

THE USE OF MACROPOROUS POLYSTYRENE-BOUND  
BENZYLTRI-N-BUTYLPHOSPHONIUM IONS  
AS TRIPHASE CATALYSTS IN A  
NUCLEOPHILIC DISPLACEMENT  
REACTION

By

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Bachelor of Science

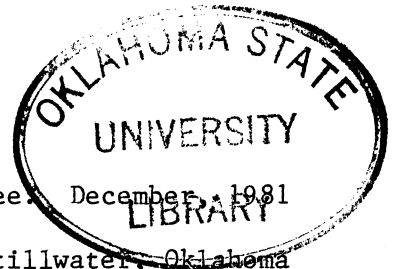
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Scope and Method of Study: The objective of this research was to find the higher activity of macroporous triphase catalysts through their higher porosities and surface areas. The rate constants of the reaction of 1-bromooctane with aqueous sodium cyanide catalyzed by a series of macroporous polystyrene-bound benzyltri-n-butylphosphonium ions were compared with those catalyzed by the analogous gel polymers. An attempt was made to understand the mechanism of catalysis.

Findings and Conclusions: The macroporous catalysts showed slightly lower activity than gel catalysts. Rates decreased as the degree of cross-linking of the macroporous polymers increased from 2% to 75%. Catalysts recovered from reaction mixtures contained more bromide than cyanide ion, indicating that slow ion exchange of the catalysts is a factor limiting the reaction rate. The slow ion transport can be explained if there is no continuous aqueous phase from the particle surface to the ion exchange sites. The failure of macroporous catalysts to improve the reaction rates is explained by failure of water to penetrate the macropores due to the lipophilic character of the catalyst surface.

ADVISER'S APPROVAL

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## CHAPTER I

### INTRODUCTION

It has been a problem for the synthetic organic chemist to carry out reactions effectively between a water-soluble reagent and a water-insoluble substrate. When a reaction is conducted as an aqueous-organic biphasic process, a very low rate is usually observed owing to the low concentration of at least one of the reactants in each phase. Rapid stirring may have an accelerating effect by increasing the interfacial contact (1, 2). Alternatively, the use of a cosolvent can increase the reaction rate by conferring homogeneity upon the system. Unfortunately, these solvents are relatively expensive, difficult to remove from products, and often undesired by-products are formed through a competing hydrolytic pathway.

A convenient solution to this problem, developed in the last few years, involves the use of so-called phase transfer catalysts (3-7). These are lipophilic quaternary ammonium or phosphonium salts, crown ethers, cryptands, or linear polyethers. In brief, the phase transfer catalyst, which is organic soluble and partially water soluble, accelerates an aqueous-organic biphasic reaction by extracting a given ionic reagent out of water and into the bulk organic phase where reaction can occur. One disadvantage is that the separation of the catalyst from the products is difficult. This becomes a problem when the relatively expensive cryptands and crown ethers are used. On the other hand, the

inexpensive ammonium and phosphonium salts sometimes form stable emulsions.

Consequently, the concept of attaching the species to a cross-linked polymer support was introduced by Regen (8, 9) in 1975. This technique of using a solid polymer-bound catalyst in an organic/aqueous mixture is called triphase catalysis. Since the solid catalysts can be separated from reaction mixtures by filtration, the product isolation and catalyst recovery are greatly simplified and improved. Also, they can be used in continuous flow systems in industry, such as in packed and fluidized bed reactors. One limitation to polymer-bound catalysts is that, in contrast to the analogous soluble phase transfer catalysts, they are less active.

After the first successful use of a polymer-supported phase transfer catalyst by Regen, investigations by others followed quickly (10, 11). Thus far, almost all the triphase catalysts introduced use cross-linked polystyrene resin and silica gel as supports. They can be divided into three categories: (1) insolubilized ammonium and phosphonium salts, (2) insolubilized crown ethers and cryptands, and (3) insolubilized cosolvents.

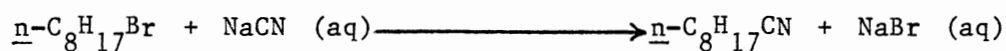
The commercial quaternary ammonium functionalized ion exchange resins are too hydrophilic to be useful for organic reactions in non-polar solvents. Regen (8) reported in 1975 that a 2% cross-linked polystyrene with only 11% ring substitution by quaternary ammonium group was a more active catalyst for reaction of cyanide ion with 1-bromooctane in a water-benzene mixture. This is the first demonstration of the feasibility of a triphase catalyst. Later work showed that the polymer-anchored phosphonium salts exhibited greater activity and thermal stability than analogous ammonium-based resins (12, 13). Silica gel

functionalized with quaternary ammonium and phosphonium groups has been used as a catalyst for nucleophilic displacements and reduction of a ketone with sodium borohydride (14-16). However, it suffers from the disadvantage of being soluble in aqueous alkali. The insolubilized crown ethers and cryptands have received limited attention thus far. They have shown significant activity for the reaction of cyanide and iodide ion with 1-bromooctane (12, 17, 18). As supported phosphonium salts, they are more useful than supported ammonium salts owing to their higher activity and thermal stability (12). To expand the utility of triphase catalysts, catalysts having cosolvent-like properties have been developed. Poly(ethylene glycol) and hexamethylphosphoramide analogues bound to cross-linked polystyrene have proved to be highly effective phase transfer catalysts (19-23).

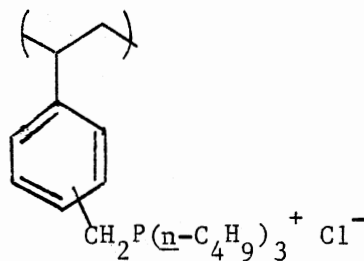
Many investigations to design more active catalysts have been reported. The structure of the ammonium or phosphonium cation has a major effect on activity in some cases (24, 25), but not in others (8, 9, 26). Brown and Jenkins (27) and Molinari et al. (28) reported that the activity of the catalyst increased as the active site was attached to the polymer matrix by long (8-39 atoms) spacer chains. The study of Reeves showed that the use of short (2 or 3 atoms) spacer chains also produced highly active catalysts (29, 30). Reaction rates decreased as the percent of cross-linking in the polystyrene increased from 2% to 10% for both microporous and macroporous catalysts (31, 32). A study of a series of polystyrene-bound phosphonium salts by Regen (33, 34) revealed that a reduced percent of ring substitution led to higher efficiency in microporous and synthetic macroporous resins. Tomoi and Ford (31, 32) found the activity of catalysts increased as the particle size decreased

up to a limit of  $1/r=1000 \text{ cm}^{-1}$ . Beyond this value, a further decrease in particle size appeared not to affect the catalytic activity. The organic solvent also affected catalytic activity: the greater its swelling power, the higher the activity (28, 32). Regen also observed the influence of aqueous salt on triphase catalytic activity (35). The catalyst activity decreased greatly as the amount of water imbibed into the catalyst increased for the reaction of chloride ion with n-decyl methanesulfonate in two phase experiments conducted with no external aqueous phase. In triphase systems, the presence of a salt reduced the water content in the catalyst through an osmotic effect and increased the activity.

Kinetic factors in heterogenous catalysis, particularly in catalysis by ion-exchange resins, have been discussed by others (36-39). Recently, a kinetic study of the reaction of 1-bromooctane with aqueous sodium cyanide catalyzed by polystyrene-bound benzyltri-n-butylphosphonium ion (32)



Catalyst =



revealed that the reaction rate can be limited by: (1) the mass transfer of the reactant from bulk liquid to the catalyst surface, (2) the diffusion of the reactant through the polymer matrix, and (3) the intrinsic reactivity at the active site. If a catalyst with the same active site structure was used in every experiment, intrinsic reactivity did

not appear to be a factor to be considered. Reaction rates depended upon the method of mixing the triphase mixture, but optimum mixing was apparently achieved at stirring speeds of 400-600 rpm. Mass transfer limitations could be overcome by employing this optimum mixing. The evidence for intraparticle diffusional limitation is that the reaction rate increases as the particle size of the catalyst decreases and the degree of cross-linking of the polymer decreases: the smaller the particle, the shorter the path to the active sites near the center of a particle and the more efficient the utilization of the active sites; the more highly cross-linked the polymer, the more tortuous the diffusion path from the particle surface to the active sites.

To overcome the slow diffusion rates, we have now examined the catalytic activity of benzyltri-n-butylphosphonium catalysts bound to macroporous polystyrene supports for the same reaction. A macroporous polymer consists of microspheres 0.01-1.0  $\mu\text{m}$  in diameter fused together into 50-1000  $\mu\text{m}$  macrospheres (40-42). It has both macropores and micropores. The macropores are the open spaces between the microspheres. The micropores are the same as those existing in the gel polymers, which are the liquid-filled spaces between polymer chains when they are in swelling solvents. Transport of a reactant molecule or an ion from the outer surface of a macroporous particle to an active site can proceed mainly through the liquid-filled macropores. This offers a shortened diffusion path from the internal surface of a macropore through the microporous polymer matrix to the active site. Consequently, if a reaction rate is limited by the intraparticle diffusion, a macroporous catalyst should provide a higher reaction rate than a gel catalyst if all other experimental variables are the same.

Through our study, the macroporous catalysts showed about equal or lower activity than the corresponding gel catalysts. Also Regen (34) reported similar results for reaction of n-decyl methanesulfonate with aqueous sodium chloride catalyzed by polystyrene-bound benzyltri-n-butylphosphonium ions, although their macroporous catalysts had BET surface areas of  $< 1 \text{ m}^2/\text{g}$ . Thus, an investigation was initiated to find out the reason for the low activity of the macroporous catalysts.

## CHAPTER II

### RESULTS

#### Macroporous Copolymer Preparation

All the macroporous polymers were synthesized by suspension copolymerization (43) of styrene, chloromethylstyrene (60/40 m/p isomers) and divinylbenzene. Copolymerization reactivity ratios for styrene ( $m_1$ ) and mixed isomers of chloromethylstyrene ( $m_2$ ) are  $r_1 = 0.72$  and  $r_2 = 1.08$ , indicating that approximately random copolymers are formed. Particles were separated with sieves after copolymerization into +40, -40+60, -60+100, -100+200, -200+325, -325+400 mesh fractions. Each batch of the polymer was examined under a microscope. Most samples consisted of opaque spherical particles. The particle size distribution and yield of each copolymer have been listed in Table I.

The only difference in the synthesis of macroporous and gel polymers is the presence or absence of an inert diluent (42), in which the monomers are soluble, but the polymer is insoluble. With added inert solvent, the cross-linked polymers precipitated as tiny particles inside each droplet during polymerization. Eventually, these particles fused together so that the final sphere was composed of many microspheres. Removal of the inert solvent left macropores of critical dimensions ranging from 50-2000 Å. The surface area of a gel polymer with the size of 500  $\mu\text{m}$  in diameter is about 0.01  $\text{m}^2/\text{g}$ , while typical macroporous polymers have surface areas of 5-1000  $\text{m}^2/\text{g}$ . The surface areas of some

TABLE I

PARTICAL SIZE DISTRIBUTION, YIELD, AND STIRRING SPEED IN MACROPOROUS POLYMER SYNTHESSES

% Cross-linking	% Chloromethyl-Styrene	Particle Distributions, wt %						Stirring Speed, rpm	Yield <sup>B</sup> %
		+40	-40+60	-60+100	-100+200	-200+325	-325		
20 <sup>a,c</sup>	25 <sup>a</sup>	0	0	17.4	63.4	14.3	5.0 <sup>e</sup>	358 <sup>f</sup>	87
20 <sup>a,c</sup>	50 <sup>a</sup>	0	0	0.2	62.6		37.2 <sup>d</sup>	350	87.4
20 <sup>a</sup>	75 <sup>a</sup>	0	13.4	21.0	34.3		31.3 <sup>d</sup>	400	74.6
50	10	25.9	36.7	29.7	6.9	0.2	0.6	231	51.8
75	10	13.3	46.5	34.3	5.6	0.3	0.3	233	37.6
50 <sup>b</sup>	10	1.1	60.2	30.8	6.9	0.2	0.8	243	85.1
75 <sup>b</sup>	10	21.7	69.1	6.1	2.9	0.1	0.1	244	85.7

<sup>a</sup> Mol % divinylbenzene and mol % chloromethylstyrene, total weight of monomers = 110 g. Others, compositions are wt %, total weight of monomers = 100 g.

<sup>b</sup> Diluent (toluene)/monomers = 1:1 (g/g). Others, diluent (4-methyl-2-pentanol)/monomers = 9:11 (g/g).

<sup>c</sup> 55% technical DVB. Others used 83% active DVB.

<sup>d</sup> -200+400 mesh size. Particles smaller than 400 mesh not collected.

<sup>e</sup> -325+400 mesh size. Particles smaller than 400 mesh not collected.

<sup>f</sup> Glass shaft stirrer with Teflon paddle was used. Others used metal stirrer with stainless steel blade.

<sup>g</sup> Yield calculated as wt % of the starting monomers isolated as cross-linked polymers.



prepared copolymers and the derived catalysts were determined by Brunauer, Emmett and Teller (BET) nitrogen adsorption method. All had values above  $1.0 \text{ m}^2/\text{g}$  which confirmed them to be macroporous polymers (Table II). The bulk densities of the macroporous polymers ( $0.3 \text{ g/ml}$ ) are shown in Table II. They are about half of those of gel polymers ( $0.65 \text{ g/ml}$  for 2% cross-linked,  $0.64 \text{ g/ml}$  for 10% cross-linked).

Increasing the stirring speed increased the amount of smaller particles except for the 20% divinylbenzene, 75% chloromethylstyrene copolymer, as shown in Table I. Although adding a surfactant, sodium dodecylbenzenesulfonate, to the aqueous phase generated smaller particles (44), the preparation of a macroporous polymer by adding this material and stirring at 300 rpm produced broken particles. By omission of the surfactant and increasing the stirring speed to 350 rpm, regular spherical particles were formed.

Since the smaller particles have higher catalytic activity (32), preparations were aimed to maximize the amount of -200+400 mesh particles. In most preparations a metal stirrer with a stainless steel blade was used. Usually at higher speed particle fragments were formed. By using a glass shaft stirrer with a Teflon paddle, more regular particles were formed. It seems that the smaller particles can be achieved by using a glass stirrer with Teflon paddle and applying higher stirring speed.

#### Catalyst Preparation

The polymer-supported catalyst was prepared by displacement of chloride with tri-n-butylphosphine or trimethylamine. Levels of ring substitution were established by analysis of the chloride contents of the catalysts (Table II). The degrees of substitution for 50% and 75%

TABLE II  
 PROPERTIES AND KINETIC ACTIVITIES OF MACROPOROUS CATALYSTS

% Cross-linking	% Chloromethylstyrene	Mesh Size	Mequiv Cl/g <sup>b</sup>	% Ring Substitution	$10^5 k_{\text{obsd}}, \text{s}^{-1} \text{e}$	% Conv. at Last Data Point	Surface Area <sup>f</sup> m <sup>2</sup> /g	Bulk Density g/ml
2	25	-100+200	1.03(1.23)	15	13.7 <sup>g</sup> (18.9) <sup>g</sup>	59	1.1	0.32
4	25	-100+200	1.01(1.23)	14	13.9 <sup>g</sup> (15.2) <sup>g</sup>	60	9.7	0.31
6	25	-100+200	0.87(1.23)	12	8.8 <sup>g</sup> (14.3) <sup>g</sup>	46	17.1	0.28
10	25	-100+200	0.81(1.23)	11	5.6 <sup>g</sup> ( 7.6) <sup>g</sup>	39	25.4	0.28
20	25	-200+400	0.59(1.23)	8	1.35	23		
20 <sup>a</sup>	50 <sup>a</sup>	-200+400	0.88(1.97)	15	5.95	46	19.4	
20 <sup>a</sup>	50 <sup>a</sup>	-200+400	0.88(1.97)	15	6.59	34	19.4	
20 <sup>a</sup>	50 <sup>a</sup>	-200+400	2.06 <sup>c</sup> (2.83)	49 <sup>c</sup>	0.32	3.1		
20 <sup>a</sup>	50 <sup>a</sup>	-200+400	0.85+0.55 <sup>d</sup>	15+9.5 <sup>d</sup>	3.44	25		
20 <sup>a</sup>	75 <sup>a</sup>	-200+400	1.38(2.46)	28	3.71	29		
20 <sup>a</sup>	75 <sup>a</sup>	-200+400	1.38(2.46)	28	4.28	32		
50	10	-40+60	0.23(0.58)	3	0.16	1.4		
75	10	-40+60	0.21(0.58)	3	0.08	1.1	588	
7	87 <sup>h</sup>	-30+40	2.24 <sup>c</sup> (2.65)	61 <sup>c</sup>	1.40	13		
Amberlyst <sup>®</sup> A-27		-20+40	2.6 <sup>c</sup>	40 <sup>c</sup>	0.00	0	46.9	0.33

<sup>a</sup> Mol % divinylbenzene and mol % chloromethylstyrene. Others, compositions are wt %.

<sup>b</sup> Values in parentheses refer to theory for complete phosphonium or ammonium ion formation.

<sup>c</sup> Benzyltrimethylammonium ion.

<sup>d</sup> 15% Benzyltri-*n*-butylphosphonium ion and 9.5% benzyltrimethylammonium ion.

<sup>e</sup> Values in parentheses refer to rate constants of the analogous gel catalysts.

<sup>f</sup> Determined by nitrogen adsorption BET method at Rohm & Haas Co.

<sup>g</sup> Determined by M. Tomoi (32).

<sup>h</sup> Rohm and Haas Co. Surface area and bulk density are from Kun, K.A.; Kunin, R. J. Polym. Sci. Part C, 1967, 16, 1457.

cross-linked polymers were very low due to the slow diffusion of reagents into the polymers. Reactions probably occurred mainly on the surface. Using a higher boiling refluxing solvent, m-xylene (B.P. 138°C), did not give any improvement. The degrees of substitution increased as the amount of tri-n-butylphosphine was increased from 1.5 molar equivalents to 5 molar equivalents and the refluxing temperature was increased to 180°C using o-dichlorobenzene as solvent (Table III).

#### Rate Measurements

Reaction rates of displacement of bromide ion from 1-bromooctane in toluene by a ten-fold excess of aqueous sodium cyanide catalyzed by macroporous polystyrene-supported benzyltri-n-butylphosphonium chloride have been listed in Table II. The dependence of reaction rate on percent divinylbenzene cross-linking for both gel and macroporous polymers has been plotted in Figure 1. All runs used 0.02 molar equivalent of catalyst. With the least active 50% and 75% cross-linked catalysts, reactions were followed to 1.4% and 1.1% conversions. For other runs 13-60% conversions were achieved at the last data points. The rate constants reported are averages calculated from 4 to 5 pairs of data points.

All experiments were performed with 400-440 rpm mechanical stirring to overcome mass transfer limitations on the rates. As the degree of cross-linking of the polymer increased, a clear decrease in reaction rate was observed. Moreover, the ammonium-based catalysts had lower activity than the phosphonium-based catalysts. The rates of reactions with macroporous catalysts appeared to be slightly lower than those with

TABLE III  
 PHOSPHONIUM SALTS FORMATION IN HIGHLY  
 CROSS-LINKED POLYMERS

% Cross-linking	Solvent	Temperature °C	Mequiv <sub>b</sub> Cl /g
50	1,2-dichloropropane	96	0.13
75	1,2-dichloropropane	96	0.14
50	<u>m</u> -xylene	138	0.13
75	<u>m</u> -xylene	138	0.11
50 <sup>a</sup>	<u>o</u> -dichlorobenzene	180	0.32
75 <sup>a</sup>	<u>o</u> -dichlorobenzene	180	0.19

<sup>a</sup> Tri-n-butylphosphine, 5.0 molar equiv. Other experiments used 1.5 molar equiv.

<sup>b</sup> Complete phosphonium salt formation corresponds to 0.58 mequiv/g.

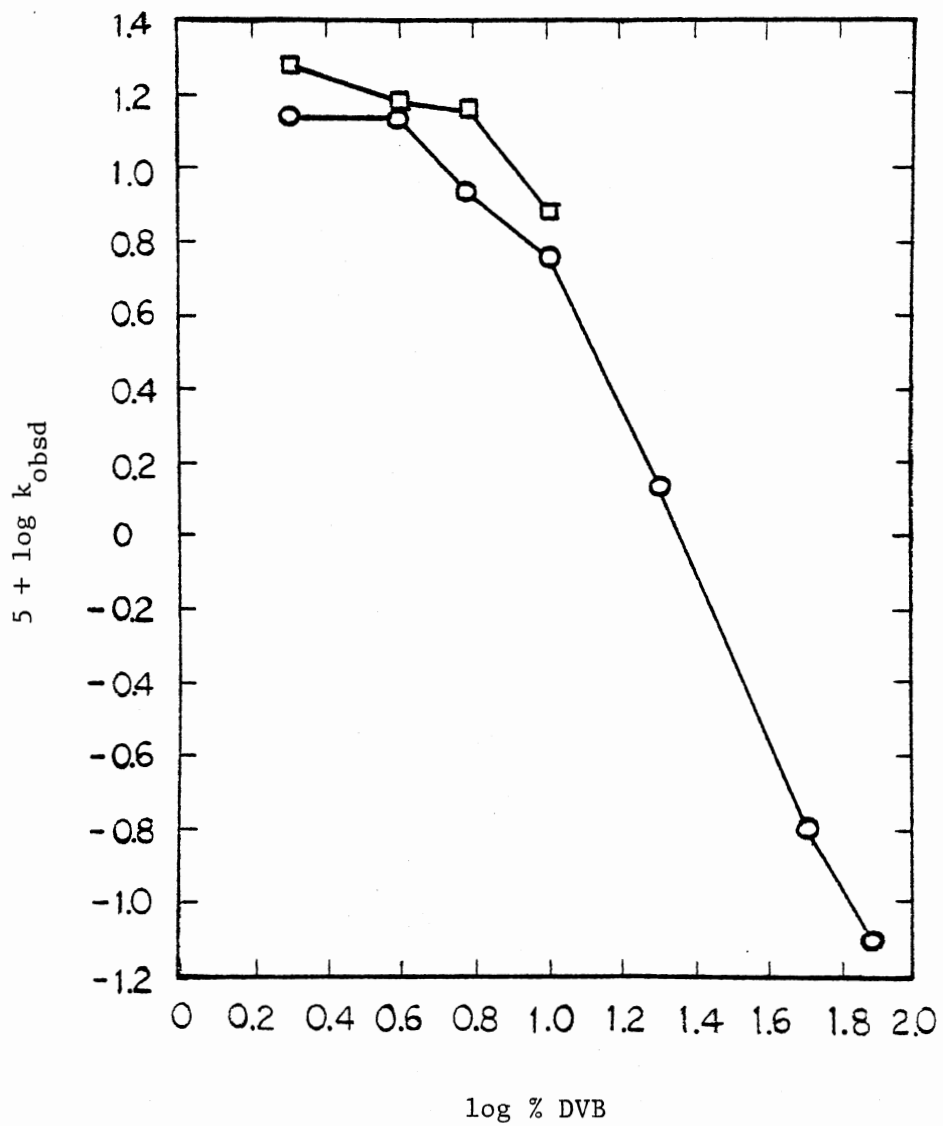


Figure 1. Dependence of  $k_{\text{obsd}}$  on Percent Cross-linker for Gel ( $\square$ ) and Macroporous ( $\circ$ ) Catalysts.

gel catalysts having the same degree of cross-linking. They are almost within experimental error of one another.

The gel and macroporous polymers having the same degree of cross-linking should have the same active site environment, so the intrinsic reactivity of cyanide ion and 1-bromooctane should be the same for both polymers. The failure of the macroporous catalysts to show higher activity than the analogous gel catalysts must be due to the slow transport of the reactants to the active sites, in spite of their increased internal surface areas.

One possible reason for slow transport is that either the aqueous or the organic phase fails to penetrate the macropores. Since the catalyst is more lipophilic than hydrophilic, the penetration of the aqueous phase must be harder. Several experiments were conducted with the 20% cross-linked, 15% ring-substituted catalyst to promote the penetration of aqueous phase. The catalyst was: (1) swollen in tetrahydrofuran (THF) before conditioning, (2) swollen in THF, and washed with water, and (3) swollen in 1,4-dioxane, and washed with water. All of the rate constants of these experiments had values  $< 1.0 \times 10^{-5} \text{ s}^{-1}$ , much less than the conventional kinetic runs. Other attempts were performed by degassing the catalyst in the presence of only the aqueous phase or in toluene only before use. Degassing in toluene provided a reaction rate the same as that of the conventional run. Degassing in aqueous phase gave a rate constant smaller than  $1.0 \times 10^{-5} \text{ s}^{-1}$ . A determination of the extent of ion exchange and the contents of the organics in the catalyst during the kinetic run should be another approach to understanding this problem.

## Bromide and Cyanide Contents in Recovered Catalysts

A series of gel and macroporous catalysts was studied for the extent of ion exchange during kinetic run. A usual kinetic run was performed. The catalyst, after partial conversion of 1-bromooctane to 1-cyanooctane, was filtered quickly through a fritted funnel. The filtration process took in 3 min or less. By comparing with the reaction time of 30-240 min after 35-86% conversion, very little ion exchange should have occurred during the time the catalyst was collected. The bromide and cyanide contents have been listed in Table IV. It shows that the catalysts contained more bromide than cyanide ion. The macroporous catalysts retained slightly less bromide ion than the gel catalysts. The ion exchange was slow for both gel and macroporous particles. Increased ratios of bromide to cyanide with increased percent of cross-linking indicated that the higher the percent of cross-linking, the slower the ion exchange rate. After 60 min of conditioning the 2% cross-linked gel catalyst retained 29% of its original chloride ion, indicating that at least 29% of the phosphonium sites were catalytically inactive.

In most catalysts the sum of bromide and cyanide ions was less than the original chloride content. The percent of active sites remaining in the recovered catalysts ranged from 54 to 106. The percent of active sites remaining was also determined by converting the 2% cross-linked gel catalyst back to its original chloride form and measuring the chloride content again.

We also attempted to determine the organic contents in the catalyst during the reaction by collecting the catalysts quickly, washing the

TABLE IV  
BROMIDE AND CYANIDE CONTENTS IN  
RECOVERED CATALYSTS

% Cross linking	Catalyst Porosity	Mequiv Cl <sup>-</sup> /g <sup>b</sup>	% Conv.	Mequiv Br <sup>-</sup> /g <sup>d</sup>	Mequiv CN <sup>-</sup> /g <sup>d</sup>	% Phosphonium Sites Remaining <sup>e</sup>
2	micro	1.12	66	0.46	0.26	65(58)
2	micro	1.12	c	0.49	0.29	71(54)
2	micro	1.12	53	0.53	0.33	79
4	micro	1.15	60	0.60	0.29	79
6	micro	1.12	74	0.72	0.28	92
10	micro	1.04	86	0.63	0.18	80
2	macro	1.03	35	0.42	0.63	106
4	macro	1.01	50	0.52	0.37	80
6	macro	0.92	35	0.45	0.48	104
10	macro	0.65	43	0.28	0.07	54
20 <sup>a</sup>	macro	1.03	65	0.55	0.19	74
2	micro	1.12	0	0.32 <sup>f</sup>	0.55	78(52)
2	micro	1.12	0	0.26 <sup>f</sup>	0.56	73(45)

<sup>a</sup> Mol % divinylbenzene, 50 mol % chloromethylstyrene.

<sup>b</sup> Others, wt % divinylbenzene, 25 wt % chloromethylstyrene.

<sup>c</sup> In starting catalyst. Estimated random error was  $\pm 0.1$  mequiv/g.

<sup>d</sup> Not measured; value is 55 calculated from reaction time.

<sup>e</sup> In recovered catalyst. Estimated random error was  $\pm 0.1$  mequiv/g.

<sup>e</sup> Determined as percent of mequiv bromide and cyanide in recovered catalyst based on mequiv chloride in starting catalyst. Values in parentheses are determined as percent of mequiv chloride regenerated with methanol/HCl based on mequiv chloride in starting catalyst. Estimated random error was  $\pm 20\%$ .

<sup>f</sup> Mequiv Cl/g.



catalyst with methanol, and determining the amount of toluene, 1-bromo-octane and 1-cyanooctane in the washings via gas chromatography. These experiments gave highly irreproducible toluene contents, probably because of variable evaporation of the toluene during isolation.

## CHAPTER III

### DISCUSSION

Previous results have shown that for a polymer-supported quaternary ammonium and phosphonium ion catalyzed reaction, mass transfer of reactants to the particle surface, intraparticle diffusion, and intrinsic reactivity were all important factors to the reaction rate (31, 32). All of the experiments in this thesis were performed under optimum mixing conditions, where mass transfer did not limit the observed reaction rate. Intrinsic reactivity influenced the reaction rate as different onium ion structures possessed different catalytic activities. To overcome the intraparticle diffusional limitation problem, we tried to use macroporous catalysts to promote the activity. Although the rates of diffusion of the reactants through the polymer matrix should be about the same for gel and macroporous resins with equal degrees of cross-linking, the macroporous resins have much greater surface area and much shorter pathways from the surface to the active sites. Rates of diffusion through the macropores should be the same as that through a quiet liquid, which is much faster than that through the cross-linked polymer network. In spite of this advantage, the macroporous catalysts did not show any improvement in the reaction rate. So further experiments were performed to obtain some mechanistic insight.

The early results from Tomoi and Ford (32) indicated that for all 2-10% cross-linked gel polystyrene supported catalysts, the intraparticle

diffusion contributed to the rate limitation. However, it did not establish whether the ion exchange (diffusion of cyanide ion from the particle surface to active sites) or the organic reactant diffusion was responsible. A ten-fold excess of cyanide ion over 1-bromooctane was used in order to make the kinetics pseudo first order, dependent only upon the overall 1-bromooctane concentration. Also, in the stirred reaction mixture both the solid catalyst particles and organic phase were suspended in the continuous aqueous phase so the particles had more complete contact with the aqueous phase than with the organic phase (32). All of these observations suggested that the diffusion of 1-bromooctane was rate-limiting. The data in Table IV shows that all of the recovered catalysts contain more bromide ion than cyanide ion. It reveals that the slow transport of cyanide ion from the concentrated aqueous solution to the active sites is at least partially responsible for limiting the reaction rates. The activity of the catalysts is limited by the number of sites in cyanide form. The loss of phosphonium sites in the catalyst is also a problem. The use of tetraalkylphosphonium ions instead of benzyltrialkylphosphonium ion should avoid the decomposition problem.

Under the phase transfer catalytic conditions the catalyst is swollen mainly by toluene. The diffusion of the bromide and cyanide ions through toluene must be slow. Recently from a study of the swelling of catalysts in the presence of sodium chloride solutions of varied concentration, Regen (45) suggested a model for the interior of the catalyst in which the aqueous phase was present in water pools around the active sites, while the organic phase was continuous through the polymer network. The slow ion transport may be due to lack of continuous aqueous phase from the particle surface to the ion exchange sites.

The determination of the bromide and cyanide contents of the recovered catalysts showed that the macroporous catalysts undergo ion exchange at about the same rate as gel catalysts in spite of the larger surface areas. This can happen only if the macropores are filled completely with organic phase rather than with water. The failure of water to penetrate the macropores may be due to the lipophilicity of the polystyrene resins. More hydrophilic polymers might provide more active catalysts.

## CHAPTER IV

### EXPERIMENTAL

#### Preparation of Poly (styrene-co-chloromethyl- styrene), 25% Divinylbenzene Cross-linked, 25% Chloromethylstyrene

In 60 mL of deionized water was dissolved 2.70 g of gelatin (pharmaceutical grade, Knox Gelatin Co.) at 50-55°C with magnetic stirring. A solution of 24.6 g of poly(diallyldimethylammonium chloride) (Calgon Corp., Cat-Floc I<sup>®</sup>) and 5.1 g of boric acid in 390 mL of deionized water was adjusted to pH 10.0 with 25% aqueous sodium hydroxide, and 0.10 g of sodium nitrite was added. The gelatin solution was mixed with the remainder of the aqueous phase. The entire mixture was added to a 1000 mL three-neck 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 35.1 g of styrene (Aldrich), 33.3 g of chloromethylstyrene (Dow, 60/40 m/p), 41.6 g of divinylbenzene (technical 55%, Polysciences), 90.0 g of 4-methyl-2-pentanol (Aldrich), and 0.55 g of azobisisobutyronitrile (Aldrich) was added. Nitrogen was swept through the flask for 30 min and a slight, positive pressure of nitrogen was maintained throughout the polymerization. A tubore glass shaft stirrer with 75 mm Teflon<sup>®</sup> paddle was used. The paddle was positioned at the organic-aqueous interface.

The stirrer was driven by a Con-torque motor (Eberbach Corp., Model 7225) with a clutch capable of maintaining speed at  $\pm 5$  rpm. The stirring speed was measured with a tachometer. Stirring was started at room temperature. The size of the droplets could be determined by stopping the stirring, sampling the mixture and examining it under a microscope. The stirring speed could be increased to obtain the desired droplet size. It was at 350 rpm in this preparation. The mixture was heated with stirring to 70°C over a period of 40-60 min. The temperature was maintained with a heating mantle on an air-driven hydraulic jack (Jack-O-Matic, I<sup>2</sup>R Corp.) connected to a temperature controller. The droplets passed through a gel point about after 60 min at 70°C. After 36 h the condenser was replaced with a distilling head and two drops of Triton CF-32 (Rohm & Haas) were added to reduce foaming. The 4-methyl-2-pentanol and any residual monomers were removed by rapid azeotropic distillation with continued stirring. More water was added to maintain the liquid level. Distillation was stopped after collection of 800 mL of organic liquid and water. The wet particles were separated into fractions with 40, 60, 100, 200, 325, and 400 mesh U.S. standard sieves. Each fraction was washed thoroughly with methanol and dried under vacuum at 60°C. Weights of dry particles were 16.7 g on 100 mesh, 60.9 g on 200 mesh, 13.7 g on 325 mesh, and 4.8 g on 400 mesh sieves (87% yield based on starting monomers). For a 100/200 mesh sample the surface area was 31 m<sup>2</sup>/g as determined by the BET nitrogen adsorption method and the pore diameter of highest probability was 0.09  $\mu$ m determined by mercury penetration porosimetry. Both the determinations were done at Rohm & Haas Co.

All of the other copolymers were prepared by the same procedure with minor changes. A metal stirrer having curved stainless steel blade with a tip-to-tip distance of 80 mm was used in other experiments. It was positioned with most of the blade in the lower aqueous phase. For the 50% and 75% cross-linked polymers 150 mL of concd HCl was added to the mixture after the distillation. The stainless stirrer was replaced with a glass stirrer with Teflon paddle before adding concd HCl. The mixture was heated at 100°C for 3 h to hydrolyze the gelatin. In an ice bath, 150 mL of 25% aq NaOH was added to the flask to reduce the acid strength to about pH = 0-1 before the washing and sieving procedures.

#### Preparation of Polystyrene-Bound Benzyltri-n- butylphosphonium Chloride

In a 250 mL three-neck round-bottom flask 10.0 g (36.2 mequiv of Cl) of poly(styrene-co-chloromethylstyrene) containing 20% divinylbenzene and 50% chloromethylstyrene was held in 125 mL of 1,2-dichloropropane for 30 min. With a syringe, 14 mL (54 mequiv) of tri-n-butylphosphine (Aldrich) was added. The mixture was heated and stirred mechanically under nitrogen at reflux for 16 h. The polymer was filtered, washed thoroughly with technical methanol, acetone, and reagent methanol, and dried under vacuum at 60°C to yield 12.2 g of catalyst. The chloride ion content was determined as follows. A 0.2 g sample was swollen in 5 mL of N,N-dimethylformamide for 2 h and 3 mL of concd aq HNO<sub>3</sub> was added. After 2 h the mixture was diluted with 100 mL of water and titrated by the Volhard method with 0.05 N AgNO<sub>3</sub>. The chloride content was 0.88 mequiv/g. Theory for complete phosphonium ion formation predicted 1.97 mequiv/g. All other catalysts were prepared by the

same procedure. For the 50% and 75% cross-linked copolymers m-xylene and o-dichlorobenzene were also used as refluxing solvents.

Some of the phosphonium salt catalysts were analyzed for surface areas by nitrogen adsorption BET method at Rohm & Haas Co. Bulk densities of some catalysts were determined by weighing 4.0 mL of the polymer in a calibrated graduated cylinder. Data are in Table II.

#### Preparation of Polystyrene-Bound Benzyltrimethylammonium Chloride

In a 250 mL three-neck round-bottom flask fitted with a dry ice condenser 10.0 g (36.2 mequiv Cl) of poly(styrene-co-chloromethylstyrene) containing 20% divinylbenzene and 50% chloromethylstyrene in 125 mL of 75/25 (v/v)  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  was stirred mechanically at 5-10°C for 30 min. Condensed trimethylamine, 9 mL (90 mequiv), was added all at once, and the mixture was stirred at room temperature for 6 h. The polymer was filtered, washed with technical methanol and reagent methanol and dried under vacuum at 60°C to yield 11.2 g of catalyst. The chloride ion content, analyzed as for the phosphonium catalysts was 2.06 mequiv/g. Theory for complete ammonium ion formation predicted 2.83 mequiv/g.

#### Kinetics

A 100 mL three-neck round-bottom flask was charged with 0.02 molar equivalent of the catalyst (based on 1-bromooctane), 20 mL of toluene, 9.8 g (0.20 mol) of sodium cyanide (Aldrich), 30 mL of deionized water, and 0.5 g of accurately weighed naphthalene (Fisher) (internal standard for GLC). The mixture was stirred mechanically (Con-Torque Stirrer,



Eberbach Co.) at 100 rpm with a standard 45 x 18 mm curved Teflon blade for 60 min at  $90.0 \pm 0.2^\circ\text{C}$  in an oil bath to condition the catalyst. The temperature of the oil bath was controlled by use of a Sargent thermometer Model 3 (E.H. Sargent & Co.). At time zero 3.5 mL (0.020 mol) of accurately weighed 1-bromooctane (Aldrich) was added, the stirring speed was increased to 400-440 rpm, and 0.2 mL samples of the organic phase were pipetted out periodically and analyzed by GLC (Hewlett-Packard, Model 5840A) on a column of 5% Carbowax 20 M on Gas-Chrom Q (6 ft x 0.125 in) in series with 5% SE-30 on Gas-Chrom Q (6 ft x 0.125 in) at  $130^\circ\text{C}$ . For each run 4-6 samples were taken over periods ranging from 110-260 min (1.1-46% conversion of 1-bromooctane to 1-cyanooctane).

The rate constant was calculated from  $k = (t_{n+1} - t_n)^{-1} \ln ([\text{RBr}]_n / [\text{RBr}]_{n+1})$  in which n and n+1 represent successive data points. It sometimes increased or decreased with time. An average of 4-5 values was taken as  $k_{\text{obsd}}$ .

#### Determinations of Bromide and Cyanide

##### Contents in Recovered Catalysts

The experiment was performed as a regular kinetic run to a degree of conversion of 35-86%, except where 0.04 molar equivalent of the catalyst was used. The organic phase was analyzed for 1-bromooctane and 1-cyanooctane by gas chromatography to establish the percent conversion. The catalyst was filtered through a medium porosity Corning glass frit (10-15  $\mu\text{m}$ ) quickly and washed with 100 mL of nitrogen-purged methanol over a period of 30 min and 100 mL of nitrogen-purged deionized water over a period of 30 min. The catalyst sample was divided into two equal parts. The first was soaked in 10 mL of N,N-dimethylformamide for 2 h,

and 20 mL of 3 N aqueous sodium nitrate was added. After 10 h the liquid was drained, and the sample was washed with 100 mL of 3 N aqueous sodium nitrate over a period of 40 min. The pH of the combined filtrate was adjusted to 1-2 by adding 6 N nitric acid, and nitrogen was purged through for 30 min to remove the liberated hydrogen cyanide (in hood). The bromide ion in the solution was determined by Volhard method. The solid was washed with 150 mL of methanol, dried under vacuum at 60°C, and weighed. The bromide contents ranged from 0.28-0.72 mequiv/g as shown in Table IV. The second half of the recovered catalyst was returned to a fresh reaction mixture containing 20 mL of toluene, 30 mL of deionized water, 1.0 g of accurately weighed 1-bromooctane, and 0.1 g of accurately weighed naphthalene. The mixture was stirred at 400 rpm at 90°C for >24 h to insure the complete conversion of cyanide ion in the catalyst to 1-cyanooctane. The organic phase was analyzed by GLC for 1-bromooctane and 1-cyanooctane. The mmol of 1-cyanooctane was calculated from the percent conversion and the weight of 1-bromooctane used. The catalyst was isolated and washed with 150 mL of methanol, dried under vacuum at 60°C, and weighed. The cyanide contents were 0.07-0.63 mequiv/g as shown in Table IV.

The 2% cross-linked gel catalyst after determining the bromide content was soaked in a mixture of 155 mL of methanol and 17 mL of concd HCl for 6 h. The solid was filtered, washed with 200 mL of methanol, and 100 mL of 3 N aqueous sodium nitrate. The chloride content in the aqueous sodium nitrate filtrate was determined by Volhard method. The same catalyst was also converted back to the chloride form after conditioning for 1 h at 90°C. The chloride contents are shown in Table IV.

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