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The Reaction Kinetics of a Polymer-Bound Phase Transfer Catalyst in a Novel Cyclic Slurry Reactor

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A novel cyclic slurry reactor was used to study the kinetics of a phase transfer catalyzed displacement reaction between 1-bromooctane in toluene and aqueous potassium cyanide using polymer-bound tri-*n*-butylphosphine. The catalyst support was 200–400 mesh low crosslinked, low percent ring substitution chloromethylated polystyrene-divinylbenzene resin. The cyclic slurry reactor allowed the immiscible reactants to contact the catalyst sites in controlled sequential steps. Results indicated that only the catalyst in a thin shell near the particle surface was utilized.

INTRODUCTION

Liquid–liquid phase transfer catalysis (PTC) is associated with reactions between an organic reactant and another species in an aqueous medium which is immiscible with the organic phase. A classic example is the displacement reaction with 1-bromooctane and aqueous sodium cyanide (*1*).

Analogous to polymer-bound organometallic catalysts, phase transfer catalysts can take advantage of a heterogeneous catalytic system if the catalyst is attached to a solid substrate. The general area of polymer-supported catalysis is well developed. The interest stems from, among other advantages, the facilitation of the catalyst separation and recovery problem. Regen (*2–4*) modified crosslinked chloromethylated polystyrene resin with quaternary ammonium groups and found the resulting resin capable of catalyzing phase transfer reactions. These catalyzed systems, consisting of two liquid phases (aqueous and organic) and one solid phase (polymer-supported catalyst), were referred to as "triphase catalysis." The chloromethylated polystyrene resins can also be quaternized with tributylphosphine, and the phosphonium ions have proven to be more active (*2–13*). Polymer-bound crown ethers and cryptands have also been studied (*10, 12, 14*).

Several interrelating factors mask the activity of polymer-bound phase transfer catalysts. These parameters—particle size, percentage crosslinking, percentage of polymer repeat units charged with catalyst groups (percent ring substitution), solvent, mixing, etc.—have been examined quite thoroughly with polystyrene resins as the support (*18*).

From all the triphase catalytic displacement reaction results, it is established that, in general, the optimum reaction conditions would require (i) very small particles to reduce intraparticle diffusional effects, (ii) low crosslinked density to enhance solvent swelling, (iii) a good swelling solvent, and (iv) a turbulently agitated reactor to eliminate external mass transfer effects.

The triphase system is also favored by low percentage ring substitution (%RS) which governs the catalyst loading or in other words, the number of charged groups on the polymer. Generally, the lower the

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catalyst loading, the higher the catalyst efficiency. The reported observation infers that catalytic activity is associated with the lipophilicity of the resin. With increasing %RS, the resin structure becomes hydrophilic and tends to retain the aqueous phase and becomes unfavorable to the organic reactant (*13, 15–18*). On the other hand, the reaction with low %RS resins can be limited by the slow diffusion of the aqueous phase.

A common feature shared by all the polymer-supported catalysts is that they exhibit lower activity than the corresponding soluble catalysts. The more encouraging results were reported by Montanari *et al.* (*12*). Their triphase reaction rates were 43% of the soluble catalyst. Regen *et al.* (*7*) found that with a very slow reaction, in which case the diffusional resistance is not expected to be as dominant, the triphase system overall rate constant approached 75% of the soluble catalyst.

Ragaini and Saed (*19*) studied the application of a fixed bed reactor in polymer-supported PTC. The two liquid phases flowed through the fixed bed concurrently. Their result indicated severe mass transfer limitations, and the operation was even less efficient than a stirred reactor triphase system. It is apparent that unconventional methods have to be devised for further investigations of polymer-supported phase transfer catalysts.

As pointed out by Telford *et al.* (*20*), a crucial point regarding mass transport effects of immiscible phases was missing in previous analyses of triphase systems. To illustrate the concept, we consider the simple nucleophilic substitution reaction:

$$RX_{(org)} + M^+Y^-_{(aq)} \rightarrow RY_{(org)} + M^+X^-_{(aq)} \quad (1)$$

where the organic reactant is denoted by RX, M^+Y^- is the reactant in the aqueous phase, and RY is the product of the displacement reaction. The overall reaction occurs in two steps by virtue of the two immiscible phases and that the onium ion, Q^+, is chemically immobilized on a solid substrate and represents a catalyst reaction site(s), viz.:

$$M^+Y^-_{(aq)} + Q^+X^-_{(s)} = Q^+Y^-_{(s)} + M^+X^-_{(aq)} \quad (2a)$$

$$Q^+Y^-_{(s)} + RX_{(org)} \rightarrow RY_{(org)} + Q^+X^-_{(s)} \quad (2b)$$

We can interpret the ion-exchange reaction, Eq. (2a), as analogous to the adsorption step in heterogeneous catalysis. The reaction in Eq. (2b) is similar to a chemical reaction between a reactant in the bulk phase with an adsorbed species on the solid surface. The entire kinetic cycle can be conceived of as an "adsorption" (ion exchange) followed by a chemical reaction. Under conventional catalysis in which case both reactants are present in proximity in a single phase, a Langmuir–Hinshelwood type kinetic expression can be derived. However, it is not valid here since for all practical purposes the reactants are in two immiscible phases. In addition, solvents interact differently with the polymer matrix. Once the resins are swollen with one liquid phase, for example the organic solvent, the subsequent penetration of the aqueous phase and displacement of the organic phase cannot be described by a simple diffusional process (*20*). Experiments which analyzed the intraparticle liquid compositions confirmed this conjecture (*15, 21*). In addition, the respective resin contact efficiencies with, and retention times in, the organic and aqueous phases also influence the intraparticle phase structure and hence the overall catalytic activity. This information cannot be obtained easily with a triphase system.

To better understand the mechanism of polymer-supported phase transfer catalysts and the detailed kinetics of the reaction, a method needs to be devised such that the solid-bound catalyst comes in contact with the two immiscible reactants in an extremely well-defined manner. Hence, the major objective of the current project specifically attempts to design a reactor to achieve this goal. The fact that the two reactants are immiscible can actually be used to our advantage. A logical solution to well-defined phase contacting would be to decouple the ion-exchange and chemical reaction steps physically (Fig. 1). The reactor should be operated in a cyclic or periodic mode—an ion-exchange step (aqueous mix time) followed by a chemical reaction step (organic mix time). They may be separated by a phase-exchange step which is a physical constraint of the reactor operation. A preliminary investigation with a spinning basket indicated that there were severe phase displacement problems within the basket. Hence, the present work employs a cyclic slurry reactor in which the catalyst particles are suspended in one phase at a time.

The decoupling of the overall kinetic mechanism with a cyclic reactor potentially enables us to examine the effect of contacting on the catalyst activity, to test the validity of the alternating shell model (*20*), and to assess the potential for improved heterogeneous phase transfer catalyst performance.

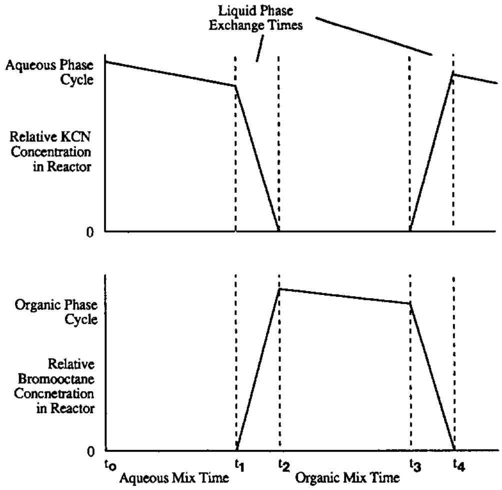

FIG. 1. Temporal relative concentration profiles of reactants over one cycle ($t_4 - t_0$) in the reactor. The aqeous mix time is ($t_1 - t_0$), and the organic mix time is ($t_3 - t_2$).

EXPERIMENTAL PROCEDURE AND APPARATUS

All chemicals and solvents were analytical reagent grade and used without further purification. Deionized water was used in the preparation of aqueous solutions. The catalyst was synthesized by chemically binding tri-*n*-butylphosphine (TBP) onto chloromethylated polystyrene beads (Bio-Rad Laboratories). The beads were 200–400 mesh and contained 1 mol% divinylbenzene (DVB) and 1.37 meq of chloromethyl groups per gram of dry resin. Details are described in Telford *et al.* (*20*).

Cyclic slurry reactor. A schematic of the reactor system is shown in Fig. 2. The entire system was constructed with glass, 316 stainless steel and Teflon. The reactor (Fig. 3) was a Pyrex tube 19 cm long, 5 cm i.d., and capped at both ends with Teflon plugs. Reactor feed was pumped in from above. The organic effluent was removed via a tube with a 1.25-cm-diameter 400 mesh screen located at the desired liquid level. The aqueous phase was removed through a sintered glass disk located on the reactor bottom. Agitation during the mix times was provided by a blunt-bladed 3.8 cm impeller at 1150 rpm. This high speed was chosen to assure that external mass transfer resistances would be minimized. Reactor temperature was monitored by a thermocouple, maintained at 70°C by a heating tape and an Omega temperature controller (Model 4001), operating through a variable autotransformer (Staco, Type 3PN1010). An Allihn condenser was used to capture escaping vapors and maintain atmospheric pressure inside the reactor.

Both reactor effluent outlets led to a pneumatically actuated three-way valve (Whitey, Assembly SS-83XTS4-153-SR). The pneumatic actuator was piloted by a quick exhaust three-way solenoid valve (Skinner, No. A3LB2127). Reactants and reactor effluent were concurrently pumped by a dual-headed peristaltic pump (Masterflex, Drive No. 7555-00, and pump heads, No. 7015) equipped with Viton tubing.

The reservoir was a 600-ml Berzelius

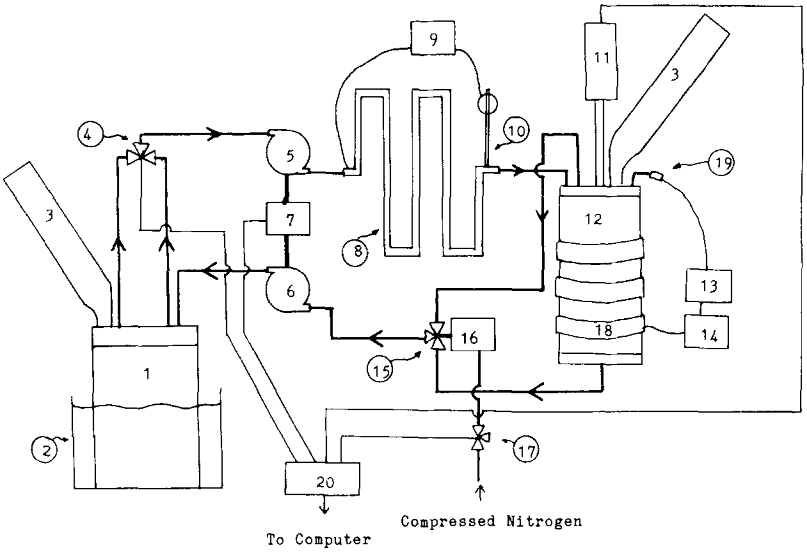

FIG. 2. Schematic of cyclic clurry reactor system. 1, reservoir; 2, cool water bath; 3, condenser; 4, three-way solenoid valve; 5, reactor feed pumphead; 6, reactor effluent pumphead; 7, pump drive; 8, preheater for reactor feed; 9, temperature controller for preheater; 10, preheater thermometer; 11, stirrer motor; 12, reactor; 13, temperature controller for reactor; 14, variable transformer; 15, three-way pneumatically actuated valve; 16, pneumatic actuator; 17, solenoid pilot valve; 18, heating tape; 19, thermocouple; 20, computer-controlled relay board.

beaker fitted with a Teflon cap. A pipe with its opening placed near the bottom operated as the aqueous outlet. The organic reactant was removed through a J-shaped tube with its opening near the air–organic interface. Reactor effluent was returned to the reservoir by a third tube, emptying its contents near the organic–aqueous interface. Samples were taken with a syringe needle through a septum. This vessel was also equipped with an Allihn condenser. Reactor feed lines, coming out of the reservoir, were controlled by a three-way solenoid valve (Kip, No. 351068-02). Valves, pump, and agitator were controlled by a time-based program run on an Apple II Plus computer with an ADALAB Data Acquisition and Control System (Interactive Microwave Inc.). The program enabled both the organic and aqueous mix (contact) times to be set, along with the time necessary for the pump to exchange the liquid phases.

Reactor operation. For each experiment, 199 ml of organic phase and 265 ml of aqueous phase were used, providing an organic phase ratio of 0.43. Before a kinetics run, 265 ml 3.2 *M* potassium cyanide, 170 ml toluene and 3.4 g quaternized resin were placed in the reservoir. The organic phase effluent port was set so that the working reactor volume would be 75 ml.

The catalyst was put through a 1-h conditioning period to induce swelling and replace the chloride ions with cyanide ions. This conditioning period was usually operated under the same control program that would be used in the actual reaction. After preconditioning, the program was halted and the reactor pumped full of the aqueous phase. It was checked that all the chloride groups present on the fresh catalyst were replaced by cyanide after the preconditioning period and confirmed by the fact that no chlorooctane was ever measured in the organic phase during the course of the reaction. To start the reaction, 29 ml 1-bromooctane was added to the reservoir and the program begun. Samples were taken from the organic phase in the reservoir at

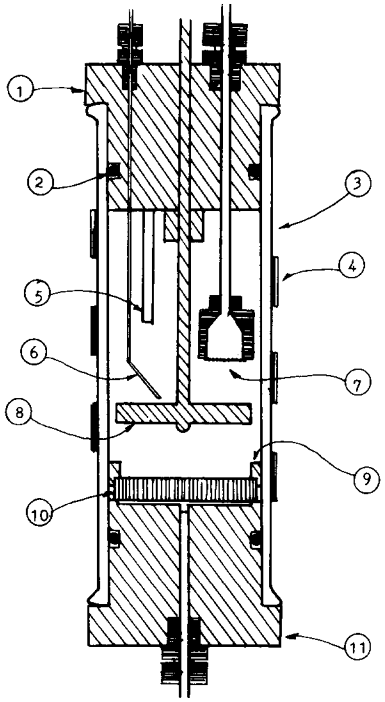

FIG. 3. Cyclic slurry reactor. 1, top Teflon cap; 2, Viton O-ring; 3, Pyrex tube; 4, heating tape; 5, entrance port; 6, thermocouple; 7, light phase exit port (with 400 mesh steel screen); 8, impeller; 9, Teflon retaining ring; 10, heavy phase exit port (sintered glass disk); 11, bottom Teflon plug.

selected intervals and were analyzed by injecting 1 μl into a Varian (Model 3700) gas chromatograph equipped with a thermal conductivity detector and a Chromosorb 101 column. Chromatograph output was monitored by a Varian CDS 111 data system.

Mixing (contact) steps were not employed in experiments performed to determine how much the liquid-phase exchange times contributed to the overall conversion of bromooctane. However, the catalyst preconditioning time did include 30 s mix (contact) times to guarantee that the catalyst was in the proper form.

Triphase catalysis experiment. To allow for comparable mixing conditions, the reactor of the cyclic slurry system was modified for triphase use (i.e., all of the reactants and catalyst were in the reactor at the same time). The feed tube port was replaced by a septum which allowed for the addition of bromooctane and for sampling.

Reactant concentrations were the same as those used in the cyclic slurry experiments. The catalyst (0.55 g) was placed in the reactor. Then 43 ml, 3.2 *M* potassium cyanide along with 27 ml of toluene were added. Agitation was initiated and the temperature set at 70°C. A conditioning time of 1 h was used. To initiate the reaction, 4.9 ml bromooctane was added. The agitator was always turned off during sample retrieval, but no longer than 30 s. Sample analysis was the same as before.

RESULTS AND DISCUSSION

We shall illustrate how the choice of cycle (phase contacting) times would influence the global reaction rate. Since both liquid phases are present during the phase-exchange periods and resemble a poorly mixed triphase system, corrections have to be made for any bromooctane conversion during phase-exchange periods. The conversion contribution during phase-exchange times was determined in a separate experiment that had no reaction mix times. Figure 4 illustrates the comparison between several cyclic slurry tests and a run with no reaction mix times. The conversion contribution *per cycle* during the phase-exchange periods was substracted from the total conversion to account for actual conversion during the organic reaction step.

$$f_{\text{mix}} = f_{\text{total}} - f_{\text{phase-exchange}}. \qquad (3)$$

The initial rate data approach is taken to evaluate the rate constant for the organic reaction (2b). This method allows us to make use of solvent displacement results (*20*) to estimate the amount of effective catalyst sites with cyanide ions. Most of the data are essentially linear over the initial 10 cycles, and is used as the basis of the initial rate analysis. Conversion of bromooctane occurs only in the organic contact period and thus only the organic mix time is used

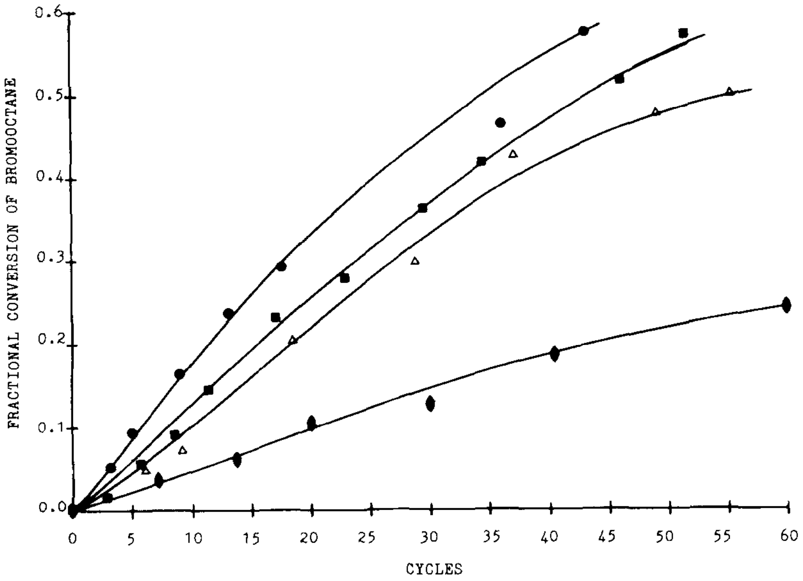

FIG. 4. Plot of the fractional conversion of bromooctane versus cycles in cyclic slurry reactor tests, and the phase-exchange-time only test. Cyclic slurry tests: (▲) Test No. 2; (■) Test No. 9; (●) Test No. 10; and (♦) phase-exchange-time only test.

to calculate the average reaction rate in the organic phase.

$$\text{Rate}_0 = -\left[\frac{d[\text{Bromooctane}]}{dt}\right]_0$$
$$= k_{2\text{obs}}[\text{QCN}]_0[\text{Bromooctane}]_0. \quad (4)$$

Here $[\text{QCN}]_0$ is the initial ionic equilibrium concentration of cyanide ion on the effective onium catalyst sites accessible to the organic reactant during a contact cycle. From a previous solvent displacement study (*20*), it is apparent that with the time scale (8 to 120 s) allowed for in the reaction mix times, $[\text{QCN}]_0$ is equivalent to only a small fraction of the total catalyst sites. In addition, we can assume that the catalyst is homogeneously dispersed throughout the gel bead. Hence, the volume fraction of the penetrating aqueous phase from the solvent displacement results can be used to estimate the fraction of effective catalyst sites, i.e., $[\text{QCN}]_0$, during a given ion-exchange mix time. Since only the solvent displacement that occurred within the initial two minutes is of any significance to the cyclic slurry reactor analysis, only the initial displacement data were needed in the analysis.

The second order rate constant should be an intrinsic rate constant if both external and intraparticle mass transport effects are eliminated. Even though the fraction of effective catalyst sites is calculated from solvent displacement tests, the time lag due to intraparticle diffusion of the organic reactant in the initial reaction cycle is not accounted for with the initial rate method. Hence, the rate is only apparent and we use $k_{2\text{obs}}$ to denote the observed second order rate constant. The observed rate constant will be influenced by the choice of organic mix times. The result is more appropriately interpreted as the average over the initial reactor cycle. As the time span over which the rate is measured (i.e., the organic mix time) decreases to zero, the resulting rate constant should approach the intrinsic value.

Table 1 summarizes the initial overall reaction rates and apparent organic phase second order rate constants. The shortest

TABLE 1

Observed Global Reaction Rate from Cyclic Slurry Reactor Tests

Test No.	Mix times (s)	Rate (g mol l^{-1} s^{-1})	$k_{2obs} \times 10^4$ ($l \cdot$ g mol^{-1} s^{-1})
A. Equal mix times for organic and aqueous phases			
	Total mix time(s)		
10	16	4.57	0.503
9	30	4.31	0.253
2	60	3.97	0.117
B. Aqueous mix times of 8 s			
	Organic mix time(s)		
10	8	4.57	0.503
13	30	1.70	0.187
C. Aqueous mix times of 30 s			
	Organic mix time(s)		
2	30	3.97	0.117
1	60	1.84	0.054
3	90	1.46	0.043
4	120	1.03	0.030
D. Organic mix times of 30 s			
	Aqueous mix time(s)		
13	8	1.70	0.187
2	30	3.94	0.117
E. Organic mix times of 90 s			
	Aqueous mix time(s)		
3	30	1.46	0.043
6	60	1.59	0.023
F. Orgaic mix times of 120 s			
	Aqueous mix time(s)		
4	30	1.03	1.030
7	60	1.13	0.017
8	90	1.51	0.015

total mix time of 16 s (8 s aqueous mixing, 8 s organic mixing) gives the highest reaction rate. As the mix times decrease, so will the depth of penetration of the liquid phases; the effective catalyst sites are restricted to a thin shell near the surface of the particle, which has minimal intraparticle diffusional effects. Hence ideally, the observed reaction rate, which has been corrected for a per effective catalyst site basis, should approach that of a intrinsic rate constant. However, further decrease of mix time is difficult with the present mechanical configuration, and further work is underway to develop improved systems.

Sections B and C of Table 1 show the rate behavior of the system in comparison among tests which had identical aqueous mix times and different organic mix times. The conversion rate of bromooctane decreased as longer organic mix times were used, regardless of the aqueous mixing times. When the results were viewed with respect to the amount of [QCN] sites available (using the solvent displacement data), the second order rate constants also exhibited a decrease with increasing organic mix times. As shown in Table 1, the organic mix (contact) times were usually longer than the aqueous contacting times. From the solvent displacement study (*20*), the organic reactant penetrates faster and deeper into the catalyst particle than the aqueous reactant in the subsequent ion-exchange step. This phenomenon results in a layer of catalyst that is complexed with bromide (from the initial cycle) and will never be regenerated to the active cyanide form. The present results conform to the alternating shell model postulated by Telford *et al.* (*20*). The decrease in rates of reaction is explained by the fact that no conversion occurs once the organic reactant diffuses past the cyanide shell and comes in contact with the inner catalyst sites with bromide ions. Excessive organic mix time will only slow down the overall observed rate.

Sections D, E, and F show comparisons among tests that had the same organic mix times but different aqueous mix times. The trends here are an increase in the rates of bromooctane conversion and a decrease in the observed rate constants with respect to increasing aqueous contacting times. The increase in the rate of reaction is explained by the longer aqueous contacting allowing for a thicker layer of renewed complexed cyanide groups to form in the particles during each cycle. The decrease in the rate constant is due to the increased diffusion resistance encountered by the organic reactant as it utilizes the deeper catalyst sites.

The fact that the reaction is favored by short contact times can be explained in another context. The volume fraction of a spherical gel bead that is accessible to reactant penetration is $1 - (r/R)^3$. The radial distance, r, is how far the penetrating liquid phase is from the center of a swollen catalyst particle of radius R. Under the assumption that the catalyst is homogeneously dispersed throughout the particle, the fraction of catalyst in the exposed volume has the same numerical value as the volume fraction. Thus the volume fraction makes its largest increase when r first starts to decrease from R (i.e., the initial contact time). The deeper the liquid reactant diffuses (smaller r), the less incremental increase in the voume of exposed catalyst. Thus the shortest contact time has the highest amount of catalyst exposed to the penetrating reactant per unit time. There is a heavy taxation to use all of the catalyst in the particle.

COMPARISON WITH TRIPHASE REACTION CONDITION

The reactor was run under triphase conditions using comparable amounts of catalyst and reactants. Comparisons are done on the pseudo-first-order rate constant basis, since we can only obtain this quantity with a triphase system. The observed pseudo-first-order rate constant of the triphase experiment was 0.178 s^{-1} mol TBP^{-1}. This value is higher than the overall pseudo-first-order rate consant of Run 10, 0.113 s^{-1} mol TBP^{-1}, after correction for the phase-exchange time periods. This result is expected, following our discussion above. The mix time of the present cyclic reactor is too long, while a triphase reactor approaches the optimal organic phase contact time. The result is a higher rate on a unit weight catalyst basis.

The triphase reaction result agrees with earlier explanations on cyclic runs with small total mix times. As the mix times decrease, the slow diffusion rate restricts the effective catalyst sites closer to the external surface of the gel beads. As a consequence, the observed reaction rate per effective catalyst site approaches that of the intrinsic value. The trade off is that the overall reaction is restricted to the catalyst sites of the periphery of the gel bead and the reaction rate is thus low. The drawback of a triphase system is that one has no easy control on the phase contact times. Hence, further work in designing a cyclic reactor capable of extremely short phase-exchange periods and utilizing well characterized thin shell catalysts is necessary to optimize a phase transfer catalytic system.

The results also explain why with a triphase system, the reaction rate is much slower than the corresponding homogeneous analogs. The alternating shell model (*20*) is a likely representation of a low %RS resin system. In systems which may allow for well controlled phase contacting, in the limit of low mix times, the reaction zone is restricted to the external surface because of diffusion limitations; the number of accessible catalyst sites is low and the overall process is limited by the organic reaction rate. With long phase contact times, the slow diffusion process of the aqueous liquid phase is obviously rate limiting. Hence, the catalyst effectiveness is low under all circumstances. With a triphase reactor, phase contacting can be adjusted via phase volume ratios and mixing. However, the relations among these operating parameters are complex.

Experiments were also performed with soluble benzyltri-*n*-butylphosphonium salt. The reaction rates obtained in the displacement reaction on bromooctane were found to be lower than those obtained in triphase catalysis. Visual observation revealed that the salt actually formed a third liquid phase, indicating a solubility problem in the organic phase. The result agrees with the available literature which does not list this particular phosphonium salt as being a good phase transfer catalyst. However, the result indicates the interesting point that a polymer-bound form can render a poor phase transfer catalyst functional.

CONCLUSION

A cyclic reactor is a useful device in studying polymer-supported phase transfer catalysts. By decoupling the ion-exchange and organic-reaction steps, the cyclic slurry reactor allows the observation of the organic phase reaction. The results with low

%RS resin strongly indicate that the displacement of organic liquid phase by the aqueous phase is rate limiting and regardless of the phase contact times, the effective catalyst sites are limited to a thin external shell. Mechanical limitations prohibit shorter contact times than are presently used. However, we believe that new cyclic reactor schemes can be designed that could use short contact times, avoid any transport of immiscible phases through a swollen porous matrix, and have negligible phase-exchange times.

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