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.

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

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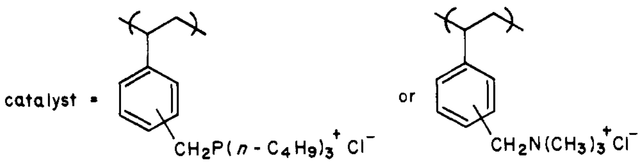
Abstract: Rates of reaction of benzyl bromide in toluene with aqueous sodium cyanide in triphase mixtures with polystyrene-supported benzyltrimethylammonium and benzyltri-*n*-butylphosphonium ions as phase-transfer catalysts depend upon mechanical stirring speed, catalyst particle size, and percent of 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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[1] On leave 1979–1980 from the Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Yokohama 240, Japan.

[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.

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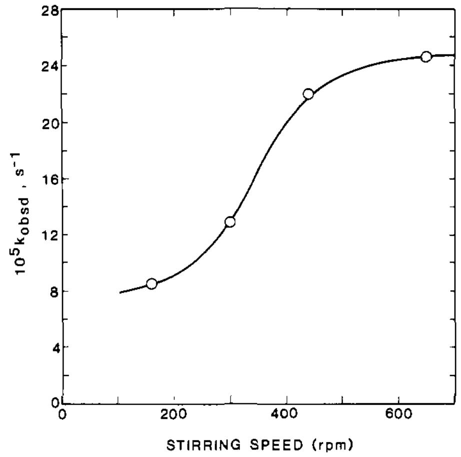

Figure 1. Dependence of k_{obsd} on mechanical stirring speed for reaction of benzyl bromide in toluene with aqueous sodium cyanide at 90 °C catalyzed by 1 mol % of -60+100 mesh 2% cross-linked polystyrene-supported benzyltrimethylammonium ion.

fractions. Treatments with tri-*n*-butylphosphine and with trimethylamine produced the quaternary onium salts, whose chloride ion contents were 0.96–1.17 mequiv of Cl^-/g (79–95% quaternized) for benzyltri-*n*-butylphosphonium catalysts and 1.26–1.42 mequiv of Cl^-/g (84–95% quaternized) for benzyltrimethylammonium catalysts. These analyses correspond to 14–18% of the polystyrene rings substituted with phosphonium ions or 16–18% of rings substituted with ammonium ions.

Rate Measurements. Phase-transfer-catalyzed reactions were conducted in 100-mL round-bottom flasks with mechanical stirring, rather than in the semi-micro flasks or test tubes with magnetic stirring as reported in similar kinetic studies in other laboratories.[4] This method has two advantages and one disadvantage. Magnetic stirring often pulverizes spherical particles of cross-linked polystyrenes to a fine powder. Since reaction rates may depend on particle size, integrity of the polymer beads must be maintained during kinetic measurements. All of the catalysts recovered from reaction mixtures were examined under a microscope and found to contain >90% of intact spherical particles. The second advantage is that a mechanically stirred mixture more closely resembles a mixture in a stirred tank reactor than does a magnetically stirred mixture. The disadvantage is that our reactions require 200–400 mg of catalyst per experiment compared with the 10–15 mg used elsewhere.[4] This makes it difficult to do many experiments with more precious catalysts. We chose to use only catalysts that can be prepared quickly on a large scale, so that we could survey the effects of a wide variety of experimental parameters on reaction rates.

Kinetic measurements were conducted by mixing all reaction components except the alkyl halide at room temperature, heating at the desired temperature for 60 min, adding the alkyl halide, and sampling the organic phase of the triphase mixture periodically. Contents of the alkyl halide and alkyl cyanide were determined by gas chromatography. All reactions were conducted with 10 molar equiv of sodium cyanide per alkyl halide and 0–2 mol % onium sites in the catalyst, based on alkyl halide. The excess sodium cyanide provided pseudo-first-order conditions. Although each kinetic run consisted of six data points, only initial rate constants are reported. They were calculated from three data points in the first 8–25% conversion. In slower reactions there was competitive slow decomposition of the benzyltri-*n*-butylphosphonium ions in the catalysts which caused decreases in observed rate constants with time.[3] Initial rate constants provided the best possible comparisons of the many experimental parameters studied. No decomposition was observed with the benzyltri-

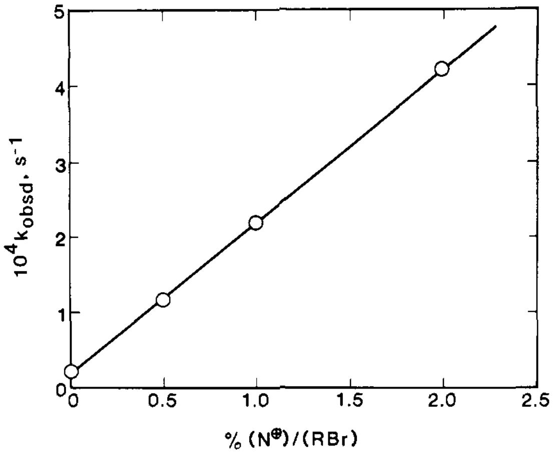

Figure 2. Dependence of k_{obsd} on mol % of 2% cross-linked -60+100 mesh benzyltrimethylammonium ion catalyst for reaction of benzyl bromide in toluene with aqueous sodium cyanide at 90 °C. Stirring speed is 420–440 rpm.

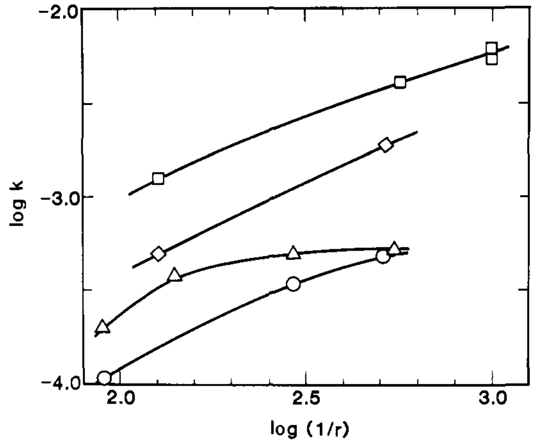

Figure 3. Dependence of rate constants on catalyst mean particle size for reaction of benzyl bromide in toluene with aqueous sodium cyanide at 90 °C: (△) benzyltrimethylammonium ion on 2% cross-linked support; (○) benzyltrimethylammonium ion, 10% cross-linked; (□) benzyltri-*n*-butylphosphonium ion, 2% cross-linked; (◇) benzyltri-*n*-butylphosphonium ion, 10% cross-linked. Ammonium ion catalysts are used at 1 mol % with 420–430-rpm stirring, and rate constants are $k_{cat} = k_{obsd} - k_0$ in s^{-1} (see text). Phosphonium ion catalysts are used at 2 mol % with 600–650-rpm stirring. Rate constants shown are $k_{obsd}/2$ (s^{-1}) for comparison of data with ammonium catalyst results.

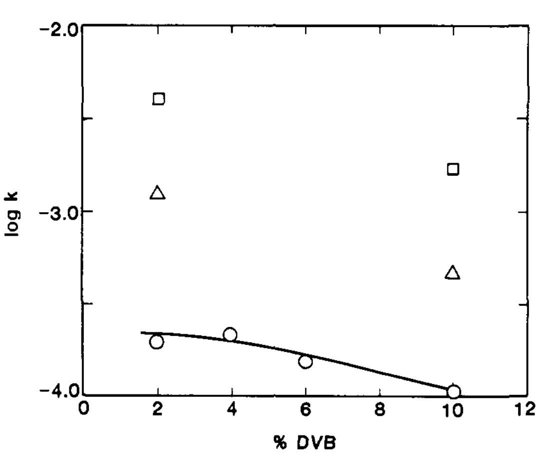

Figure 4. Dependence of rate constants on degree of cross-linking for reaction of benzyl bromide with aqueous sodium cyanide at 90 °C: (○) benzyltrimethylammonium ion, 1 mol %, 420–430-rpm stirring, -60+100 mesh, $k_{cat} = k_{obsd} - k_0$ (s^{-1}); (△) benzyltri-*n*-butylphosphonium ion, 1 mol %, 600–650 rpm, -100+200 mesh, k_{obsd} (s^{-1}); (□) benzyltri-*n*-butylphosphonium ion, 1 mol %, 600–650 rpm, -325+400 mesh, k_{obsd} (s^{-1}).

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(4) (a) Regen, S. L. *J. Am. Chem. Soc.* **1976**, *98*, 6270–6274; (b) Molinari, H.; Montanari, F.; Quici, S.; Tundo, P. *J. Am. Chem. Soc.* **1979**, *101*, 3920–3927; (c) Regen, S. L.; Besse, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 4059–4063.

Table I. Influence of Particle Size and Degree of Cross-linking of Benzyltrimethylammonium Catalysts on Activation Parameters for Reaction of Benzyl Bromide with Aqueous Sodium Cyanide[a]

particle size, mesh	% DVB	E_{app},[b] kcal/mol	$\Delta S^{\ddagger}$,[c] cal deg^{-1} mol^{-1}
	no catalyst	12.1	−46.8
−60 + 100	2	15.3	−33.4
−325 + 400	2	13.0	−37.9
−60 + 100	10	12.5	−42.6
−325 + 400	10	12.6	−39.4
−60 + 100	2	21.1[d]	−22.6[d]

[a] Experimental conditions: toluene solvent, 1 mol % catalyst, 430–440-rpm stirring. [b] Arrhenius activation energy. [c] At 80 °C. [d] Reaction of 1-bromooctane with sodium cyanide.

Table II. Dependence of Reaction Rates in Toluene at 90 °C on Substrate Structure

catalyst		10^5k_{obsd}, s^{-1}			
% DVB	size, mesh	n-$C_8H_{17}Br$[a]	n-$C_{16}H_{33}Br$[a]	$C_6H_5CH_2Br$[b]	$C_6H_5CH_2Cl$[a]
Benzyltri-*n*-butylphosphonium Catalysts[c]					
2	−100 + 200	21		125	
2	−200 + 325	31	13		
2	−325 + 400	38	16	400	
2	−400	40	17	580	
10	−100 + 200	9		47	
10	−325 + 400	26		170	
Benzyltrimethylammonium Catalysts[d]					
2	−60 + 100	1.4	0.21	44	5.9
2	−325 + 400	1.4	0.52	112	6.1
10	−60 + 100	1.0		26	6.3
10	−325 + 400	1.8		99	7.8

[a] 2.0 mol % catalyst. [b] 0.5, 1.0, or 2.0 mol % catalyst. Rate constants are normalized to those for 2.0% catalyst, assuming k_{obsd} is directly proportional to catalyst concentration. [c] 600–650-rpm mechanical stirring. [d] 420–440-rpm mechanical stirring.

Table III. Effects of Experimental Parameters on Rate-Limiting Processes

process	stirring speed	particle size	degree of cross-linking
mass transfer	dependent	rate inversely proportional to radius	independent
matrix diffusion and intrinsic reactivity	independent	dependent	dependent
intrinsic reactivity	independent	independent	uncertain

methylammonium ion catalysts.

Benzyl Halides. Effects of stirring speed, amount of catalyst, particle size of catalyst, degree of catalyst crosslinking, and catalyst structure on rates of reaction between benzyl bromide in toluene and aqueous sodium cyanide are in Figures 1–4. The rate increases with stirring speed up to a limit at ~600 rpm with −60+100 mesh ammonium catalyst. Most other experiments were conducted at 420–430 rpm, which gives rate constants no more than 10–12% smaller than the value that would be obtained with 600-rpm stirring. (Stirring effects on k_{obsd} are greatest with the largest catalyst particles. Figure 1 is based on the largest particles used in this investigation.) The rate of reaction is linearly related to the amount of catalyst used from 0 to 2 mol % ammonium catalyst (Figure 2), and there is a slow reaction even in the absence of onium ions in the polymer. An amount of 2% cross-linked poly(styrene-*co*-chloromethylstyrene) equal in weight to 1 mol % catalyst was used for "no catalyst" control experiments. Most of the benzyltrimethylammonium ion catalysis data are reported as $k_{cat} = k_{obsd} - k_0$, where k_0 is the rate constant with no onium ions in the polymer.

Figure 3 shows effects of catalyst structure and particle size on rate constants. The benzyltri-*n*-butylphosphonium ions are more active than benzyltrimethylammonium ions, and the activity difference increases as the particle size decreases when using 2% cross-linked catalyst supports. Within the practical limit of particle size attainable by suspension polymerization ($r \geq 5$ μm), maximum activity of the phosphonium catalysts for the reaction of benzyl bromide with aqueous sodium cyanide could not be achieved. The rate constants with the 2% cross-linked ammonium catalyst reach a maximum value when $1/r \geq 500$ cm^{-1} ($r \leq 20$ μm). Available data for the 10% cross-linked ammonium catalyst indicate that the maximum rate is not reached when $1/r = 500$ cm^{-1}.

Figure 4 shows decreases in rate constants with increased cross-linking for −60+100 mesh ammonium catalyst and −100+200 and −325+400 mesh phosphonium catalysts. Comparison with Figure 3 suggests, however, that there would be little or no dependence of rate constants on percent of cross-linking of the ammonium catalysts if −325+400 mesh or smaller particles were used.

Temperature dependences at 70–90 °C of rates of reaction for reactions of benzyl bromide with aqueous sodium cyanide, using benzyltrimethylammonium ion catalysts of various particle sizes and cross-linking, are in Table I. Data for 1-bromooctane, a much less active substrate, are included for comparison.

Comparisons of Alkyl Halides. Table II reports rate constants for reactions of sodium cyanide with alkyl halides in toluene at 90 °C. With all catalysts employed, the reactivity order is benzyl bromide > benzyl chloride > 1-bromooctane > 1-bromohexadecane. Rates depend upon catalyst particle size except for the reactions of 1-bromooctane and benzyl chloride catalyzed by benzyltrimethylammonium ions. All of the rates are affected by the degree of polymer cross-linking.

Discussion

Rates of reactions in heterogeneous catalysis may be limited by (1) mass transfer of reactant from bulk liquid to the surface of the catalyst, (2) intraparticle diffusion of the reactant to an active site, (3) intrinsic reactivity at the active site, (4) intraparticle diffusion or mass transfer of the product to the bulk liquid.[5,6] Reactions between alkyl halides and cyanide ion catalyzed by anion-exchange resins could be limited by mass transfer or intraparticle diffusion of either the alkyl halide or the cyanide ion. All of the experiments here used 10 molar equiv of cyanide ion per alkyl halide. Observed first-order rate constants decreased slowly with time with benzyltri-*n*-butylphosphonium ion catalysts. Such deviations did not occur with the benzyltrimethylammonium ion catalysts. The decreases in rate with phosphonium catalysts could be due either to retention of bromide ion and depletion of the cyanide ion in the ion-exchange sites of the catalyst or to decomposition of benzyltri-*n*-butylphosphonium ions. Evidence in the accompanying paper on reactions of 1-bromooctane with cyanide ion indicates that catalyst decomposition is responsible.[3] Therefore, ion exchange of bromide for cyanide is not a rate-limiting factor.

In each reaction the product alkyl cyanide is almost the same molecular size as the reactant alkyl bromide. Reactant and product should have nearly equal diffusivities. The chemical reactions are irreversible. Mass transfer and intraparticle diffusion of the product should have little or no effect on reaction rates. Therefore, the data will be discussed only in terms of mass transfer of alkyl halide, intraparticle diffusion of alkyl halide, and intrinsic reactivity.

Table III summarizes how stirring speed, particle size, and degree of cross-linking affect reaction rates controlled by mass transfer, a combination of intraparticle diffusion and intrinsic

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(5) Helfferich, F. "Ion Exchange"; McGraw-Hill: New York, 1962; Chapter 11.

(6) (a) Satterfield, C. N. "Mass Transfer in Heterogeneous Catalysis"; M.I.T. Press: Cambridge, MA, 1970; (b) Thomas, J. M.; Thomas, W. J. "Introduction to the Principles of Heterogeneous Catalysis"; Academic Press: New York, 1967, Chapter 4.

reactivity, and intrinsic reactivity alone.[5,6]

Only mass transfer is affected by stirring speed. Data for benzyl bromide in toluene with a −60+100 mesh ammonium catalyst at 90 °C in Figure 1 and for 1-bromooctane in toluene with various sizes of phosphonium catalysts[3] indicate that at 600 rpm mixing is fast enough to remove mass transfer as a rate-limiting factor. The rate of mass transfer is proportional to the surface area of the catalyst and therefore to $1/r$, where r is the particle radius.[6] The experimental conditions that lead to the greatest mass transfer control of observed reaction rates are large particles, slow stirring, and fast intrinsic reaction rates.[6] Since the data in Figure 1 were obtained with the largest particles, −60+100 mesh, and the most reactive alkyl halide, benzyl bromide, the stirring speed effects on all of the other observed reaction rates of benzyl bromide, benzyl chloride, and 1-bromooctane should be less than those shown in Figure 1. Most of the data for reaction using ammonium catalysts were obtained at 420–440-rpm stirring. In Figure 1, $k_{\text{obsd}}(400 \text{ rpm}) = 0.89\ k_{\text{obsd}}(650 \text{ rpm})$. Therefore, rate constants at 420–440 rpm with less reactive alkyl halides or smaller ammonium ion catalyst particles deviate ≤11% from rate constants that would be obtained at 650 rpm, and mass transfer is no more than a minor factor limiting rates with 420–440-rpm stirring. We shall discuss the rest of the data qualitatively in terms of intraparticle diffusivity and intrinsic reactivity, neglecting possible small contributions to rate limitation by mass transfer.

Both intraparticle diffusion and mass transfer limitations on observed rates depend on particle size. Under conditions where mass transfer contributions are negligible, the particle size dependences in Figure 3 demonstrate that a combination of intraparticle diffusion and intrinsic reactivity limits the reaction rates of benzyl bromide with both benzyltri-*n*-butylphosphonium and benzyltrimethylammonium catalysts. The data suggest that with 2% cross-linked ammonium ion catalyst, one might attain conditions where only intrinsic reactivity limits the reaction rate by using smaller particles with $1/r > 500$ cm^{-1} ($r < 20\ \mu$m). This small particle size is near the lower limit attainable by suspension polymerization and near the lower limit of particles easily separated from reaction mixtures by simple filtration. In practical applications of polymer-supported phase-transfer catalysts, more active catalysts than benzyltrimethylammonium ions and more rigid, more highly cross-linked supports than one with 2% divinylbenzene are likely to be used. With such catalysts and reactions having as high intrinsic rates as benzyl bromide and cyanide ion, slow intraparticle diffusivity will slow the reaction rates. Consequently, polymer-supported catalysts should never be as active as soluble catalysts for such reactions. In cases of high reactivity, however, the ease of separation and the reuse of a heterogeneous catalyst are probably more important than its activity.

Figure 4 shows how polymer cross-linking affects the intrinsically fast reaction of benzyl bromide with cyanide ion. Increased cross-linking decreases reactant diffusivity, but the difference in observed rate constants between catalysts on 2% and 10% cross-linked supports is less than a factor of 3 in all cases. If catalyst activity is not a major consideration, the more cross-linked catalyst should be preferred because of its greater rigidity and durability in filtrations and in packed-bed reactors.

Table I shows temperature dependences of reactions of benzyl bromide and cyanide ion. Even the least active catalyst studied, a 10% cross-linked −60+100 mesh benzyltrimethylammonium catalyst, provided a rate increase of a factor of 11 over the rate of the reaction with no catalyst at 90 °C. When intraparticle diffusion strongly limits the rates of first-order irreversible reactions with a heterogeneous catalyst, the apparent activation energy approaches as a lower limit the mean of the activation energies for intraparticle diffusion and intrinsic reactivity ($E_{\text{app}} = E_{\text{diff}}/2 + E_r/2$).[5] As the rate limitation by diffusion decreases, E_{app} approaches the limit E_r, the activation energy of intrinsic reactivity. All of the catalyzed benzyl bromide reactions in Table I are cases of rate limitation by a combination of intraparticle diffusion and intrinsic reactivity. In anion-exchange resins in water, E_{diff} of monovalent anions is 4–10 kcal/mol and the entropy of diffusion is positive.[7] Similar E_{diff} values are reported for diffusion of small molecules through polymers above T_g.[8] If E_{diff} values for benzyl bromide in the cross-linked polystyrene-supported catalysts are 4–10 kcal/mol also, values of E_r must be higher than the E_{app} values of 12.5–15.3 kcal/mol. Values of E_{app} and $\Delta S^{\ddagger}$ for reactions of iodide ion with 1-bromooctane and of chloride ion with 1-decyl methanesulfonate in triphase systems with polymer-bound benzyltri-*n*-butylphosphonium ion catalysts[3b,c] are about the same as E_{app} and $\Delta S^{\ddagger}$ for reactions of cyanide ion with 1-bromooctane. For comparison, Table I includes a case of rate limitation only by intrinsic reactivity, reaction of 1-bromooctane with cyanide catalyzed by polymer-bound benzyltrimethylammonium ions. It has a much higher E_{app} and less negative $\Delta S^{\ddagger}$ than the benzyl bromide reactions. Since the faster benzyl bromide reactions should have smaller E_r values than the 1-bromooctane reaction, we estimate that their E_r values are 16–20 kcal/mol. The data indicate also that the entropies of the diffusion processes are more negative than the entropies of activation for intrinsic reactivity. The E_{app} values for the 10% cross-linked catalysts are smaller than the E_{app} values for the 2% cross-linked catalysts as expected if there is stronger limitation of observed reaction rates by diffusion in the more highly cross-linked polymers. The 2.3 kcal/mol difference in E_{app} for two different particle sizes of 2% cross-linked catalysts is an unexplained anomaly. If there should be any dependence of E_{app} on particle size, the diffusion limitation should be greater with the larger particles, and consequently E_{app} should be smaller for larger particles. This prediction is opposite to what is observed.

Data in Table II show how rates of polymer-supported phase-transfer-catalyzed reactions depend on substrate size and reactivity and on catalyst activity. With catalysts of low activity, such as the benzyltrimethylammonium ions, and less reactive small molecule substrates that can diffuse rapidly, such as 1-bromooctane and benzyl chloride, k_{obsd} does not depend on particle size, and therefore only intrinsic reactivity is rate limiting. With the same catalyst and a reactant with lower diffusivity, such as 1-bromohexadecane, k_{obsd} increases as particle size decreases, and therefore diffusion contributes to rate limitation. In the absence of diffusional limitations, 1-bromooctane and 1-bromohexadecane undergo S_N2 reactions at almost the same rate.[9] Selectivity effects due to molecular size have been reported for reactions using polystyrene-supported transition metal catalysts[10] and polystyrene-supported phase transfer catalysts,[11] but there is no evidence to tell whether intraparticle diffusion or mass transfer differences were responsible for the selectivities.

With a much more reactive substrate, benzyl bromide, and the same benzyltrimethylammonium ion catalysts, diffusivity again contributes to rate limitation. Normally benzyl bromide reacts 50 times faster than benzyl chloride and 300 times faster than 1-bromooctane in S_N2 displacements.[12] The rate differences with polymer-bound catalysts are much smaller because intraparticle diffusion slows reaction rates of benzyl bromide but not of benzyl chloride and 1-bromooctane. With the more active benzyltri-*n*-butylphosphonium ion catalysts, even lower rate ratios k(benzyl bromide)/k(1-bromooctane) are observed.

Increased cross-linking of the benzyltrimethylammonium catalysts decreases rates of reaction of benzyl bromide with cyanide ion (Table II). The 10% cross-linked ammonium catalyst is less active than the 2% cross-linked catalyst as −60+100 mesh particles but more active as −325+400 mesh particles for reactions of 1-bromooctane with cyanide ion. Slower rates in 10% than in 2%

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(7) Soldano, B. A.; Boyd, G. E. *J. Am. Chem. Soc.* **1953**, *75*, 6099–6104.

(8) (a) Stannett, V. in "Diffusion in Polymers"; Crank, J.; Park, G. S., Eds.; Academic Press: New York, **1968**; pp 41–73; (b) Fujita, H. in "Diffusion in Polymers"; Crank, J; Park, G. S., Eds.; Academic Press: New York, 1968; pp 75–105.

(9) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed; Cornell University Press: Ithaca, NY, 1969; p 432.

(10) (a) Grubbs, R. H.; Kroll, L. C. *J. Am. Chem. Soc.* **1971**, *93*, 3062–3063; (b) Regen, S. L.; Lee, D. P. *Isr. J. Chem.* **1978**, *17*, 284–286.

(11) Regen, S. L.; Nigam, A. *J. Am. Chem. Soc.* **1978**, *100*, 7773–7775.

(12) Streitwieser, Jr., A. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962; pp 13–30.

J. Am. Chem. Soc. **1981**, *103*, 3832–3837

cross-linked catalysts are explained by slower diffusion of reactant. The cases of faster rates of reaction of benzyl chloride and of 1-bromooctane with cyanide ion in a 10% cross-linked catalyst than in a 2% cross-linked catalyst are surprising. They are probably due to a microenvironmental effect on intrinsic reactivity. With the more active benzyltri-*n*-butylphosphonium catalysts, increases in reaction rates of all three alkyl bromides with decreases in catalyst particle sizes indicate that all of the rates are controlled by intraparticle diffusion and intrinsic reactivity.

The overall effects of intraparticle diffusion on reaction rates fall into two classes. If two substrates have nearly equal diffusivities, heterogeneous catalysts reduce differences in observed rates because diffusion limits the reaction rate of the more active substrate more than that of the less reactive substrate. If two substrates have nearly equal intrinsic reactivities and different diffusivities, heterogeneous catalysts give faster reaction rates with the faster diffusing species.

Conclusions

Mass transfer of reactant from bulk liquid to the catalyst surface is an important factor limiting rates of polymer-bound phase-transfer-catalyzed reactions of alkyl halides with aqueous sodium cyanide unless rapid mechanical stirring is used. In our experiments, at least 400 rpm, and preferably ≥600 rpm, is required to make rate limitation by mass transfer negligible. With use of other reaction vessels and mixing methods, the conditions required to attain reaction rates not limited by mass transfer will vary, and control experiments will be required to establish that mixing is effective enough to avoid mass transfer control. If mass transfer limitations are overcome, most rates of reactions of alkyl halides with sodium cyanide are limited by a combination of intraparticle diffusion and the intrinsic rate at the active site. Smaller catalyst particles, lower degrees of cross-linking of the polymer, less active catalysts, and less active substrates all decrease the contribution of intraparticle diffusion to rate limitation. In this study, only the reactions of 1-bromooctane and benzyl chloride using 2% cross-linked benzyltrimethylammonium ion catalysts were controlled strictly by intrinsic reactivity.

Experimental Section

All chemicals were reagent grade and were used without further purification. Catalyst preparations and analyses and kinetic procedures were the same as in the preceding paper.[3]

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Reactivity of Carbonyl Oxides. Characteristic Nucleophilic Oxygen Atom Transfer from R_2COO beside Electrophilic and Radical Reactions[1a]

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Abstract: According to a MINDO/3 calculation, carbonyl oxide H_2COO has a large contribution of zwitterionic structure **1a**, which is not altered by phenyl substituent. The dye-sensitized photooxidation of diazomethanes in CH_2Cl_2–MeOH afforded ca. 30% yield of α-methoxy hydroperoxides as product from **1a** and MeOH. Relative reactivities of various types of substrates toward the carbonyl oxide from diazofluorene and $^1O_2$ have been determined. While benzene gave phenol in a low yield, substituted benzenes such as toluene or anisole yielded products by hydrogen atom abstraction on the side chain as a major reaction. Olefins gave a rather minor amount of epoxides: the predominant reaction was C–C cleavage or allylic hydrogen abstraction. The relative reactivity with carbonyl oxide is in the order $Ph_2SO \gg Ph_2S > C{=}C >$ benzene, where C=C means α-methylstyrene. This order is in sharp contrast to the case of peroxy acid, $Ph_2S \gg Ph_2SO \gg C{=}C$, or to the order with acylperoxy radical, $C{=}C \gg Ph_2S, Ph_2SO$. The above order with carbonyl oxide indicates a nucleophilic oxygen atom transfer as a characteristic reaction; this was clearly shown by the positive ρ value of +0.26 for substituted diphenyl sulfoxides. The reactivities of various substrates revealed that another characteristic reaction is hydrogen atom abstraction as a radical, and carbonyl oxides could be regarded as a rather poor electrophilic O-transfer agent. These features may be understood by representing carbonyl oxides as a resonance hybrid of $R_2C{=}O^+{-}O^-$ (**1a**) and $R_2\dot{C}{-}O{-}\dot{O}$ (**1c**).

Oxygen-atom transfer reactions are of current interest as a model of monooxygenase enzymes.[2] Much attention has been concentrated on the reactivity of carbonyl oxides,[3] which are believed to be formed in the ozonolysis of alkenes[3] and alkynes[4] or in the direct[5] or sensitized[6] photooxidation of diazo compounds. Carbonyl oxides can transfer oxygen atom to alkanes,[7] olefins,[3b,4,8] sulfides,[9] sulfoxides,[9] and aromatic rings.[10] They are also believed to be intermediates effecting the Baeyer-Villiger reaction in the decomposition of furan endoperoxides.[11] Recently, a metal ion coordinated carbonyl oxide has been reported to lead to an effective epoxidation of olefins.[12]

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[2] G. A. Hamilton, "Molecular Mechanism of Oxygen Activation", O. Hayaishi, Ed., Academic Press, New York, 1974, p 405.

[3] (a) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **14**, 745 (1975); (b) H. Kwart and D. H. Hoffman, *J. Org. Chem.*, **31**, 419 (1966).

[4] R. E. Keay and G. A. Hamilton, *J. Am. Chem. Soc.*, **98**, 6578 (1976).

[5] (a) W. Kirmse, L. Horner, and L. Hoffman, *Justus Liebigs Ann. Chem.*, **614**, 22 (1958); (b) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **84**, 3408 (1962); (c) R. W. Murray and A. Suzui, *ibid.*, **95**, 3343 (1973).

[6] D. P. Higley and R. W. Murray, *J. Am. Chem. Soc.*, **96**, 3330 (1974).

[7] G. A. Hamilton and J. R. Giacin, giacin, *J. Am. Chem. Soc.*, **88**, 1584 (1966).

[8] T. A. Hinricks, V. Ramachandran, and R. W. Murray, *J. Am. Chem. Soc.*, **101**, 1282 (1979).

[9] (a) W. Ando, S. Kohmoto, and K. Nishizawa, *J. Chem. Soc., Chem. Commun.*, 894 (1978); (b) W. Ando, H. Miyazaki, and S. Kohmoto, *Tetrahedron Lett.*, 1317 (1979).

[10] (a) J. W. Jerina, D. M. Jerina, and B. Witkop, *Experimentia*, **28**, 1129 (1972); (b) S. K. Chaudhary, R. A. Hoyt, and R. W. Murray, *Tetrahedron Lett.*, 4235 (1976).

[11] W. Adam and A. Rodriquez, *J. Am. Chem. Soc.*, **102**, 404 (1980).

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