nonaqueous media and the possibility of formation of a series of hydrogen-bonded structures involving catalyst and reactant molecules as well as acetone (*9*).

The rate data can be summarized in a simple equation:

$$k_0 = k_1 C_{\text{PTSA}} + k_2 C^2_{\text{PTSA}} \qquad (2)$$

Fitting the full set of data to Eq. (2) yields nearly linear Arrhenius plots and the following summary of the results:

$$k_1 = 1.92 \times 10^{11} \exp(-19{,}000/RT) \qquad (3)$$

$$k_2 = 3.20 \times 10^{11} \exp(-17{,}000/RT) \qquad (4)$$

The good fit to the data by Eqs. (2) to (4) is shown in Fig. 1.

In the experiments with the solid catalyst, liquid-phase mass transfer had a negligible effect on rates (since variations in stirring rate and in the ratio of reactant to catalyst mass did not affect reaction rates), but the influence of intraparticle diffusion could not be evaluated, since the pertinent diffusion length (the average diameter of the microspherules comprising the polymer) could not be varied. In general, catalysis by macroporous polymers must be expected to be influenced by internal diffusion.

To provide kinetics data for comparison with the kinetics of the solution reaction, initial rates of reaction were measured with various concentrations of $-SO_3H$ groups in the resin, the remaining groups being $-SO_3M$. The results are summarized in Fig. 2. The salt forms of the resin had negligible catalytic activity, and the Na, K, and Rb ions all had nearly the same effect, which implies that the $-SO_3M$ groups simply diluted the catalytically active acid groups. The $-SO_3Li$ groups, however, were different, contributing some activity. This result is similar to earlier results with a similar set of catalysts used for alcohol dehydration (*18*).

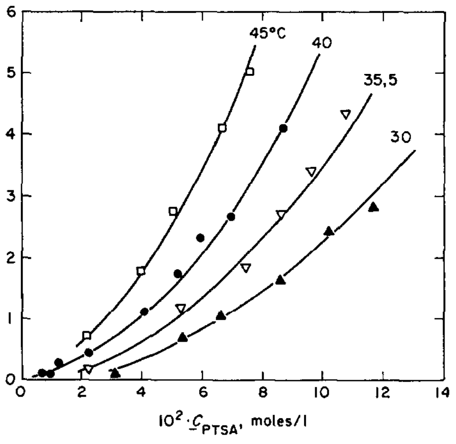

FIG. 1. Cumene hydroperoxide decomposition catalyzed by anhydrous *p*-toluenesulfonic acid in acetone: determination of the order of reaction in catalyst. The curves are predicted by Eqs. (2) to (4).

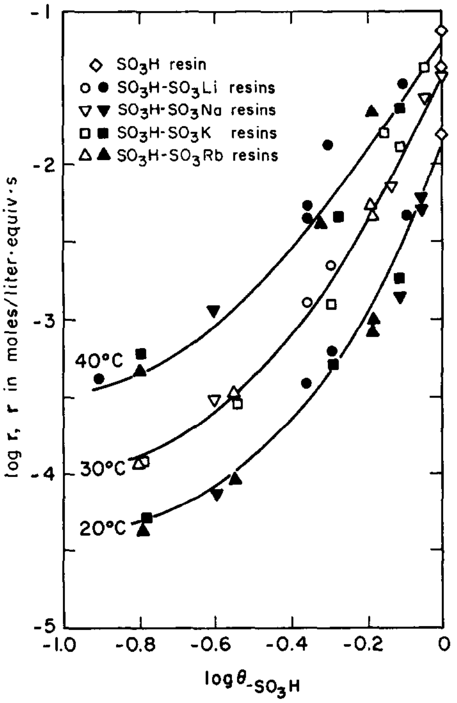

FIG. 2. Cumene hydroperoxide decomposition catalyzed by macroporous sulfonated poly(styrene–divinylbenzene): dependence of initial reaction rate on catalyst $-SO_3H$ group concentration. The initial reactant concentration in acetone was 0.1 *M*. The curves are predicted by Eqs. (5) to (7).

The data for the solid catalyst are qualitatively like those for the soluble catalyst in showing an increasing order of reaction in $-SO_3H$ groups with an increasing concentration of these groups. Again, at the lowest concentrations the reaction order in acid groups is roughly 1, but at the highest concentrations it increases to about 4. The following equation was found to fit the data better than any of comparable complexity:

$$\mathbf{r} = \mathbf{k}_1\theta_{-SO_3H} + \mathbf{k}_4\theta^4_{-SO_3H} \tag{5}$$

The data give nearly linear Arrhenius plots, and the following equations summarize the results:

$$\mathbf{k}_1 = 1.65 \times 10^{10} \exp(-18{,}600/RT) \tag{6}$$

$$\mathbf{k}_4 = 1.13 \times 10^{10} \exp(-16{,}000/RT) \tag{7}$$

The good fit of the data by Eqs. (5) to (7) is shown in Fig. 2.

The similarity in the kinetics of the resin-phase and solution-phase reactions suggests some similarity in their mechanisms, but the differences in concentrations of the various species in the liquid and polymer phases preclude any mechanistic conclusions.

ACKNOWLEDGMENT

This work was supported in part by a Fulbright Grant to C. I. for research at Rensselaer Polytechnic Institute. We thank Professor David Aikens for providing research facilities.

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Received February 10, 1978; revised May 30, 1978

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