Acknowledgment. We thank the National Science Foundation for financial support.

Appendix: Derivation of Equation 8

Except at the very lowest buffer concentrations the $k_p{}^B[B]$ and $k_{-p}{}^B[BH]$ terms in eq 4a and 4b, respectively, are dominant. This permits eq 7 to be written as

$$\frac{1}{\tau} = \frac{k_1 k_p{}^B[B]}{k_{-p}{}^B[BH] + k_1} + \frac{k_{-1} k_{-p}{}^B[BH]}{k_{-p}{}^B[BH] + k_1} \tag{15}$$

Inverting and rearranging leads to

$$\tau = \frac{k_{-p}{}^B[BH] + k_1}{k_1 k_p{}^B[B] + k_{-1} k_{-p}{}^B[BH]} \tag{16}$$

Dividing both the numerator and the denominator of eq 16 by $k_{-p}{}^B[BH]$ affords

$$\tau = \frac{1 + k_1/k_{-p}{}^B[BH]}{k_1 k_p{}^B[B]/k_{-p}{}^B[BH] + k_{-1}} \tag{17}$$

Since the relation

$$k_p{}^B[B]/k_{-p}{}^B[BH] = K_a/a_{H^+} \tag{18}$$

holds, eq 17 becomes

$$\tau_{hi} + \tau_{hi}(k_1/k_{-p}{}^B[BH]) \tag{19}$$

with τ_{hi} given by eq 9. Substituting $[B]_0 a_{H^+}/(K_a{}^B + a_{H^+})$ for $[BH]$ then affords eq 8.

References and Notes

(1) This is part 15 in the series "Intermediates in Nucleophilic Aromatic Substitution". Part 14: C. F. Bernasconi and F. Terrier, *J. Am. Chem. Soc.*, **97**, 7458 (1975).

(2) M. R. Crampton, *J. Chem. Soc., Perkin Trans. 2*, 2157 (1973).

(3) C. F. Bernasconi and R. H. de Rossi, *J. Org. Chem.*, **38**, 500 (1973).

(4) C. F. Bernasconi and H. S. Cross, *J. Org. Chem.*, **39**, 1054 (1974).

(5) M. R. Crampton and M. J. Willison, *J. Chem. Soc., Perkin Trans. 2*, 1681, 1686 (1974).

(6) M. R. Crampton and M. J. Willison, *J. Chem. Soc., Perkin Trans. 2*, 155 (1976).

(7) C. F. Bernasconi and C. L. Gehriger, *J. Am. Chem. Soc.*, **96**, 1092 (1974).

(8) For recent reviews, see (a) M. R. Crampton, *Adv. Phys. Org. Chem.*, **7**, 211 (1969); (b) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).

(9) (a) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964); (b) C. F. Bernasconi, "Relaxation Kinetics", Academic Press, New York, N.Y., 1976, Chapter 4.

(10) M.-L. Ahrens and G. Maass, *Angew. Chem., Int. Ed. Engl.*, **7**, 818 (1968).

(11) The error limits given in Table IV are standard deviations and thus do not take into account the potential source of error from a salt effect and a possibly somewhat erroneous value of $k_{-p}{}^B$ (B = chloroacetate).

(12) J.-C. Hallé, R. Gaboriaud, and R. Schaal, *Bull. Soc. Chim. Fr.*, 2047 (1970). Note that the comparison is somewhat crude because the temperature and ionic strength are not identical in the two systems.

(13) V. N. Knyazev, A. A. Klimov, N. G. Yaryshev, and V. N. Drozd, *Zh. Org. Khim.*, **10**, 2587 (1974).

(14) $K_a k_1$ calculated by multiplying Crampton and Willison's[5] $K_{OH}k_1$ (K_{OH} = $[\mathbf{8}]/[\mathbf{7}]a_{OH^-}$) with 10^{-14}

(15) P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, **82**, 795 (1960).

(16) It is interesting to note that the situation in reaction 3 is somewhat intermediate between that of reactions 2 and 5. Deprotonation of **5** occurs mainly by the $k_p{}^{OH}$ and $k_p{}^B$ steps because $k_p{}^S$ is small (like $k_{-p}{}^{OH}$ in system 5). However $k_{-1} = 2 \times 10^5\ s^{-1}$ is only moderately high (like k_1 in system 2); as a consequence proton transfer is rate limiting ($k_{-1} > k_p$) at low pH and low [B], but becomes very fast ($k_{-1} \ll k_p$) at high pH and/or high [B].

(17) For the system 1-(β-hydroxyethoxy)-2,4-dinitrobenzene, $K_{OH}k_1$ (K_{OH} defined analogously as in ref 14) is 67-fold larger in 50% Me_2SO–50% water compared to water,[4] presumably mainly due to an increase in k_1.

(18) J. J. Ryan and A. A. Humffray, *J. Chem. Soc. B*, 1300 (1967).

(19) L. H. Gan and A. R. Norris, *Can. J. Chem.*, **52**, 18 (1974).

(20) J. Murto, *Acta Chem. Scand.*, **20**, 303 (1966).

(21) V. N. Drozd, V. N. Knyazev, and A. A. Klimov, *Zh. Org. Khim.*, **10**, 826 (1974).

(22) J.-C. Hallé, R. Gaboriaud, and R. Schaal, *Bull. Soc. Chim. Fr.*, 1851 (1969). Note that the value of K_s given is only approximate, since our conditions of temperature and ionic strength are different.

Triphase Catalysis. Kinetics of Cyanide Displacement on 1-Bromooctane[1]

Steven L. Regen

Contribution from the Department of Chemistry, Marquette University,
Milwaukee, Wisconsin 53233. Received February 4, 1976

Abstract: The kinetics of the triphase-catalyzed displacement of cyanide ion (aqueous phase) on 1-bromooctane (organic phase) employing cross-linked polystyrene resins (solid phase) bearing a variety of quaternary ammonium groups has been investigated. The rate of the displacement exhibited a first-order dependency on the 1-bromooctane concentration and was linearly dependent on the amount of catalyst used. Comparison of the catalytic activity for resins having 1, 10, and 21% ring substitution indicates that within this range of ring substitution, resin activity is directly related to the number of quaternary ammonium groups present. Examination of the activity displayed by various other polystyrene ion-exchange resins further revealed that, at the 8–10% ring substitution level, the structure of the quaternary ammonium group bound to the polymer backbone has little influence in determining the catalyst's activity. Polystyrene in the "popcorn" form yielded a resin catalyst which exhibited activity similar to that produced from the microporous form; macroporous polystyrene afforded a significantly less active catalyst. Increasing the level of ring substitution in microporous polystyrene with $CH_2N(CH_3)_3Cl$ groups to 46, 70, and 76% resulted in a sharp drop in catalyst activity accompanied by a significant change in swelling properties of the resin.

A new type of heterogeneous catalysis termed "triphase catalysis" has recently been introduced.[2] The underlying feature which distinguishes this from other forms of heterogeneous catalysis is that both the catalyst and each one of a pair of reactants are located in separate phases. This principle has been successfully applied to certain *aqueous phase–organic phase* reactions employing a *solid phase* catalyst.

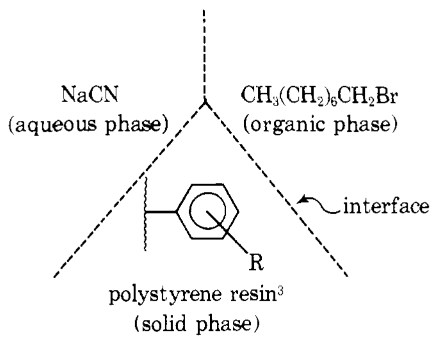
In the present work we have examined in detail the kinetics of one such triphase-catalyzed process. The system chosen was the displacement of cyanide ion (aqueous phase) on 1-bromooctane (organic phase) catalyzed by one of several different types of polystyrene ion-exchange resins (solid phase); an illustration of the three-phase system is presented in Scheme I. This investigation was carried out for the dual purpose of (1)

Table I. Dependence of k^m on Catalyst Employed[a]

Catalyst	Polystyrene matrix	% ring substitution	R[b]	k^m, s^{-1} [c]
1	Microporous (2% divinylbenzene)	10	$CH_2N(CH_3)_2(n\text{-}C_4H_9)Cl$	2.2
2		1		1.9
3		21		2.2
4		10	$CH_2N(CH_3)_3Cl$	3.0
5		46		0.015
6		76		<0.015[d]
7	AG 1-X2	70		<0.015[d,e]
8	Microporous (2% divinylbenzene)	10	$CH_2N(CH_3)_2(n\text{-}C_8H_{17})Cl$	4.4
9		10	$CH_2N(CH_3)_2(n\text{-}C_{12}H_{25})Cl$	3.0
10		9	$CH_2N(CH_3)_2(n\text{-}C_{14}H_{29})Cl$	3.7
11		8	$CH_2N(C_2H_5)_3Cl$	1.5
12		9	$CH_2N(CH_3)_2(CH_2C_6H_5)Cl$	2.6
13		8	$CH_2N(CH_3)_2(C_2H_4OH)Cl$	1.1
14	Microporous (1% divinylbenzene)	10	$CH_2N(CH_3)_2(n\text{-}C_4H_9)Cl$	2.2
15	Microporous (4% divinylbenzene)	9		2.7
16	Macroporous	8		0.22
17	"Popcorn"	10		2.5

[a] Reaction of 0.289 mmol of 1-bromooctane in 2 ml of toluene with 24.5 mmol of sodium cyanide dissolved in 2 ml of water catalyzed by 0.06 g of catalyst at 110 °C. [b] R represents the pendant group shown in Scheme I. [c] Represents the first-order rate constant divided by the molar amount of quaternary ammonium groups present. [d] Reaction was sufficiently slow that competing hydrolysis of sodium cyanide made determination of k^m impossible; the yield of 1-cyanooctane produced after 72 h using either catalyst **6** or **7** was <6%. [e] Commercially available resin from Bio-Rad Laboratories (R = $CH_2N(CH_3)_3Cl$).

Scheme I



clarifying the kinetic features of this one specific transformation and (2) defining parameters pertinent to achieving optimum resin activity.

Results and Discussion

Evidence for Triphase Catalysis. The apparatus used for all of the triphase-catalyzed experiments described in this work consisted of a Corning No. 9826 culture tube equipped with a Teflon-lined screw cap. When the tube was charged with an aqueous sodium cyanide solution plus a toluene solution of 1-bromooctane and resin **1** (Table I) was added, the polymer beads resided at the organic-aqueous interface (Figure 1). We have found that heating such heterogeneous mixtures at 110 °C resulted in the production of 1-cyanooctane in high yield. Control experiments outlined in the Experimental Section established that when unfunctionalized polystyrene was used as the solid phase for similar reactions, the alkyl bromide remained unchanged.

In order to ensure that this displacement reaction was, in fact, being catalyzed by the solid phase, the reaction of cyanide ion with 1-bromooctane in the presence of **1** was repeated, but stopped after a 15% yield of 1-cyanooctane was obtained. A portion of both the aqueous phase and the organic phase was transferred to a second tube, which, along with the original tube, was heated for an additional period of time at 110 °C. Analysis of the product mixture in the tube containing **1** showed an increased yield (64%) of 1-cyanooctane. In the absence of **1**, the yield of 1-cyanooctane remained unchanged.

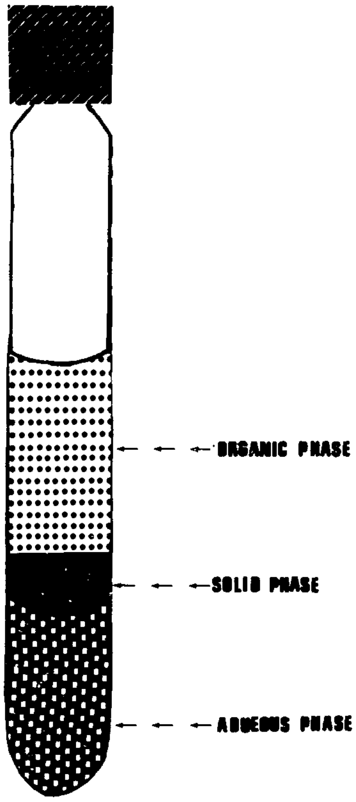


Figure 1. Corning No. 9826 culture tube containing organic, aqueous, and solid phases.

Kinetic Features of the Displacement. Despite the complexities inherent in a three-phase system, we have found that under appropriate conditions the above displacement reaction obeyed simple first-order kinetics; i.e., the rate showed a first-order dependency on the 1-bromooctane concentration. Figure 2 illustrates typical kinetic data obtained. Examination of the dependency of the observed first-order rate constant (k_{obsd}) on the amount of cyanide present in the reaction mixture revealed that within the limits of experimental error, a tenfold increase in the amount of sodium cyanide employed

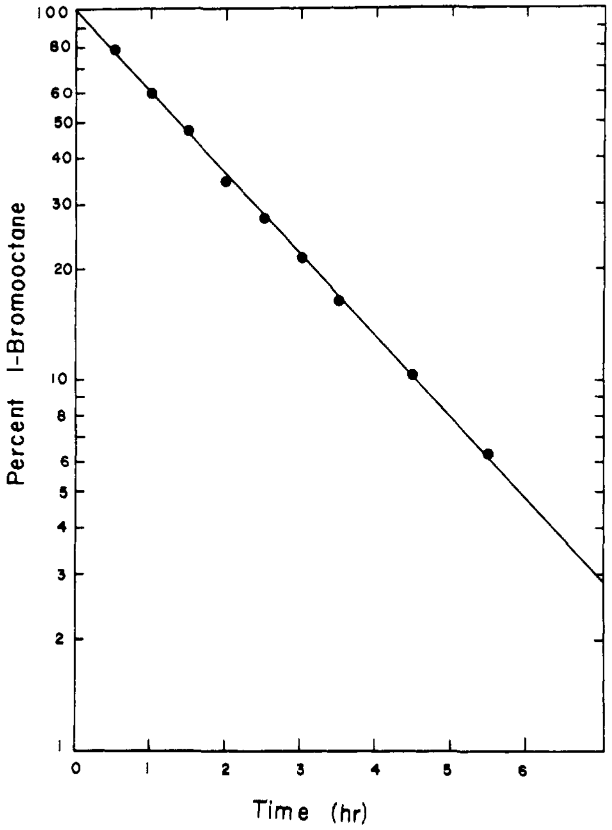


Figure 2. Plot of percent of 1-bromooctane in the organic phase as a function of time for the reaction of 0.289 mmol of 1-bromooctane in 1 ml of toluene with 12.2 mmol of sodium cyanide dissolved in 1 ml of water catalyzed by 0.074 g of **1** at 110 °C.

Table II. Dependence of k_{obsd} on the Amount of Sodium Cyanide Present[a]

NaCN, mmol	$10^5 k_{obsd}$ s^{-1} [b]
1.2	5.1 ± 0.4[c]
4.1	5.7 ± 0.8
8.2	5.3 ± 1.0
12.2	6.8 ± 2.0

[a] Reaction of 0.289 mmol of 1-bromooctane in 1 ml of toluene with the indicated amount of sodium cyanide dissolved in 1 ml of water catalyzed by 0.030 g of **1** at 110 °C. [b] Average of three reactions along with the standard deviation. [c] For this reaction, 0.145 mmol of 1-bromooctane was used.

produced no significant change in the observed rate of reaction (Table II).

A plot of k_{obsd} as a function of the amount of resin **1** used for the cyanide displacement reaction is shown in Figure 3. These data demonstrate that the rate of reaction is linearly dependent on the amount of catalyst present.

In order to determine the dependency of k_{obsd} on the concentration of ionic groups along the polymer backbone we have measured the resin activity of **1**, **2**, and **3**. For purposes of comparison, first order rate constants listed in Table I are expressed as k^m values, where $k^m = k_{obsd}$/mol of quaternary ammonium groups. The similarity of these values indicates that resin activity is directly related to the number of quaternary ammonium groups present.

A kinetic description for this triphase-catalyzed reaction consistent with all of the above observations is summarized below (eq 1-4). Equation 1 depicts an equilibrium between the chloride and cyanide forms of the resin, where P_{cl} and P_{cn}

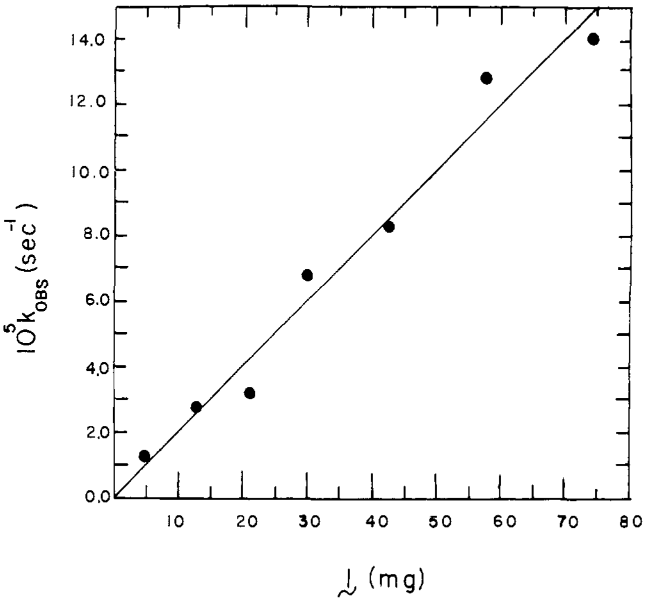


Figure 3. Plot of $10^5 k_{obsd}$ as a function of the amount of catalyst used for the reaction of 0.289 mmol of 1-bromooctane in 1 ml of toluene with 12.2 mmol of sodium cyanide dissolved in 1 ml of water catalyzed by the indicated amount of **1** at 110 °C.

represent single quaternary ammonium chloride and quaternary ammonium cyanide groups bound to the polystyrene framework, respectively.

$$P_{cl} + CN_{aq}^- \overset{K}{\rightleftharpoons} P_{cn} + Cl_{aq}^- \qquad (1)$$

If P_{cl}^m and P_{cn}^m represent the corresponding molar quantities of these groups present and $P_t^m = P_{cl}^m + P_{cn}^m$, then P_{cn}^m may be alternatively expressed as shown

$$P_{cn}^m = \frac{K(CN^-)_{aq}P_t^m}{(Cl^-)_{aq} + K(CN^-)_{aq}} \qquad (2)$$

If it is assumed that the rate-determining step for the conversion of 1-bromooctane into 1-cyanooctane is the displacement of P_{cn} on 1-bromooctane (eq 3) and also that $K(CN^-)_{aq} \gg (Cl^-)_{aq}$, then the rate equation describing the disappearance of 1-bromooctane reduces to eq 4, where $k_{obsd} = k^m P_t^m$.[4]

$$-d(\text{1-bromooctane})/dt = k^m P_{cn}^m (\text{1-bromooctane})_{org} \qquad (3)$$

$$-d(\text{1-bromooctane})/dt = k_{obsd}(\text{1-bromooctane})_{org} \qquad (4)$$

Additional support for the above scheme was provided by the following observations. When catalyst **1** was subjected to the conditions used for the triphase-catalyzed cyanide displacement reaction for 0.5 h, recovered by filtration, washed thoroughly with distilled water and tetrahydrofuran, and dried under vacuum, microanalysis revealed that all of the chloride had been replaced by cyanide ions. We have found that the resulting cyanide form of **1** reacts with 1-bromooctane in toluene as a two-phase reaction to give high yields of 1-cyanooctane. Thus, when the cyanide form of **1** was treated with excess 1-bromooctane in toluene for 24 h at 110 °C, an 85% yield of 1-cyanooctane was produced, based upon the amount of resin employed. Examination of the rate of disappearance of 1-bromooctane for this two-phase reaction using a large excess of resin revealed a simple first-order dependency on the concentration of 1-bromooctane (Figure 4). Doubling the amount of resin used increased the observed first-order rate constant by a factor of two. Similar kinetic behavior was observed for the displacement of the same cyanide resin on 1-bromooctane when a third phase, water, was introduced. The k^m value determined for the two-phase displacement was 22.0,

Table III. Swelling of Ion-Exchange Resins in Toluene and Water[a]

Resin	q_{toluene}	q_{water}
4	2.3	1.7
3	2.3	1.8
5	1.3	3.5
7	1.3	4.7

[a] Degree of swelling values, q (swelled volume/dry volume) were determined from the measured density of the dry resin and the weight of imbibed solvent using established procedures and are accurate to ±10%.[17]

approximately one order of magnitude faster than the corresponding three-phase reaction (2.0). Within experimental error, the latter value was identical with that recorded for resin **1** under catalytic conditions.

Dependence of Catalytic Activity on the Structure of the Quaternary Ammonium Group and the Type of Polystyrene Used. Examination of the activity displayed by catalysts **1, 4, 8–13** (Table I) reveals that, at the 8–10% level of ring substitution, the structure of the quaternary ammonium group bound to the polymer backbone appears to have little influence in determining the catalyst's activity. We have also tested other types of polystyrene lattices (catalysts **14–17**) and with the exception of the macroporous modification, little differences were noted between the support material. Sano et al. have previously shown that macroporous polystyrene can, in certain instances, allow for faster rates of two-phase reactions relative to the more conventional microporous form.[5,6] We were, therefore, somewhat surprised to find a *lower* activity for catalyst **16** relative to **14, 15,** and **17.** The reason for this result is not presently clear.

One interesting observation made, which may have important practical consequences for synthetic applications of triphase catalysis, is seen through comparison of the activity exhibited in catalysts **4–6.** Although k^{m} showed little dependency on the percent ring substitution between 1 and 20%, increasing the level of substitution to 46, 70, and 76% resulted in a sharp drop in catalyst activity. Accompanying this loss in activity was a significant change in swelling properties of the resins (Table III). Thus, we have noted that those resins which were more compatible with the organic phase (larger degree of swelling) than with the aqueous phase exhibited greater catalytic activity. Although neither the origin nor the generality of this effect has yet been established, this finding does suggest that most commercially available ion-exchange resins (typically >60% ring substitution with high swelling capacities in water) will not be ideally suited for use in triphase catalysis.

The kinetic features for this specific triphase-catalyzed process bears a resemblance to that observed for the displacement of cyanide ion on 1-bromooctane using the recently developed "phase-transfer catalysis" technique.[7,8] In both systems, the rate of displacement exhibits a first-order dependency on the 1-bromooctane concentration and is also linearly dependent on the amount of catalyst used. For the phase-transfer reaction it has been proposed that the organic-soluble catalyst acts by repeatedly bringing cyanide ions located in an aqueous phase into the bulk organic phase where the displacement occurs. It has also been suggested that micellar catalysis, in which reverse micelles could bring small amounts of aqueous sodium cyanide into the organic phase in a form suitable for displacement, is of negligible importance. Whether a related mechanistic pathway exists for the case of the triphase reaction, however, remains to be established.

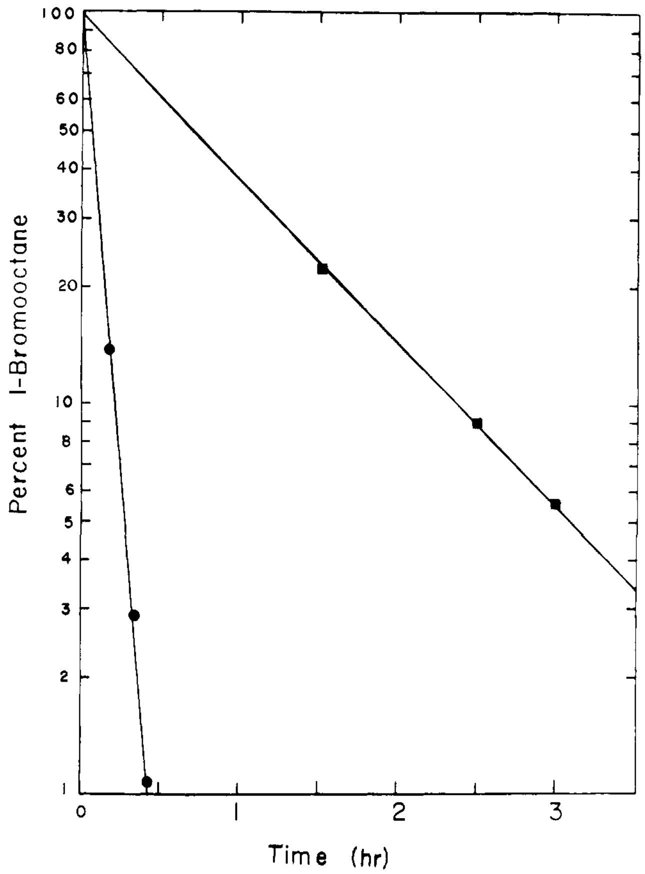


Figure 4. Plot of percent of 1-bromooctane as a function of time for the reaction of 4.0×10^{-3} mmol of 1-bromooctane in 2 ml of toluene with 0.085 g of the cyanide form of **1** (●) and 4.0×10^{-3} mmol of 1-bromooctane in 2 ml of toluene with 0.089 g of the cyanide form of **1** in the presence of 2 ml of water (■).

Before a more detailed description of this triphase-catalyzed transformation is possible the physical state of the swelled resin needs to be defined. In particular, the degree of aggregation of the quaternary ammonium groups along the polymer backbone as well as the extent to which they are solvated by the organic and aqueous phases must be ascertained.[9]

Experimental Section

General Methods. Unless stated otherwise, all reagents were obtained commercially and used without further purification. Microporous polystyrene beads S-X1, S-X2, and S-X4 (200–400 mesh) were purchased from Bio-Rad Laboratories, the number following the letter X indicates the percent of divinylbenzene incorporated into the polymer beads.

The macroporous modification of polystyrene was commercially available (Pierce Chemical Co.) and purchased in the chloromethylated form (0.66 mmol of chlorine/g of resin). Cross-linked polystyrene in the "popcorn" form (0.5% divinylbenzene) was prepared following procedures described in the literature.[10] All of the microporous and "popcorn" copolymers were chloromethylated using established procedures.[11] Benzene, tetrahydrofuran, and toluene were each dried by distillation from sodium and benzophenone under a nitrogen atmosphere. *N,N*-dimethyl-*n*-butylamine and *N,N*-dimethyl-*n*-octylamine were purchased from K & K Laboratories and were used without further purification. Trimethylamine, triethylamine, *N,N*-dimethyl-*n*-dodecylamine, *N,N*-dimethyl-*n*-tetradecylamine, *N,N*-dimethylethanolamine, *N,N*-dimethylbenzylamine, 1-cyanooctane, and 1-bromooctane were available from Aldrich Chemical Co. and used as obtained. All ^{1}H NMR spectra were recorded using a Varian A-60 spectrometer. Product mixtures were analyzed by GLC on a Hewlett-Packard Model 5710A flame ionization instrument (4 ft × 0.125 in. 5% Carbowax 20M on 80–100 mesh Chromasorb P at 110 °C) equipped with a Hewlett-Packard Model 3380A integrator. The oil bath used for the kinetic experiments was maintained at 110 ± 0.5 °C with the aid of a "THERM-O-WATCH" Electronic Controller Model L6-1000 (I^2R Co., Cheltenhan, Pa.) attached to a thermometer. Culture tubes (Corning No. 9826, 13 × 100 mm) equipped with Teflon-lined screw caps were used as reaction vessels for all of the experiments described. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

General Procedure for Preparation of Ion-Exchange Resins. Procedures similar to that described for the quaternization of chloromethylated polystyrene (microporous) with *N,N*-dimethyl-*n*-butylamine were followed for the preparation of all polymeric catalysts described in Table II.[12] Chloromethylated polystyrene (1.0 g, 1.0 mmol of chlorine; 2% divinylbenzene) was swelled in 5 ml of a benzene solution of *N,N*-dimethyl-*n*-butylamine (0.2 M, 1.0 mmol) in a Corning No. 9826 culture tube sealed with a Teflon-lined screw cap. The tube was placed in an oil bath maintained at 75 °C for 100 h, withdrawn, and cooled to room temperature. The resin was filtered, washed with 100 ml of benzene, and dried under vacuum [12 h, 110 °C (0.05 mm)]. Chloride-ion analysis indicated that the resulting resin contained 0.86 mmol of Cl^-/g of resin (100% quaternization corresponds to 0.91 mmol of Cl^-/g of resin).[13]

Anal. Calcd for **1a**: N, 1.27. Found: N, 1.21.

General Procedure for Triphase-Catalyzed Displacement of Cyanide Ion on 1-Bromooctane. To a Corning No. 9826 culture tube containing 0.074 g of **1** was added a solution of 0.6 g (12.2 mmol) of sodium cyanide dissolved in 1 ml of water followed by 0.112 g (0.6 mmol) of 1-bromooctane plus 1 ml of toluene. An internal standard (*n*-dodecane) was added to the reaction mixture and the tube was shaken vigorously for 2 min, placed in an oil bath maintained at 110 °C for 5.5 h, withdrawn, and cooled to room temperature. Analysis of the organic phase by GLC indicated a yield of 1-cyanooctane of 90%. Identification of 1-cyanooctane was made by comparison of its NMR spectrum and GLC retention time with those of an authentic sample.[15,16]

When similar experiments were carried out in which **1** was either omitted or replaced with unfunctionalized polystyrene, 100% of the alkyl bromide remained unchanged.

Control Experiment Confirming Triphase Catalysis. To a Corning No. 9826 culture tube containing 0.08 g of **1** was added a solution of 1.2 g (24.4 mmol) of sodium cyanide dissolved in 2 ml of water followed by 0.224 g (1.2 mmol) of 1-bromooctane plus 2 ml of toluene. After an internal standard was added to the mixture, the tube was sealed, shaken vigorously for 2 min, placed in an oil bath maintained at 110 °C for 0.3 h, withdrawn, and cooled to room temperature. Analysis of the organic phase by GLC indicated a yield of 1-cyanooctane of 15%. A portion of the organic phase (0.4 ml) and the aqueous phase (0.4 ml) was transferred to a second culture tube, which, along with the original tube, was heated for an additional 1.5 h. Analysis of the product mixture in the vial containing **1** showed a 64% yield of 1-cyanooctane. In the absence of **1**, the yield remained at 15%.

Isolation of the Cyanide Form of 1. Catalyst **1** (0.3 g, 0.26 mmol of chloride ion) along with a solution of 2.4 g (48.8 mmol) of sodium cyanide dissolved in 4 ml of water plus 3 ml of toluene was added to a culture tube. The tube was shaken vigorously for 2 min, placed in an oil bath maintained at 110 °C for 0.5 h, withdrawn, and cooled to room temperature. The aqueous phase was diluted with distilled water and the resin was filtered, washed successively with water, 3:1 tetrahydrofuran-water, tetrahydrofuran, and dried under vacuum [12 h, 65 °C (0.05 mm)]. Microanalysis indicated that the resulting resin contained <0.1% chlorine. When the cyanide form of **1** (0.1 g) was heated in the presence of an excess of a toluene solution of 1-bromooctane (2 ml of 0.145 M 1-bromooctane solution) for 24 h at 110 °C, 0.072 mmol of 1-cyanooctane was produced (100% replacement of chloride by cyanide ion corresponds to 0.86 mmol of CN^-/g of resin).

Kinetics of Triphase-Catalyzed Displacement on 1-Bromooctane. Kinetic experiments were carried out by placing culture tubes containing the appropriate components (after having been shaken vigorously for 2 min) in an oil bath maintained at 110 °C. Reactions were monitored by withdrawing 1 μl samples from the organic phase at no less than 30-min time intervals. Sampling was carried out by removing a given tube from the oil bath, allowing it to cool for a 1-min period, withdrawing a sample, and quickly returning the tube to the oil bath. Plots made on semilogarithmic paper of the percent of 1-bromooctane remaining as a function of time gave straight lines; slopes were used to calculate first-order rate constants.

Kinetics of Displacement of 1-Bromooctane by the Cyanide Form of 1. The cyanide form of **1** (0.085 g) was placed in a culture tube followed by the addition of 2 ml of 2.0×10^{-3} M 1-bromooctane in toluene containing an internal standard. The mixture was placed in an oil bath maintained at 110 °C and the disappearance of 1-bromooctane was monitored as a function of time. When analogous three-phase reactions were investigated (addition of 2 ml of water to the above mixture provided three distinct phases) the tubes were shaken vigorously for 2 min prior to analysis.

Acknowledgment. We wish to thank Mr. Warren Kupin for help with the chloride-ion analyses and also with the preparation of certain of the ion-exchange resins used.

References and Notes

(1) Supported by the National Science Foundation, Grant No. MPS74-23925.

(2) S. L. Regen, *J. Am. Chem. Soc.*, **97**, 5956 (1975).

(3) Polymer-bound quaternary ammonium groups (R) investigated in this work are listed in Table I.

(4) Cyanide forms of certain anion-exchange resins have previously been found capable of converting alkyl halides into cyanoalkanes: M. Gordon, M. L. DePamphilis, and C. E. Griffin, *J. Org. Chem.*, **28**, 698 (1963). In addition, anion-exchange resins have previously been found to catalyze certain cyanide-displacement reactions: H. B. Copelin and G. B. Crane, U.S. Patent 2 779 781 (1957). Although such systems bear a resemblance to the triphase-catalyzed process described herein, the fact that these reactions proceed at a significant rate in the absence of suitable resins makes their relationship to triphase-catalysis questionable.

(5) S. Sano, R. Tokunaga, and K. A. Kun, *Biochim. Biophys. Acta*, **244**, 201 (1971).

(6) The macroporous polystyrene resin obtained from Pierce Chemical Co. contained 8% divinylbenzene and was available in 200–400 mesh.

(7) C. M. Starks and R. M. Owens, *J. Am. Chem. Soc.*, **95**, 3613 (1973).

(8) In phase-transfer catalysis, an organic-soluble catalyst (tetraalkylammonium or tetraalkylphosphonium salt) is used to accelerate the reaction between two substances separated by an aqueous phase–organic phase boundary.

(9) A recent report dealing with the mobility of benzene-swelled polystyrene ion-exchange resins similar to those used in this work suggests that for such systems charge clustering may be extensive: S. L. Regen and D. P. Lee, *J. Am. Chem. Soc.*, **96**, 294 (1974).

(10) R. L. Letsinger, M. J. Kornet, V. Mahadevan, and D. M. Jerina, *J. Am. Chem. Soc.*, **86**, 5163 (1964).

(11) K. W. Pepper, H. M. Paisley, and M. A. Young, *J. Chem. Soc.*, 4097 (1953).

(12) Tetrahydrofuran was used as the solvent in the preparation of ion-exchange resins derived from trimethylamine (25% aqueous solution). The resulting resins were filtered, washed successively with water, 3:1 tetrahydrofuran–water, tetrahydrofuran, and dried under vacuum [12 h, 110 °C (0.05 mm)].

(13) The amount of chlorine present in the form of chloride ion was determined by a modified Volhard titration using procedures described elsewhere.[14]

(14) J. M. Stewart and J. D. Young, "Solid Phase Peptide Synthesis", W. H. Freeman, San Francisco, Calif., 1969, p 55.

(15) ^1H NMR comparisons were made when toluene-d_8 was used as the solvent for the organic phase of the reaction. In this case, the internal standard was omitted, and the NMR spectrum observed for the organic phase was identical with that of the toluene-d_8 solution of authentic 1-cyanooctane.

(16) A referee has pointed out that other workers using ion-exchange resins to catalyze cyanide displacement on alkyl halides have found a moderate rate of decomposition of the quaternary groups on the resin (a private communication). Under the conditions used for the triphase-catalyzed displacement of cyanide ion on 1-bromooctane with **1a**, there appears to be little if any catalyst decomposition; i.e., good first-order plots could be obtained over 90% of the reaction (Figure 2). In addition, reuse of **1a** in a second catalyzed cyanide displacement on 1-bromooctane gave, again, a good first-order plot with no detectable change in k^m. These results, however, do not rule out the possibility of significant resin decomposition in other triphase-catalyzed cyanide-displacement reactions. Work in progress is aimed at establishing the synthetic utility of this technique for cyanide displacement as well as other transformations.

(17) H. P. Gregor, G. K. Hoeschele, J. Potenza, A. G. Tsuk, R. Feinland, M. Shida and P. Teyssie, *J. Am. Chem. Soc.*, **87**, 5525 (1965).