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Mechanisms of Polymer-Supported Catalysis. 1. Reaction of 1-Bromooctane with Aqueous Sodium Cyanide Catalyzed by Polystyrene-Bound Benzyltri-*n*-butylphosphonium Ion

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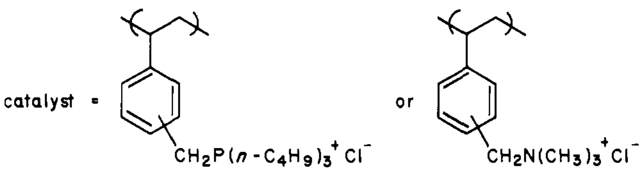
Abstract: The rate of reaction of 1-bromooctane with aqueous sodium cyanide catalyzed by insoluble polystyrene-bound benzyltri-*n*-butylphosphonium salts has been studied as a function of the method of mixing of the triphase system, catalyst particle size, degree of polymer cross-linking, solvent, and temperature. Reaction rates increase as the speed of mechanical stirring increases to a maximum rate at 600 rpm. Turbulent vibromixing and ultrasonic mixing do not cause any additional reaction rate increase. Reaction rates increase as catalyst particle sizes decrease, even at the maximum stirring speed. Reaction rates decrease as percent of divinylbenzene cross-linking in the polymer increases from 2% to 10%. Reaction rates increase with increasing swelling power of the solvent in the order decane < toluene < chlorobenzene. The results are discussed in terms of mass transfer and intraparticle diffusion limitations on the reaction rates. The polymer-bound benzyltri-*n*-butylphosphonium ion gives reaction rates ≥28 times faster than polymer-bound benzyltrimethylammonium when mass transfer and intraparticle diffusion do not limit the rates.

Insoluble polymer-supported phase-transfer catalysts promote reactions between water-soluble anions and organic substrates under triphase conditions.[2,3] The catalysts can be separated from reaction mixtures and can be reused, or they can be used in flow systems such as packed and fluidized bed reactors. There are also drawbacks to the known polymer-supported phase-transfer catalysts. Their activity is often less than that of soluble phase-transfer catalysts. The most commonly used support for phase-transfer catalysts, polystyrene cross-linked with 2% divinylbenzene, may be too gelatinous in swelling solvents for use in many large-scale flow systems and filtrations. The 2% cross-linked polystyrene is used most often because of its commercial availability as "Merrifield resin" for solid-phase peptide synthesis. More highly cross-linked polystyrenes are more rigid and could be used as catalyst supports, but they have not been tested systematically. A better fundamental understanding of the factors that control activity of polymer-supported phase-transfer catalysts is needed to attain both the higher activity and the greater ridigity required of practical heterogeneous catalysts.

This paper is the first of a series on the experimental parameters that control rates of reactions promoted by polymer-bound phase-transfer catalysts. It is devoted to a single prototypical phase-transfer-catalyzed reaction, that of 1-bromooctane with aqueous sodium cyanide catalyzed by benzyltri-*n*-butylphosphonium and benzyltrimethylammonium ions bound covalently to cross-linked polystyrenes. The experimental parameters include mixing of the triphase system, catalyst particle size, degree of cross-linking of the polymeric support, solvent, and temperature. Earlier papers on mechanisms of polymer-supported phase-transfer catalysis have not considered all of these parameters. We shall show how all of them are important. Still more parameters affect observed rates of reaction of cyanide with alkyl halides, such as the separation of the active site from the polymer backbone, the degree of substitution of the polymeric support, and the structure of the substrate, but they will not be evaluated here.

$$n\text{-}C_8H_{17}Br + NaCN(aq) \longrightarrow n\text{-}C_8H_{17}CN + NaBr(aq)$$



Quaternary onium salts bound to cross-linked polystyrenes are ion-exchange resins. The fundamental kinetic steps that influence reactions catalyzed by ion-exchange resins have been known for years.[4] The reaction of cyanide with 1-bromooctane differs from earlier ion-exchange resin catalysis in only one major respect, the presence of two liquid phases instead of just one liquid phase. The fundamental kinetic steps in ion-exchange resin catalysis are as follows (Figure 1): (1) mass transfer of reactant from bulk liquid to the surface of the catalyst particle, (2) diffusion of reactant through the polymer matrix to the active sites, (3) intrinsic reaction rate at the active sites, (4) diffusion of product through the polymer matrix to the particle surface and mass transfer of product to bulk solution. The same four fundamental kinetic steps must occur with both 1-bromooctane and cyanide ion for the bimolecular

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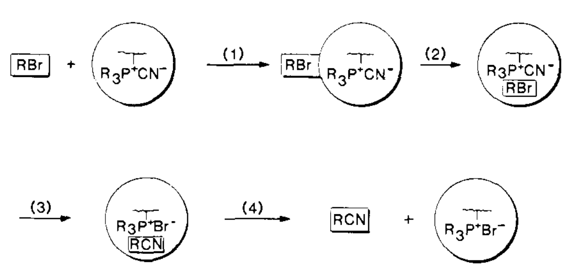

Figure 1. Fundamental kinetic steps in polymer-supported phase-transfer catalysis. (1) Mass transfer to reactant from bulk solution to catalyst surface. (2) Diffusion of reactant through polymer matrix to active site. (3) Reaction at active site. (4) Diffusion of product to surface of catalyst and mass transfer of product to bulk solution.

reaction to occur, although only the 1-bromooctane steps are shown in Figure 1. In the absence of catalyst the insolubility of 1-bromooctane in water and of sodium cyanide in organic media prevents reaction. In this paper we focus on experimental parameters that affect the contributions of mass transfer, intraparticle diffusion, and intrinsic reactivity to control of observed rates.

Results

Catalyst Preparation. All catalysts were synthesized by suspension copolymerization of styrene, chloromethylstyrenes (25 wt%, 60:40 meta/para isomers), and a cross-linker, followed by displacement of chloride with tri-*n*-butylphosphine or trimethylamine. Particles were separated with sieves at the copolymer stage into −40+60, −60+100, −100+200, −200+325, −325+400, and −400 mesh fractions, and sometimes separations were repeated at the catalyst stage. Each catalyst had 14–18% of the polymer repeat units substituted with phosphonium ions or 16–18% substituted with ammonium ions. Levels of substitution were established by analysis of the chloride ions contents of the catalysts. All of the 2% cross-linked phosphonium catalysts were prepared independently 2–4 times. Rate data were obtained with 45 different batches of catalysts with variations in cross-linking, particle size, and active-site structure.

Rate Measurements. Reaction rates were measured by using a large excess of aqueous sodium cyanide, usually 10 mol of NaCN/mol of $C_8H_{17}Br$. Conversion of 1-bromooctane to 1-cyanooctane was followed for 25–80% conversion with phosphonium catalysts and 5–25% conversion with ammonium catalysts. With benzyltri-*n*-butylphosphonium ion catalysts, pseudo-first-order k_{obsd} decreased with time due to catalyst decomposition, so all rate constants reported are initial values for 5–25% reaction. Other evidence of slow catalyst decomposition includes: (1) Reaction rates were slower when the catalyst was conditioned for 2 h at 90 °C with all reaction components except 1-bromooctane than when the catalyst was conditioned for 1 h. Exacly 1 h was used as the standard conditioning time. (2) One batch of catalyst recovered after 3-h reaction time was recycled, and a 32% decrease in rate constant occurred. (3) The chloride ion content of the same batch of recovered catalyst was 12% less than the original value. In spite of the catalyst decomposition, data are reliable for comparative purposes because the catalysts were conditioned identically in all experiments and the data points used to calculate initial rate constants were taken in 25 min or less, during which time the decrease in phosphonium sites is calculated to be <2%. The observed first-order rate constants were linearly dependent on the amount of catalyst from 0 to 4 mol % on the basis of 1-bromooctane. With no catalyst present, <0.1% conversion was observed in 4 h, a time equal to 12 half-lives when using 2 mol % of −400-mesh catalyst with turbulent mixing.

Methods of Mixing. Most reaction mixtures were stirred mechanically in a round-bottom flask. Plots of pseudo-first-order rate constant vs. stirring speed are in Figures 2 and 3. Rate constants increased with stirring speed up to about 400 rpm and increased only a little more up to 600–650 rpm. the dependence of the rate constant on stirring speed decreased as the particle size decreased, as can be seen in Figure 3 by comparison of k_{obsd} at 200 rpm with k_{obsd} at 600 rpm.

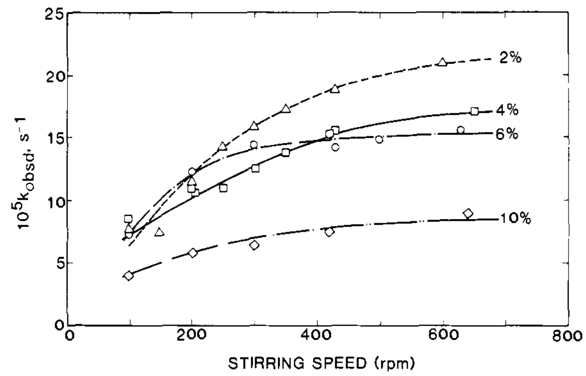

Figure 2. Effects of stirring speed and percent divinylbenzene cross-linker on k_{obsd} at 90 °C for reaction of 1-bromooctane in toluene with 10 molar equiv of sodium cyanide in water and 0.02 molar equiv of polystyrene-bound benzyltri-*n*-butylphosphonium salt catalyst. Particle sizes were −100+200 mesh at the copolymer stage.

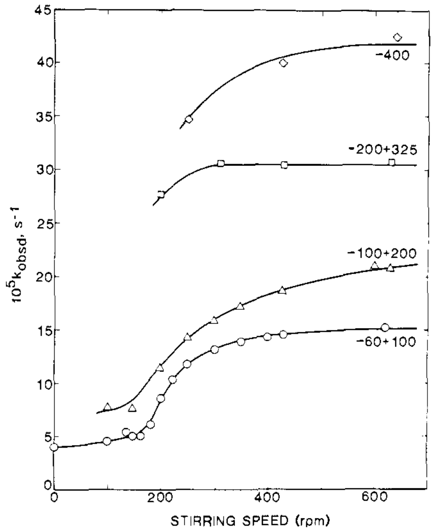

Figure 3. Dependence of k_{obsd} on stirring speed and mean particle size of 2% divinylbenzene cross-linked catalysts. Experimental conditions are the same as in Figure 2.

Although rate constants appeared nearly independent of stirring speed at >600 rpm, we were not certain that optimum mixing had been attained. So turbulent mixing was studied with a vibromixer and with an ultrasonic probe. Figure 4 shows dramatically different oil-in-water dispersions from the three methods of mixing. In a quiet mixture, the toluene solution is the upper phase, and the catalyst rests at the organic/aqueous interface. Mixing disperses droplets of organic phase and the solid catalyst particles throughout the continuous aqueous phase. The sizes of organic droplets with 600 rpm mechanical stirring, vibromixing, and ultrasonic mixing are ~5–30, ~0.5–3, and <0.05 mm. (The <0.05-mm droplets are too small to see in the photographs.) The ultrasonic mixture looks like a milky emulsion. Ultrasound makes the catalyst particles clump together. Any of the three mixing methods carried out too vigorously splashes catalyst particles out of the reaction mixtures onto the upper walls of the flask out of contact with the reactants. For reaction to occur, both liquid phases must contact the catalyst particles so that 1-broooctane and cyanide ion are transported into the particles and 1-cyanooctane and bromide ion are transported out of the particles. The effects of mixing methods on observed rate constants are in Table I. Even though the turbulent mixing methods give much finer oil-in-water dispersions, 600-rpm mechanical stirring gives rates as fast or faster than turbulent mixing. Therefore, the other experimental parameters were studied by stirring at 600–650 rpm.

Catalyst Particle Sizes. The particle size of a heterogeneous catalyst may strongly affect its activity. Figures 3 and 5 show dependence of k_{obsd} on mean particle sizes at different stirring

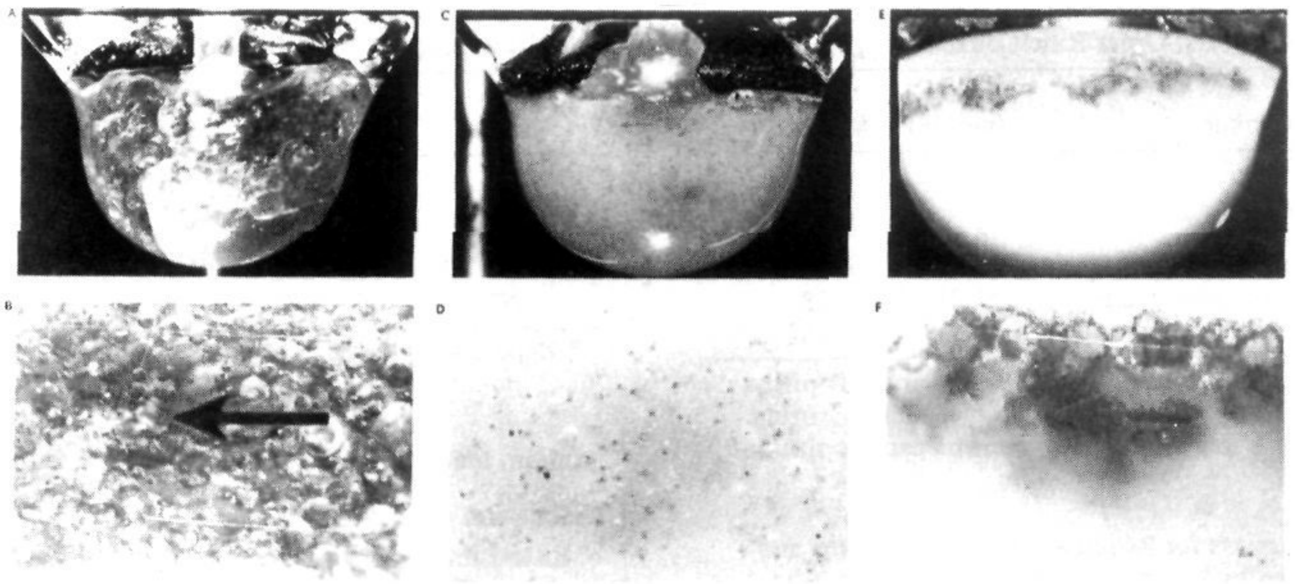

Figure 4. (A) Mechanical stirring at 300 rpm. (B) Mechanical stirring at 600 rpm. In all photographs catalyst particles appear as dark spots 150–300 μm in diameter. The diameter of the arrow shaft is 550 μm. (C) Vibromixing "upwards" creates a fountain around the mixer shaft in the center of the flask. (D) Enlargement of vibromixing. (E) Ultrasonic mixing emulsifies the organic/aqueous mixture and causes clumping of catalysts. (F) Enlargment of ultrasonic mixing.

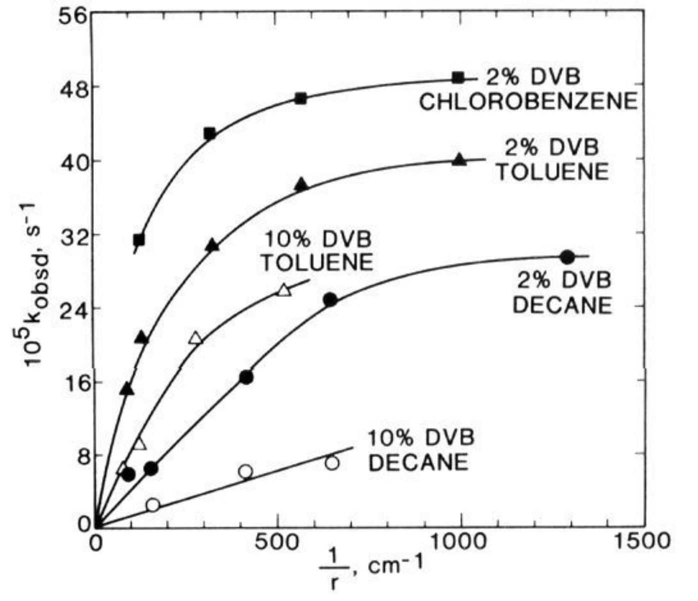

Figure 5. Dependence of k_{obsd} on mean catalyst particle size and solvent. Stirring speed is 600–650 rpm, and other experimental conditions are the same as in Figure 2.

Table I. Dependence of the Observed Pseudo-First-Order Rate Constants on the Method of Stirring[a]

method of stirring	swollen particle size, μm	$10^5 k_{obsd}$, s^{-1} [d]
mechanical, 600 rpm	150–300	15
	100–200	21
vibromixer, upward[b]	150–300	15
vibromixer, downward[b]	150–300	14
	100–200	19
ultrasonic wave[c]	150–300	11

[a] $C_8H_{17}Br$, 0.02 mol; toluene, 20 mL; 0.02 molar equiv of the phosphonium catalyst cross-linked by 2% divinylbenzene; 90 °C. [b] Two kinds of virbromixing were used. The disk with holes tapering upward forces the mixture to flow rapidly upward around the stirrer shaft. The disk with holes tapering downward forces the mixture to flow rapidly downward from the bottom of the disk. The vibrational amplitude was adjusted to prevent the catalyst from splashing out of the reaction mixture. [c] A 21-kHz probe placed directly in the reaction mixture. Many of the catalyst particles formed large clusters. We suspect reduced activity of the clusters is responsible for the slower rate. [d] Rate constants are reproducible to ±5% with mechanical stirring and to ±10% with vibromixing and ultrasonic mixing.

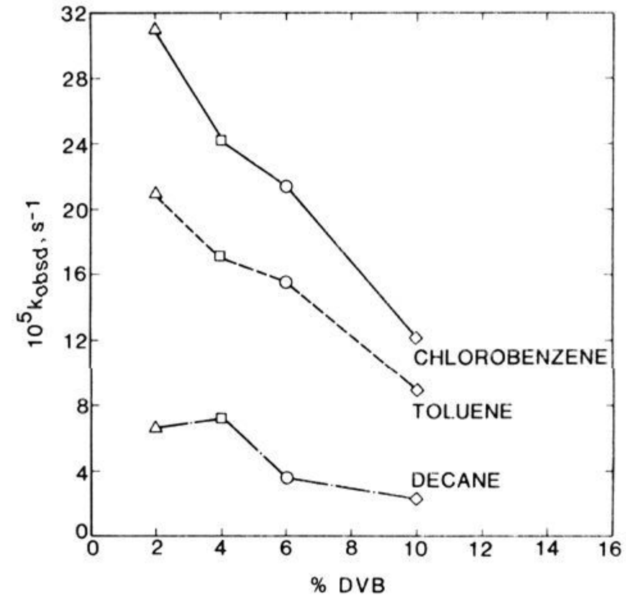

Figure 6. Effects of solvent and percent cross-linker on k_{obsd}. Stirring speed is 600–650 rpm, and other experimental conditions are the same as in Figure 2.

Table II. Volume Swelling of Catalysts at 25 °C

		swollen volume/dry volume[a]			
active site	% divinylbenzene	water	toluene	chlorobenzene	decane
P^+	2	1.8	2.2	3.0	1.0
P^+	4	1.2	2.0	2.7	1.0
P^+	6	1.0	1.6	1.9	1.0
P^+	10	1.0	1.4	1.7	*b*
N^+	2	2.0	1.6	3.0	*b*
N^+	10	1.0	1.4	2.0	1.0

[a] See Experimental Section for procedures. [b] Not measured; value presumably is 1.0.

speeds and in three different solvents. Sizes of catalyst particles recovered from reaction mixtures were measured with a microscope with a movable stage calibrated in micrometers. In Figure 5, with 2% divinylbenzene-cross-linked catalysts, rate constants increase as particle size decreases up to a limiting value of $1/r = 1000$ cm^{-1}, beyond which further decreases in particle size appear not to affect k_{obsd}. The maximum rate is attained at a particle diameter of 20 μm, near the lower limit of particle sizes that can be prepared by suspension polymerization and near the lower limit of particle sizes that can be separated from reaction mixtures by simple filtration without resorting to ultrafiltration or dialysis. Figure 5 shows that k_{obsd} increases as particle size decreases also with 10% divinylbenzene-cross-linked catalysts, but experiments were not carried out with small enough particles to maximize k_{obsd}.

Effect of Solvent. In Figures 5 and 6, k_{obsd} decreases with solvent in the order chlorobenzene > toluene > decane over wide ranges of particle sizes and polymer cross-linking. The ability of the solvent to swell the catalysts decreases in the same order, as shown in Table II.

Polymer Cross-linking. Increasing the level of divinylbenzene cross-linking in the polymeric support decreases k_{obsd}, as shown

Table III. Effect of the Structure and Content of the Cross-linker on the Observed Pseudo-First-Order Rate Constants[a]

cross-linker	wt % (mol %)	$10^5 \cdot k_{obsd}$, s^{-1}
divinylbenzene	2	21
divinylbenzene	4	17
divinylbenzene	6 (5.3)	16
divinylbenzene	10	9.1
1,6-hexanediol dimethacrylate	(5.3)	18
1,10-decanediol dimethacrylate	(5.3)	18

[a] $C_8H_{17}Br$, 0.02 mol; toluene, 20 mL; 0.02 molar equiv of the phosphonium catalyst; 90 °C, 600–650-rpm mechanical stirring. The catalysts were prepared from copolymers of particle size 75–150 μm.

Table IV. Rate Constants for Reaction of 1-Bromooctane and Cyanide Ion Catalyzed by Polymer-Bound Benzyltrimethylammonium Ions[a]

% DVB	particle size, mesh	solvent	$10^5 \cdot k_{obsd}$, s^{-1}
2	−60+100	toluene	1.44
2	−60+100	decane	0.36
2	−60+100	chlorobenzene	1.55
2	−200+325	toluene	1.41
2	−325+400	toluene	1.40
2	−325+400	decane	1.34
2	−325+400	chlorobenzene	1.74
4	−60+100	toluene	1.46
6	−60+100	toluene	1.32
10	−60+100	toluene	0.98
10	−60+100	chlorobenzene	0.92
10	−100+200	toluene	1.54
10	−200+325	toluene	1.65
10	−325+400	toluene	1.77

[a] With 420–430-rpm mechanical stirring at 90 °C. All other experimental conditions are the same as in Figure 2.

in Figures 2, 5, and 6. The same effect was observed in three solvents. Increasing the cross-linking decreases the extent of swelling of the catalysts as shown in Table II. With use of divinylbenzene as the cross-linker, the extent of catalyst swelling can be controlled by either the level of cross-linking or the swelling power of the solvent. With either method k_{obsd} increases as the degree of swelling increases.

The effect of crosslinking was also examined by use of aliphatic bismethacrylates instead of divinylbenzene to cross-link the styrene/chloromethylstyrene copolymers. We thought that if intraparticle diffusion limited reaction rates, more flexible aliphatic cross-linkers might give more active catalysts by providing faster intraparticle diffusion. Comparisons of catalysts that contain 5.3 mol % cross-linker (equivalent to 6.0 wt % divinylbenzene) in Table III shows that cross-linker structure has little effect on k_{obsd}.

Benzyltrimethylammonium Ion Catalysts. All rate constants with benzyltrimethylammonium ion catalysts are at least a factor of 10 smaller than those with the corresponding quaternary phosphonium ion catalysts. Data are in Table IV. With 2% cross-linked −60+100 mesh catalyst, the rate in toluene was independent of stirring speed from 300 to 600 rpm. Rate contants with 2% cross-linked catalysts are independent of particle size in toluene, highly dependent on particle size in decane, and perhaps slightly dependent on particle size in chlorobenzene. Rate constants with 10% cross-linked catalysts in toluene increase as particle size decreases. With −60+100 mesh particles, rate constants in toluene and chlorobenzene decrease as percent of cross-linking increases. With −200+325 and −325+400 mesh particles in toluene, rate constants are higher than with 10% cross-linking than with 2% cross-linking.

Effect of Temperature. Activation parameters calculated from Arrhenius plots of kinetic data are in Table V. Each plot consisted of data at 50, 70, and 90 °C. The percent of cross-linking has no measurable effect on apparent activation energy E_{app} or ΔS^* with −100+200 mesh phosphonium ion catalysts. Small particles, −400 mesh, increase E_{app} and decrease slightly ΔS^*. The ammonium ion catalyst is much less active due to a much larger E_{app}.

Table V. Influence of Particle Size and Degree of Cross-linking on Activation Parameters in Toluene[a]

active site	particle size, mesh	% DVB	E_{app}, kcal/mol	$\Delta S^{\ddagger}$,[b] cal deg^{-1} mol^{-1}
P^+	−60+100	2	11.4	−44.9
P^+	−100+200	2	11.7	−43.4
P^+	−400	2	13.5	−37.0
P^+	−100+200	10	11.7	−45.0
N^+	−60+100	2	21.1	−22.6

[a] Experimental conditions are the same as in Figure 2. [b] At 70 °C.

Discussion

Rate-Limiting Processes in Heterogeneous Catalysis. Previous analyses of the kinetic factors in heterogeneous catalysis,[5] particularly in catalysis by ion-exchange resins,[4,6] provide the foundation for discussion of the mechanisms of catalysis by polymer-bound onium salts in triphase systems. The fundamental steps that may affect rates of reaction between cyanide ion and 1-bromooctane in triphase experiments are shown in Figure 1. Detailed mathematical models of the intraparticle diffusion and intrinsic reactivity contributions to kinetics of catalysis by ion-exchange resins are available,[6] but they do not include mass transfer. A model for supported enzyme catalysis includes mass transfer.[7] None of the models considers triphase systems. At this time we discuss our data qualitatively in terms of the concepts provided by the models.

1. *Mass transfer* of 1-bromooctane from bulk organic phase to the surface of a catalyst particle depends upon contact between polymer particles and organic droplets, both of which are suspended in a continuous phase of aqueous sodium cyanide. Any dependence of observed reaction rates on the method of mixing or speed of stirring must be due to at least partial limitation of the reaction rate by slow mass transfer. In the extreme case of a rate controlled only by mass transfer, the reaction takes place exclusively on the catalyst particle surface.

In any agitated solid/liquid system, the rate of fluid flow increases with distance from the solid surface. The liquid phase nearest the solid surface is essentially quiet even when the bulk liquid undergoes turbulent flow. This phenomenon is most familiar to chemists as the "Nernst layer" around the electrode in electrochemistry and the "wall effect" in liquid flow through a pipe. The thickness of the quiet layer, or film, at the surface of a solid depends on the degree of agitation of the mixture. The more turbulent the mixing or the faster the liquid flow, the thinner the film at the solid surface. Molecular transport through the film occurs as diffusion through a quiet liquid.

In catalysis by spherical particles, the rate of mass transfer refers to the rate at which reactant molecules from bulk liquid reach the surface of the catalyst. This rate depends on both the degree of agitation of the mixture, which affects the thickness of the quiet film, and the diffusion coefficient of the reactant in the quiet film. Whenever mass transfer limits the observed reaction rate, there is a gradient of decreasing concentration of reactant from bulk liquid across the quiet film to the catalyst surface.

Control of observed reaction rates only by mass transfer occurs when the catalyst is highly active, and reaction proceeds on the surface much faster than the reactant diffuses into the catalyst matrix. Under these conditions the structure of the active site and the structure of the polymer matrix do not affect observed reaction rates. The only experimental parameters that affect reaction rates are the method of mixing, the catalyst particle size,

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and the number of active sites on the catalyst surface. The reaction rates is directly proportional to the surface area of the catalyst and inversely proportional to the radius of spherical catalyst particles.

2. *Diffusion* of reactant *through the polymer matrix* may limit reaction rates when mass transfer of reactant is fast and low surface activity of the catalyst permits reactant molecules to diffuse into the catalyst particles and react at interior active sites. If the activity of the catalyst is high, the reaction may proceed entirely on the catalyst surface, and the rate is controlled either by mass transfer or by the intrinsic reactivity at the catalyst surface. If the intrinsic reaction rate is slow compared with the intraparticle diffusion, a uniform distribution of reactant throughout the catalyst particle is attained, and the rate is controlled by intrinsic reactivity at all of the active sites. Intraparticle diffusion influences reaction rates only in intermediate cases where a decreasing concentration gradient of reactant is established from the surface to the center of the spherical catalyst. Under these conditions both diffusion and intrinsic reactivity limit the reaction rate. Intraparticle diffusion can never be the only rate-limiting process.

Experimental parameters that may reveal intraparticle diffusion effects on reaction rates are catalyst particle size, degree of cross-linking, and solvent. The diffusion rate through the polymer matrix does not depend on particle size, but smaller particles provide more efficient utilization of active sites. The larger the particle, the longer the diffusion path to an active site near the center of the particle and the less that active site is used.

The degree of cross-linking controls diffusion rates by controlling the swelling of the polymer matrix. The lower the degree of cross-linking, the greater the swelling and the greater the volume fraction of the more mobile liquid phase in the catalyst. Increased cross-linking could also render some catalytic sites completely inaccessible to 1-bromooctane. Cross-linking can decrease the equilibrium capacity of cation-exchange resins for tetraalkylammonium ions,[8], and the greater the cross-linking in solvent-swollen polystyrene gels, the lower their molecular weight exclusion limit in gel permeation chromatography.[9]

The solvent may affect catalytic activity in several ways. The greater its swelling power, the larger the volume fraction of catalytic occupied by the more mobile liquid, and the smaller the volume fraction of the more rigid polymer network. The degree of swelling and the viscosity within the polymer matrix affect intraparticle diffusion rates. The solvent may also affect intrinsic reactivity at the active site. Experimentally it is difficult to distinguish solvent effects on diffusivity from solvent effects on reactivity.

3. The *intrinsic reactivity* at the active site may partly or completely control reaction rates. Active-site structure is the experimental parameter most thoroughly investigated in previous reports of polymer-supported phase-transfer catalysis.[2,3] We have used the same active-site structure for most experiments so that attention could be concentrated on mass transfer and diffusion effects. In some papers active-site structure has been invoked to explain reactivity differences in experiments where other important parameters, such as mixing method, catalyst particle size, and degree of cross-linking, have not been carefully controlled. Regen[3d] and Cinouini and co-workers[3b] have shown that active-site structure is important in nucleophilic substitutions, and our observations of higher activity with benzyltri-*n*-butylphosphonium ions than with benzyltrimethylammonium ions confirm their earlier conclusions.

4. *Diffusion* of product out of the polymer matrix *and mass transfer of product* from catalyst particle surface to bulk liquid also could affect observed reaction rates. In the reaction of 1-bromooctane with cyanide ion, the product 1-cyanooctane has almost the same molecular size and shape as the reactant 1-bromooctane. Rates of matrix diffusion of 1-bromooctane and 1-cyanooctane should be almost equal and so should their rates of mass transfer be almost equal. Most likely during reactions a balance is reached in which the sum of 1-bromooctane and 1-cyanooctane concentrations inside the catalyst remains constant with a flux of 1-bromooctane into the catalyst and a flux of 1-cyanooctane out of the catalyst. Since the conversion of 1-bromooctane to 1-cyanooctane is irreversible, the concentration of 1-cyanooctane in the catalyst does not appear in the rate law and can cause at most a small solvent effect on the reaction rate.

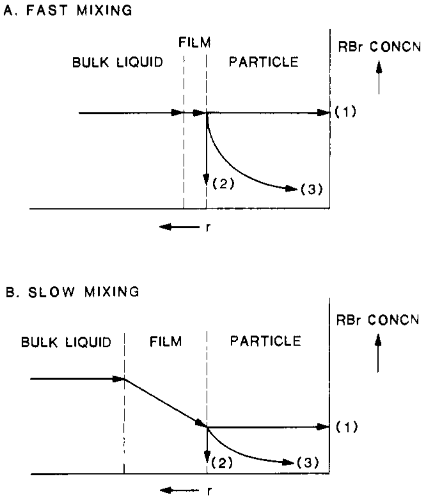

Figure 7. Reactant concentration as a function of distance from the center of a catalyst particle for fast mixing (A) and slow mixing (B). In both figures, (1) represents a reaction rate limited by intrinsic reactivity at the active site, (2) represents a reaction rate limited by mass transfer, and (3) represents a reaction rate limited by a combination of intraparticle diffusion and intrinsic reactivity.

5. The *rate of ion exchange* of the original chloride or the product bromide for cyanide in the ion-exchange resin catalyst also could limit the reaction rate. Ion exchange is subject to mass-transfer and matrix-diffusion effects similar to those with the organic reactant, except that ion exchange is complicated by electrostatic phenomena. We have avoided rate-limiting ion exchange by use of 10 molar equiv of sodium cyanide per mol of 1-bromootane. Pseudo-first-order kinetics using only 0.02 molar equiv of catalyst indicate that ion exchange is not a rate-limiting factor.

The conditions employed for kinetics of reaction of 1-bromooctane and cyanide ion make factors 4 and 5 negligible to a first approximation. Therefore, interpretation of the results will be confined to factors (1) mass transfer of 1-bromooctane to the catalyst surface, (2) diffusion of 1-bromooctane through the polymer matrix, and (3) intrinsic reactivity at the active site. We find helpful in this interpretation Figure 7, in which idealized one-dimensional reactant concentration profiles as a function of distance from the center of a catalyst particle are presented for fast- and slow-mixing conditions. The main difference between fast mixing in Figure 7A and slow mixing in Figure 7B is that fast mixing greatly reduces the thickness of the quiet film on the catalyst surface so that there is little or no concentration gradient between bulk liquid and the catalyst surface. With slow mixing there is a large decrease in concentration of reactant across a thicker quiet film. In both Figure 7A and Figure 7B, three concentration profiles are pictured inside the catalyst particle. In (1) the intrinsic reaction rate is slow relative to matrix diffusion, so there is no concentration gradient from the surface to the center of the particle. In (3) matrix diffusion and chemical reaction proceed at similar rates, and there is an exponential decrease in reactant concentration from the surface to the center of the catalyst. In (2) intrinsic reactivity at an active site is so high (or intraparticle diffusion is so slow) that reaction occurs only on the catalyst surface, and no matrix diffusion of reactant is required.

Interpretation of Kinetic Data. Observed rate constants for benzytri-*n*-butylphosphonium ion catalyzed reaction of 1-bromooctane with cyanide ion increase with stirring rates up to a limiting rate constant that is approximately the same as that attained with turbulent vibromixing or ultrasonic mixing. This

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(8) Lieser, K. H. *Pure Appl. Chem.* **1979**, *51*, 1503–1517.
(9) Heitz, W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 689–702.

phenomenon occurs with all catalyst particle sizes and all degrees of cross-linking in toluene, and we assume that similar results would be obtained in chlorobenzene and in decane. The only kinetic process limited by mixing is mass transfer. Therefore, in all experiments carried out at stirring speeds less than that required to attain the maximum k_{obsd} with a given catalyst, Figure 7B applies and mass transfer is a factor limiting reaction rates. At stirring speeds that give the maximum value of k_{obsd} with a given catalyst, Figure 7A applies and mass transfer is not rate limiting.

Reaction rates increase as catalyst particle size decreases. Both mass transfer and the efficiency of utilization of active sites (which depends on intraparticle diffusion) depend on particle size. If only mass transfer limits rates, k_{obsd} is proportional to $1/r$. If a combination of matrix diffusion and intrinsic reactivity limits the rates, the dependence of rate on particle size can vary from zero at the limit of exclusive intrinsic reactivity control to $1/r$ at the limit where diffusion is so slow that all reaction takes place on the particle surface. The experiments in Figure 5 were carried out at stirring speeds of 600–640 rpm where mass transfer is not rate limiting. Therefore, Figure 5 is strong evidence for rate limitation by a combination of intraparticle diffusion and intrinsic reactivity. As catalyst particle size decreases, the dependence of k_{obsd} on $1/r$ decreases, indicating that intrinsic reactivity becomes more important and matrix diffusion becomes less important as particle size decreases. The curves in Figure 5 indicate that if one used still smaller catalyst particles k_{obsd} would become independent of particle size and depend only on intrinsic reactivity.

Reaction rates decrease as catalyst cross-linking increases when using −100+200 mesh catalyst particles and 600–650 rpm stirring (Figure 6). Increased cross-linking decreases the ability of the polymer matrix to swell in solvents (Table II). The more cross-linked the polymer matrix, the smaller the volume fraction of liquid phase, and the lower the diffusivity of the 1-bromooctane.

The solvent also affects the observed reaction rate, increasing in the order decane < toluene < chlorobenzene. This order corresponds with increasing solvent dielectric constant[10] and with increasing swelling of the catalyst particles (Table II). Thus, one effect of solvent could be the same as the cross-linking effect: the more swollen the catalyst, the faster the intraparticle diffusion and the faster the reaction. But there is a solvent effect in Figure 5 even when reaction rates approach their maximum value with decreasing particle size, where the observed rate constants are due only to intrinsic reactivity. Solvent effects on intrinsic reactivity must be due to different environments at the active site. The actual aqueous vs. organic composition at the active site is not known, but the hydration numbers of the halide ions in polymer-bound benzyltri-*n*-butylphosphonium catalysts swollen in toluene are 3.5 water molecules per Cl^- and 2.0 water molecules per Br^-.[3x] The degree of hydration of CN^- should be similar. Use of decane or chlorobenzene may alter the degree of hydration of cyanide ion, or increasing polarity of organic solvent may cause a more rapid reaction at an aqueous/organic interface at an ion-exchange site. Rates of conventional phase-transfer-catalyzed displacement reactions similar to that of 1-bromooctane with cyanide ion increase as the dielectric constant of the solvent increases,[11] probably because the solubility of the quaternary onium cyanide in the organic phase increases with increasing solvent polarity.

Reaction rates were low with the benzyltrimethylammonium ion catalysts (Table IV). The intrinsic reactivity difference between phosphonium and ammonium catalysts is a factor of at least 28, which is the ratio of the rate constant for 2% cross-linked −400 mesh phosphonium catalyst at 640-rpm stirring in toluene at 90 °C to the rate constant for 2% cross-linked −325+400 mesh ammonium catalyst at 420-rpm stirring. Since the largest particles with the least cross-linking show no influence of stirring speed from 300 to 600 rpm in toluene, none of the rate constants in Table IV are limited by mass transfer. With 2% cross-linked catalysts in toluene, particle size does not affect the rates, so matrix diffusion is not rate limiting either. Intrinsic reactivity is completely rate limiting with 2% cross-linked benzyltrimethylammonium ion catalysts. With 10% cross-linked ammonium catalysts in toluene, rate constants increase as particle size decreases, indicating that a combination of intraparticle diffusion and intrinsic reactivity limits rates. The higher rate constants with 10% than with 2% cross-linked −200+325 and −325+400 mesh ammonium catalysts in toluene are an unexplained anomaly. Limited data with 2% cross-linked ammonium catalyst in decane and chlorobenzene suggest that both intraparticle diffusion and intrinsic reactivity limit rates. Again the solvent effect on rates is decane < toluene < chlorobenzene.

When intraparticle diffusion and intrinsic reactivity together limit reaction rates, the apparent Arrhenius activation energy E_{app} may range from

$$E_{app} = E_{diff}/2 + E_r/2$$

for the case of strongly diffusion limited rates, to

$$E_{app} = E_r$$

for the case of rates limited only by intrinsic reactivity.[4] E_{diff} is the Arrhenius energy for intraparticle diffusion, the E_r is the Arrhenius energy for intrinsic reaction rates. The activation parameters in Table V for reactions using phosphonium catalysts were obtained under conditions where a combination of intraparticle diffusion and intrinsic reactivity limits reaction rates, although the data with −400 mesh particles approach the limit of control by intrinsic reactivity alone. The data for the benzyltrimethylammonium ion catalysts are a case of strict intrinsic reactivity control. Thus, the benzyltrimethylammonium ion catalyzed reaction has a higher E_{app} (and higher $\Delta G^{\ddagger}$) and a less negative $\Delta S^{\ddagger}$ than the benzyltri-*n*-butylphosphonium ion catalyzed reaction. Since the −400 mesh catalyst gives more intrinsic reactivity control, the E_{app} data indicate that $E_r > E_{diff}$, and the entropy of diffusion is more negative than the $\Delta S^{\ddagger}$ for intrinsic reaction rates with the phosphonium catalysts. We estimate that $E_r \approx 13.5$ kcal/mol and $E_{diff} \approx 9-10$ kcal/mol for catalysis by phosphonium ions in the 2% cross-linked polymer. This estimate E_{diff} is similar to obervations of $E_{diff} = 5-10$ kcal/mol for intraparticle diffusion of anions in anion-exchange resins in aqueous solutions.[4]

Conclusions

In a prototypical example of polymer-bound phase-transfer catalysis (triphase catalysis), the reaction of 1-bromooctane with aqueous sodium cyanide catalyzed by polystyrene-bound benzyltri-*n*-butylphosphonium ion, mass transfer of reactant from bulk liquid phase to the catalyst surface, diffusion of reactant through the polymer matrix, and intrinsic reactivity at the active site all can limit observed reaction rates. The experimental conditions that favor intrinsic reactivity control are (1) turbulent mixing, (2) small particle size, preferably smaller than 400 mesh, (3) low degree of polymer cross-linking, which provides greater catalyst swelling, (4) increased swelling power of solvent, (5) lower temperature, and (6) less active catalytic sites. Parameters 1–4 increase reaction rates, but 5 and 6 decrease reaction rates. Strict control of rates by intrinsic reactivity at the active sites is often not desirable in polymer-supported phase-transfer catalysis. We and others who wish to prepare more useful polymer-bound phase-transfer catalysts must consider the following points in the design of new catalysis experiments. (1) Smaller polymer particles are likely to produce more active catalysts, but the particles must be large enough to separate from reaction mixtures by filtration. More laborious separation procedures would defeat the major advantages of polymer-bound catlaysts over soluble catalysts—ease of separation from reaction mixtures and reuse, and suitability for use in flow reactors. (2) Lower degrees of cross-linking may

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(10) Dielectric constants are decane 2.0, toluene 2.4, and chlorobenzene 5.6 at 20–25 °C: Riddick, J. A., Bunger, W. B. "Organic Solvents", 3rd ed; Wiley: New York, 1970.

(11) Starks, C. M., Liotta, C. "Phase Transfer Catalysis"; Academic Press: New York, 1978; p 94. When onium salts such as hexadecyltributylphosphonium bromide are highly soluble in highly nonpolar solvents, nucleophilic substitution rates have been observed to be even faster in cyclohexane than in chlorobenzene: Landini, D.; Maia, A.; Montanari, F. *Nouv. J. Chim.* **1979**, 575–577.

give more active catalysts, but they may also give catalysts that are too gelatinous to filter on a large scale. Even the 2% cross-linked Merrifield resin in many cases may fail the requirements for ease of filtration and suitability in flow reactors. More highly cross-linked instead of less cross-linked polymers likely will be needed. (3) In many known examples, polymer-bound phase-transfer catalysts are less active than their soluble onium salt analogues, probably because of mass-transfer and matrix-diffusion limitations on reaction rates. More active catalytic sites are needed, but the more active the catalyst, the more likely the reaction rates will be controlled by mass transfer or matrix diffusion rather than intrinsic reactivity.

Experimental Section

General Methods. All reagents were obtained commerically and used without further purification. The temperature of the oil bath used for kinetic experiments was controlled (±0.1 °C) by use of a Sargent thermonitor Model 3 (E.H. Sargent & Co.). Reaction systems were stirred by a mechanical stirrer (Con-Torque Stirrer, Eberbach Co., for speeds ≤440 rpm; T-Line Stirrer, Talboys Co., for speeds >440 rpm), a vibromixer (Model E-1, Chemapec, Inc.), or a 21-kHz ultrasonic mixer (Blackstone Ultrasonics, Inc., Sheffield, PA, Model SS-2A). Reaction mixtures were analyzed by GLC on a Hewlett-Packard Model 5840A thermal conductivity instrument with a 6 ft × 0.125 in. column of 5% Carbowax 20 M on Gas-Chrom Q at 140 °C.

Poly(styrene-*co*-chloromethylstyrene), 2% Divinylbenzene Cross-linked. A solution of 1.35 g of gelatin, 12.3 g of poly(diallyldimethylammonium chloride) (Calgon Corp., Cat-Floc T), and 5.1 g of boric acid in 450 g of water was adjusted to pH 10.0 with 25% aqueous sodium hydroxide and added to a 1000-mL round-bottom flask fitted with reflux condenser, mechanical stirrer, and thermocouple connected to a proportional temperature controller (Love Controls Corp., Model 49). A solution of 214 g of styrene (Aldrich), 75 g of chloromethylstyrene (Dow, 64:40 meta/para), 10.9 g of technical 55% divinylbenzene (Polysciences), and 1.5 g of azobisisobutyronitrile (Aldrich) was added. No attempt was made to remove polymerization inhibitors from the monomers. The flask was purged with nitrogen for 30 min, and a nitrogen atmosphere was maintained throughout polymerization. The stirrer had a curved blade whose tip-to-tip distance is 80 mm. It was positioned in the quiet mixture with most of the blade in the lower aqueous phase. The stirrer was driven by a Model 7225 Con-Torque motor (Eberbach Corp., Ann Arbor, MI) with a clutch capable of maintaining stirring speed at ±5 rpm in the range 0–400 rpm. Stirring was started at room temperature. The size of the orgainic droplets suspended in water can be determined by sampling the mixture and examining it under a microscope. If smaller droplets are desired, the stirring speed can be increased. Stirring speed in this preparation was 305 rpm. Provided no breakage of polymer spheres occurs, the size of droplets corresponds with the size of the cross-linked product after the decrease in volume during polymerization is taken into account. After droplet size was established, the mixture was heated with stirring to 70 ± 1 °C for 17 h. Insoluble polymer was collected on sieves and washed thoroughly with water. Volumes of wet polymer collected were 115 mL on 60-mesh, 182 mL on 100-mesh, 65 mL on 200-mesh, and 9 mL on 325-mesh sieves. All of the other copolymers were prepared by the same procedure with minor changes. Smaller particles sizes were obtained by faster stirring and by addition of 0.3–1.2 mM sodium dodecylbenzenesulfonate to the starting aqueous phase. Smaller particles were isolated by using a 400-mesh sieve and a Corning fine-porosity (4–5.5 μm) fritted glass funnel.

Polymer-Bound Benzyltri-*n*-butylphosphonium Chloride. A mixture of 10.0 g (16.4 mmol of Cl) of poly(styrene-*co*-chloromethylstyrene) and 1.5 molar equiv of tri-*n*-butylphosphine (Aldrich) in 125 mL of 1,2-dichloropropane was heated and stirred mechanically under nitrogen at reflux for 16 h. The polymer was filtered, washed with technical methanol, acetone, and anhydrous methanol, and dried under vacuum at 85 °C to yield 13.1 g of catalyst. Chloride ion content was determined as follows. A 0.2-g sample of resin was held in 4 mL of *N*,*N*-dimethylformamide for 0.5 h, and 4 mL of concentrated aqueous HNO_3 was added. After 2 h the mixture was diluted with 100 mL of water and titrated by the Volhard method. Chloride contents were 0.96–1.17 mequiv/g (79–95% quaternization).

Polymer-Bound Benzyltrimethylammonium Chloride. A mixture of 10.0 g (16.4 mmol of Cl) of poly(styrene-*co*-chloromethylstyrene) and 150 mL of 75:25 (v/v) CH_2Cl_2/CH_3OH was stirred mechanically at 5–10 °C for 30 min in a flask fitted with dry-ice condenser. Condensed trimethylamine (4 mL, 40 mmol) was added all at once, and the mixture was stirred 3 h at room temperature. The polymer was isolated, washed, dried, and analyzed for Cl^- as described for the phosphonium catalysts. Chloride contents were 1.26–1.42 mequiv/g (84–95% quaternization).

Table VI. Data from a Fast Kinetic Run, MT-451B[a]

time, min[b]	$[RBr]/[RBr]_0$, % (av)[c]	Δt, min	k_{obsd}, s^{-1} [d]	
5	88.87, 88.82 (88.84)			
		10	38.35	37.48
15	70.54, 70.61 (70.58)			
		20	36.60	
25	57.46, 57.07 (57.26)			
		30	35.35	
35	47.15, 46.89 (47.02)			
		45	33.74	
50	35.66, 35.80 (35.73)			
		65	32.31	
70	25.14, 25.25 (25.20)			

[a] Reaction mixture contained 9.8 g of NaCN, 30 mL of H_2O, 20 mL of toluene, 0.5464 g of *o*-dichlorobenzene (GC standard), 0.396 g of −400-mesh 2% cross-linked benzyltri-*n*-butylphosphonium chloride catalyst containing 1.01 mequiv of Cl/g (0.400 mmol), and 3.5 mL of 1-bromooctane (20.0 mmol). Mixture was stirred at 600 rpm at 90 °C. [b] Mixture excluding 1-bromooctane was conditioned 60 m in at 90 °C. 1-Bromooctane was added at $t = 0$. [c] Duplicate GLC analyses of 0.1-mL samples of organic phase. [d] $k_{obsd} = (1/\Delta t) \ln([RBr]_0/[RBr]_t)$, where $[RBr]_0$ is the amount of RBr remaining at the first data point.

Table VII. Data from a Slow Kinetic Run, MT-468B[a]

time, min	$[RBr]/[RBr]_0$, % (av)	Δt, min	k_{obsd}, s^{-1}	
10	94.08, 94.10 (94.09)			
		20	9.20	9.12
30	84.25, 84.25 (84.25)			
		40	9.04	
50	75.69, 75.77 (75.73)			
		60	8.93	
70	68.23, 68.23 (68.23)			
		80	8.75	
90	61.76, 61.87 (61.81)			
		110	8.63	
120	53.23, 53.26 (53.24)			

[a] Reaction mixture contents were the same as in Table VI except 0.360 g of −100+200 mesh 10% cross-linked benzyltri-*n*-butylphosphonium chloride catalyst, 1.11 mequiv of Cl/g, was used (0.400 mmol). Mixture was stirred at 600 rpm at 90 °C. For further details, see footnotes in Table VI.

Kinetics. Cyanide displacement reactions were studied between 50 and 90 °C. In a typical run, a 100-mL three-neck flask was charged with 0.02 molar equiv of the catalyst (based on 1-bromooctane), 20 mL of toluene, 9.8 g (0.20 mol) of sodium cyanide, 30 mL of water, and 0.5 g of *o*-dichlorobenzene or naphthalene (internal standard for GLC). The mixture was stirred mechanically at 100 rpm with a standard 45 × 18 mm curved Teflon blade for 60 min to condition the catalyst. The stirring speed, which was measured by using a tachometer (James G. Biddle Co., Plymouth Meeting, PA) or a strobe light, was increased, 1-bromooctane (Aldrich, 0.02 mol) was added at zero time, and 0.1-mL samples of the organic phase were analyzed periodically by GLC. Stirring was stopped 10–15 s each time for sampling. Every GLC analysis was done twice, and average values were used in calculations. Each run consisted of six samples taken over periods ranging from 50 to 240 min (25–80% conversion of 1-bromooctane to 1-cyanooctane in the final sample), using phosphonium catalysts, or from 3 to 4 h (5–25% conversion in the final sample), using ammonium catalysts. Typical data from slow and fast runs using phosphonium catalysts are in Table VI and VII. In all runs using phosphonium catalysts, k_{obsd} decreased noticeably with time, and an average of the first two calculated values was taken as k_{obsd}. All phosphonium ion catalysis data in the figures and tables are initial rate constants. No deviations from pseudo-first-order kinetics were observed with benzyltrimethylammonium ion catalysts. Estimated random errors in k_{obsd} are ±5% for mechanically stirred reactions and ±10% for vibromixed or ultrasonically mixed reactions. In a few kinetic runs, some of the catalyst splashed and stuck onto the upper wall of the flask out of contact with liquid. Such runs were discarded.

Control Experiments. Reaction rates were slower when the catalyst was conditioned at 90 °C for 2 h than when the catalyst was conditioned 1 h because of slow decomposition of the benzyltri-*n*-butylphosphonium ions. For example, one pseudo-first-order rate constant changed from 11.0×10^{-5} s^{-1} to 8.7×10^{-5} s^{-1}. In all experiments reported in this paper, exactly 1 h was used as the standard conditioning time.

A 2% cross-linked −60+100 mesh benzyltri-*n*-butylphosphonium catalyst was recovered after 3-h reaction time and washed with a large excess of aqueous NaCl, water, and methanol. The recovered catalyst compared with the original catalyst gave a decrease in k_{obsd} from 9.2×10^{-5} s^{-1} to 6.3×10^{-5} s^{-1} and had a decrease in its chloride analysis from 1.10 to 0.97 mequiv/g.

In the absence of catalyst, <0.1% conversion was observed in 5 h with turbulent mixing (vibromixer).

Distribution of 1-Bromooctane between Catalyst and Liquid Phases. A 2% cross-linked benzyltri-*n*-butylphosphonium catalyst was added to a mixture of 15 mL of water, 4.9 g of NaCN, 5 mL of toluene, and 1.8 mL of bromooctane. After the mixture had been stirred for 2 h at room temperature, the catalyst was filtered in a small fritted tube, and excess liquids were removed by centrifugation for 30 min. The organic materials absorbed in the catalyst were extracted with 3 × 2.5 mL of CH_2Cl_2. The combined extract was analyzed by GLC (*o*-dichlorobenzene was used as an internal standard) as $(C_8H_{17}Br + C_8H_{17}CN)$/toluene = 0.183 compared with $(C_8H_{17}Br)$/toluene = 0.174 in the original solution. In similar experiments, in the absence of aqueous NaCN the distribution of 1-bromooctane was the same.

Swelling of Catalyst. Dry catalyst was weighed into a tared fritted tube. The catalyst was soaked at room temperature for 2 h in toluene or chlorobenzene or for 12 h in decane. Excess liquid was removed by centrifugation. The tube was weighed after 5, 10, 25, and 120 min. The weight of imbibed solvent was taken as the nearly constant value reached after 5 or 10 min. Swelling in water was determined by swelling the catalyst in methanol and washing out the methanol with 8–10 portions of water before centrifugation. Volume ratios were calculated by assuming the polymer density was 1.06 g/mL (vs. 1.04–1.065 g/mL for amorphous polystyrene) and assuming the densities of the solvent and polymer components of the gels were the same as those of pure solvent and pure polymer. Some of the measurements were confirmed by adding 2 mL of dry polymer to a 10-mL graduated cylinder, swelling in solvent for ≥12 h, and measuring the swollen volume. Data in Table II are considered reliable to ±0.2 or ±10%, whichever is smaller.

Acknowledgment. This research was supported by an Oklahoma State University Presidential Challenge Grant. T. Balakrishnan, Margaret Bernard, Jeanne Lee, and Saada Yacoub made experimental contributions. Professors Billy Crynes and Gil Mains provided some critical insight on mass transfer and diffusion phenomena.

Mechanisms of Polymer-Supported Catalysis. 2. Reaction of Benzyl Bromide with Aqueous Sodium Cyanide Catalyzed by Polystyrene-Bound Onium Ions

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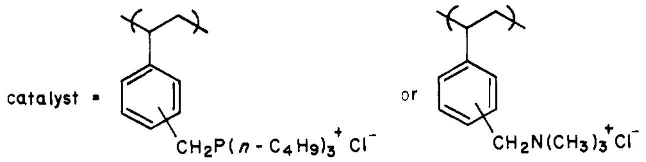
Abstract: Rates of reaction of benzyl bromide in toluene with aqueous sodium cyanide in triphase mixtures with polystyrene-supported benzyltrimethylammonium and benzyltri-*n*-butylphosphonium ions as phase-transfer catalysts depend upon mechanical stirring speed, catalyst particle size, and percent of cross-linking of the polymer support. Increases in stirring speed increase reaction rates up to a maximum at about 600 rpm. Decreases in particle size increase reaction rates. Increases in polymer cross-linking decrease reaction rates. Apparent activation energies with benzyltrimethylammonium ion catalysts are 12–15 kcal/mol at 70–90 °C. Rates of reaction of benzyl bromide, benzyl chloride, 1-bromooctane, and 1-bromohexadecane all are affected differently by variations in catalyst structure, particle size, and cross-linking. The results are discussed in terms of mass transfer, intraparticle diffusion, and intrinsic reactivity limitations on reaction rates. Slow intraparticle diffusion reduces the reactivity differences between benzyl bromide and 1-bromooctane and between benzyl bromide and benzyl chloride and causes 1-bromohexadecane to react much slower than 1-bromooctane.

Polymer-supported quaternary ammonium and phosphonium ions are phase-transfer catalysts for reactions between water-soluble salts and water-insoluble organic substrates. When the polymer is insoluble, the reaction mixture is triphase, and the catalyst can be separated from the reaction products by simple filtration.[2] Ease of separation in batch reactions, suitability for use in flow reactors, and reuse of the catalyst make polymer-supported catalysts attractive for new industrial chemical processes.

One drawback to polymer-supported catalysts is that their activity may be substantially lower than that of soluble catalysts. Detailed investigation of the experimental parameters that affect the triphase reaction of 1-bromooctane with aqueous sodium cyanide catalyzed by polystyrene-bound benzyltri-*n*-butylphosphonium and benzyltrimethylammonium ions showed that the structure of the active site, the method of stirring the triphase mixture, the particle size of the catalyst, the degree of cross-linking of the polymer support, and the solvent all affect the rate of reaction.[3] This paper reports how the intrinsic reactivity and the molecular size of the organic substrate are interrelated with these same experimental parameters in triphase reactions of benzyl bromide, benzyl chloride, 1-bromooctane, and 1-bromohexadecane with aqueous sodium cyanide.

$$RX + NaCN(aq) \longrightarrow RCN + NaX(aq)$$



Results

Catalyst Preparation. Poly(styrene-*co*-chloromethylstyrene)s containing 25 wt % chloromethylstyrenes and cross-linked with 2–10 wt % divinylbenzene were prepared by suspension copolymerization. The spherical bead polymers were sieved into −60+100 −100+200, −200+325, −325+400, and −400 mesh

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(2) For a review, see Regen, S. L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 421–429.

(3) M. Tomoi and W. T. Ford, preceding paper in this issue.