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Studies on Triphase Catalysis:[1] Effects of Structure of the Immobilized Quaternary Salt on the Catalytic Activity

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The catalytic activities of eight different types of triphase catalyst (immobilized phase transfer catalyst) were examined in the displacement reaction of several anions with benzyl bromide and *n*-octyl methanesulfonate at 70 and 90 °C, respectively. The catalysts were prepared by the reaction of 1% cross-linked chloromethylated polystyrene with such tertiary amines as R_3N (R = ethyl, *n*-propyl, *n*-butyl) and $R(CH_3)_2N$ (R = ethyl, *n*-butyl, *n*-dodecyl, *n*-hexadecyl) and tri-*n*-butylphosphine.

The catalytic activity for the reaction of *n*-octyl methanesulfonate increased with increasing size of the immobilized quaternary cation. The catalysts with bulky cations having different central atoms ([resin]–$CH_2N^+(C_4H_9)_3$, [resin]–$CH_2P^+(C_4H_9)_3$) showed almost the same catalytic activity in every reaction tested.

Variation of the structure of the immobilized cation was concluded to modify the catalytic activity not only by changing the anion–cation interaction energy but also by changing the reaction environment around the active site.

Keywords——triphase catalysis; phase transfer catalysis; anion displacement; quaternary cation structure; catalytic activity comparison; polystyrene resin; *n*-octyl methanesulfonate

In liquid–liquid phase transfer catalysis of a displacement reaction catalyzed by quaternary salts, the relationship between the structure of the quaternary salts and the catalytic activity has been studied in detail by Herriott *et al.*[2] According to their results, larger and more symmetrical cations are most effective. This conclusion is widely accepted, and a bulky and symmetrical cation, $N^+(C_4H_9)_4$, has frequently been used as a highly effective catalyst. The poor activity of relatively smaller quaternary cations is mainly attributed to their hydrophilic nature, that is, partitioning to the aqueous phase in liquid–liquid phase transfer catalysis.

In the case of triphase catalysis, the partitioning factor can be neglected because the quaternary cation is immobilized on a lipophilic support. Therefore, it seemed interesting to test the effectiveness of triphase catalysts having different quaternary cation structures. In general, a triphase catalyst with a bulky cation ([resin]–$CH_2N^+(C_4H_9)_3$ or [resin]–$CH_2P^+(C_4H_9)_3$) is expected to be effective, and a catalyst having a small cation ([resin]–$CH_2N^+(CH_3)_3$) is expected to be a very poor catalyst.[3,4] However, there are few papers dealing with quantitative aspects of such differences in catalytic activity. Such an analysis is also important in order to clarify the mechanism of triphase catalysis.

In this paper, the relationship between the structure of the quaternary cation anchored to polystyrene resin and the triphase catalytic activity was examined in detail. The catalytic activity of several different catalysts for the anion displacement reactions (1) and (2) was determined under reaction conditions where the effect of mass transfer resistance on the rate of reaction was negligible. The difference in the activity of different catalysts was interpreted in terms of both the difference in the anion–cation interaction energy of the quaternary salt and the nature of the nucleophile. On the basis of the analysis, two structural effects of the supported cation on the catalytic activity were confirmed. The relationship between the structure of the immobilized quaternary cation and the reaction order with respect to benzyl bromide was also examined.

$$\text{Ph–CH}_2\text{Br}+\text{KX} \longrightarrow \text{Ph–CH}_2\text{X}+\text{KBr} \qquad (1)$$

$$\text{X}=\text{Cl, I, CN, OAc}$$

$$\text{C}_8\text{H}_{17}\text{OSO}_2\text{CH}_3+\text{KX} \longrightarrow \text{C}_8\text{H}_{17}\text{X}+\text{KOSO}_2\text{CH}_3 \qquad (2)$$

$$\text{X}=\text{Cl, Br, I}$$

Experimental

Materials——Benzyl bromide, all *n*-alkanes (internal standards), toluene and all potassium salts were used as obtained. Triethylamine and dimethylformamide (DMF) were used after distillation. Other amines and tri-*n*-butylphosphine were purchased from Tokyo Kasei Kogyo Co., Ltd., and were used as such without distillation. *n*-Octyl methanesulfonate was prepared by the procedure described by Williams *et al.*[5] Chloromethylated polystyrene cross-linked by 1% divinylbenzene (Bio-Beads S-X1, 1.26 or 1.34 meq. chlorine/g-resin, 200—400 mesh) was purchased from Bio-Rad Laboratories.

Catalysts——All catalysts were prepared by the reaction of the chloromethylated resin with tertiary amines and phosphine. The reaction was conducted in a culture tube for 70 h, at 70 °C for amines and 90 °C for phosphine. Toluene or DMF was used as a solvent for amines or phosphine, respectively. The resin was filtered off, and washed first with toluene then with methanol and distilled water alternately. It was dried overnight under reduced pressure at 70 °C. The contents of quaternary salts in catalyst samples were determined by elemental analysis and are shown in Table I. The reactivity of symmetrical amines as a whole was low and the content of active sites in catalyst 7 was so low that the rate of reaction (2) could not be measured. A higher content for catalyst 7 was obtained by conducting the quaternization in DMF solution instead of toluene.

TABLE I. Catalysts Tested in This Work

Catalyst		Elemental analysis for N or P (%)		Content of quaternary cation (mmol/g-catalyst)
No.	Structure of cation	Obsd	Calcd	
1	$-\text{N}^+(\text{Me})_2\text{Et}$	1.72	1.71	1.23
2	$-\text{N}^+(\text{Me})_2\text{Bu}$	1.70	1.65	1.21
3	$-\text{N}^+(\text{Me})_2\text{dodecyl}$	1.46	1.46	1.04
4	$-\text{N}^+(\text{Me})_2\text{hexadecyl}$	1.38	1.37	0.99
5	$-\text{N}^+(\text{Et})_3$	0.85	1.65	0.61
6	$-\text{N}^+(\text{Pr})_3$	0.75	1.57	0.54
7	$-\text{N}^+(\text{Bu})_3$	0.19	1.50	0.14
		1.19[a]		0.85
8	$-\text{P}^+(\text{Bu})_3$	2.14	3.27	0.69

a) The quaternization was carried out in DMF solution.

Procedure——A test tube (cross-sectional area: $1.43\,cm^2$) equipped with a Teflon-lined screw cap was used as a reaction vessel.

All runs were carried out in an unstirred system, and the procedure was as follows. Five mg of catalyst was placed in the test tube, then 2 ml of aqueous solution containing a nucleophile (3.6 M) was added, and the catalyst was well dispersed on the surface of the solution. The tube was sealed and placed in an oil bath, the reaction was started by adding 1 ml of toluene solution of a substrate containing an internal standard. The reaction was followed by withdrawing samples (1 μl each) from the organic phase at appropriate intervals. The reaction temperature was 70 °C for reaction (1) and 90 °C for reaction (2).

The observed rate constant (k_0) or initial rate of reaction (r_0) was determined in the same way as described in the previous paper.[1] As the same amount of each type of catalyst was used, the relative catalytic activity was determined by dividing r_0 or k_0 by the concentration of quaternary cation [mol of quaternary cation contained in the catalyst used/volume of organic phase].[6]

The concentrations of reactant and product in the sample were determined by gas chromatography. For the analysis, two types of columns were used: silicone DC550 on Celite 545BW (60—80 mesh) for reaction (1) and 2% silicone GE SE-30 on Chromosorb W (AW-DMCS, 80—100 mesh) for reaction (2).

Results and Discussion

Kinetic Aspects

In the previous paper,[1] reaction of benzyl bromide with potassium chloride catalyzed by a polymer-supported phosphonium cation was chosen as a model reaction to study the mechanism of triphase catalysis, and it was concluded that the rate-determining step is the chloride displacement reaction of benzyl bromide (reaction 3).

$$\text{[resin]–}CH_2P^+(C_4H_9)_3Cl^- + Ph\text{–}CH_2Br \longrightarrow \text{[resin]–}CH_2P^+(C_4H_9)_3Br^- + Ph\text{–}CH_2Cl \qquad (3)$$

As the observed reaction order with respect to benzyl bromide was 0.73 it was supposed that (i) the adsorption of organic reactant on the catalyst surface or (ii) its entrapment in the polymer matrix occurred in reaction (3). If this is the case, the reaction order may be influenced by the nature of the catalyst or substrate. Thus, before comparing the catalytic activities, the relationship between the structure of the supported quaternary cation or substrate and the reaction order was examined.

Reaction orders were determined by plotting the logarithm of the initial rate of reaction r_0 *vs.* the initial concentration of substrate C_0. As shown in Figs. 1 (I) and (II), the observed order with respect to benzyl bromide was found to be affected by the structure of the supported quaternary cation, but almost unaffected by the nature of the nucleophile. The orders for catalysts 7 and 8 (having bulky cations) were in the range of 0.7—0.8, whereas in the case of catalysts 1 and 2 (having small quaternary cations, that is, hydrophilic cations) the observed orders were nearly first-order. Catalysts 3 and 4, whose quaternary cations were considered to be of medium size, were found to show intermediate values of reaction order between those of catalyst 1 or 2 and catalyst 7 or 8. On the other hand, in the case of reaction (2), first-order dependency was observed for the reaction catalyzed by catalyst 4 or 8, as shown in Fig. 1 (III).

It was concluded that these reaction orders are dependent on the nature of the substrate and that of the supported quaternary cation. If the observed reaction order can be interpreted in terms of a Langmuir–Hinshelwood or Michaelis–Menten type equation, the smaller value of the reaction order may reflect higher affinity of the substrate. From this point of view, the observed relationship between the reaction order and the lipophilicity of the supported quaternary cation is reasonable, and it suggests the occurrence of adsorption or entrapment of the substrate in the case of reaction (1).

Effect of Structure of the Supported Quaternary Cation on Catalytic Activity

The initial rates of reaction (1) catalyzed by catalysts 1—4, 7, and 8 under the same

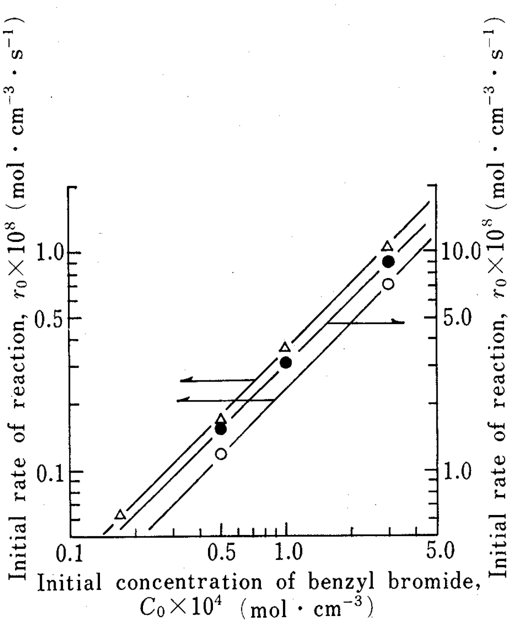

Fig. 1 (I). Effect of Initial Concentration of Benzyl Bromide on the Rate of Reaction (1) Catalyzed by Catalysts 1 and 2

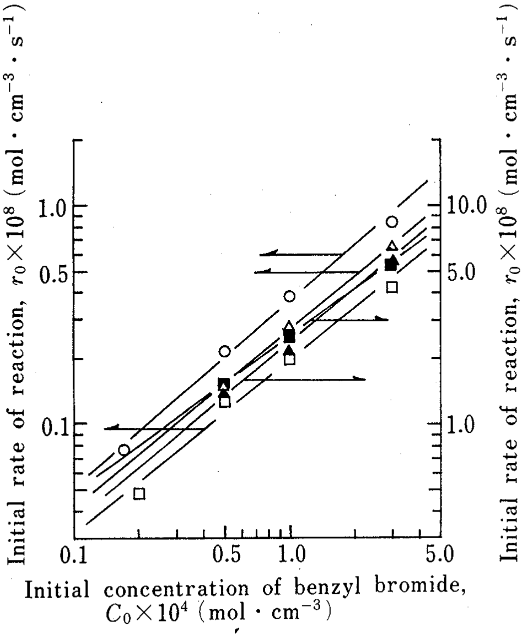

Fig. 1 (II). Effect of Initial Concentration of Benzyl Bromide on the Rate of Reaction (1) Catalyzed by Catalysts 3, 4, 7, and 8

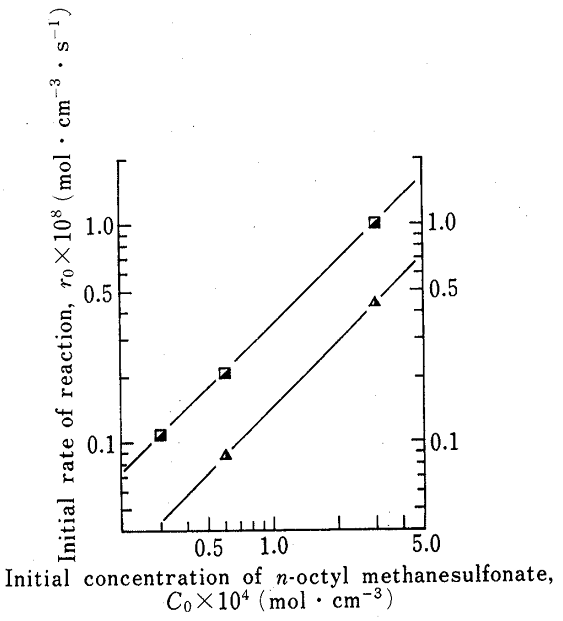

Fig. 1 (III). Effect of Initial Concentration of *n*-Octyl Methanesulfonate on the Rate of Reaction (2) Catalyzed by Catalysts 4 and 8

Reaction conditions

Initial concentration of KCl or KI: 3.6×10^{-3} mol·cm^{-3}.

Volume: org. phase, 1 cm^3; aq. phase, 2 cm^3.

Amount of catalyst: 5 mg.

Reaction temperature: 70 °C for reaction (1), 90 °C for reaction (2).

Symbols and observed reaction orders

	Symbol	Catalyst	Nucleophile	Reaction order
(I)	—○—	1	Cl	1.00
	—△—	2	Cl	0.97
	—●—	1	I	0.95
(II)	—○—	3	Cl	0.84
	—△—	4	Cl	0.81
	—□—	7	Cl	0.76
	—▲—	4	I	0.78
	—■—	8	I	0.73
(III)	—△—	4	Br	1.00
	—□—	8	Br	1.00

conditions are summarized in Table II. The different reaction orders (Fig. 1) do not permit direct comparison of the catalytic activities. However, the following conclusions were obtained from these results.

i) The sequence of nucleophilic reactivity of the anions was in the order of

TABLE II. Initial Rate of Reaction (1) with Different Catalysts

Catalyst No.	$r \times 10^3$ (s^{-1})[a] (Relative rate[b])			
	X=OAc	X=Cl	X=CN	X=I
1	0.54 (0.04)	1.2 (0.08)	7.0 (0.47)	15.0 (1.0)
2	—	1.7 (0.10)	—	18.2 (1.0)
3	—	1.6 (0.14)	—	11.1 (1.0)
4	1.1 (0.11)	1.4 (0.15)	3.6 (0.38)	9.5 (1.0)
7	3.9 (0.25)	6.0 (0.39)	17.6 (1.15)	15.3 (1.0)
8	3.1 (0.20)	6.6 (0.41)	15.8 (0.98)	16.2 (1.0)

[a] r was determined by dividing r_0 ($mol \cdot cm^{-3} \cdot s^{-1}$) by the concentration of quaternary cation ($mol \cdot cm^{-3}$) as mentioned in the experimental section.
[b] For each catalyst, relative to iodide.

Reaction conditions
Initial concentration of benzyl bromide, $0.3 \times 10^{-3}\ mol \cdot cm^{-3}$; solvent, toluene; initial concentration of potassium salts, $3.6 \times 10^{-3}\ mol \cdot cm^{-3}$.
Volume: org. phase, $1\ cm^3$; aq. phase, $2\ cm^3$.
Amount of catalyst: 5 mg.
Reaction temperature: 70 °C.

$I \gtrsim CN > Cl > OAc$ in each case, but the difference in relative reactivity was larger for catalysts 1—4 than for catalysts 7 and 8.

ii) Little difference in catalytic activity was observed between catalyst 7 and catalyst 8 having a different central atom of the quaternary cation.
The difference in relative reactivity of halide ions with different catalysts will be discussed later.

Next, the catalytic activity was examined by taking into account reaction (2). The reactivity of *n*-octyl methanesulfonate as a substrate is lower than that of benzyl bromide, so the intraparticle mass transfer resistance may also be neglected in reaction (2) under our conditions. Therefore, it was confirmed that the rate-determining step in this reaction under our experimental conditions is reaction (4).

$$\text{[resin]–}CH_2N^+R_3X^- + C_8H_{17}OSO_2CH_3 \longrightarrow \text{[resin]–}CH_2N^+R_3{}^-OSO_2CH_3 + C_8H_{17}X \qquad (4)$$

The second-order rate constants of reaction (2) catalyzed by catalysts 1—8 are listed in Table III. The catalytic activity was found to be closely related to the size of the immobilized quaternary cation, contrary to the result reported by Regen.[7] Comparing the values for catalysts 1, 5, 6, and 7, it was concluded that the triphase catalytic activity increases monotonously with increasing size of immobilized quaternary cation. Although the actual size of the quaternary cation of catalyst 2 or 4 is unknown, the observed catalytic activity may be consistent with the above conclusion.

According to Coulomb's law, the anion–cation interaction energy (E) decreases with increase in the distance between the ions as shown below.

$$E = e^2 \cdot N/\varepsilon \cdot r = 33.18/\varepsilon \cdot r \quad \text{(kcal/mol)} \qquad (5)$$

where e is the charge of the electron, ε the dielectric constant, r (Å) the effective distance separating the centers of positive and negative charge, and N Avogadro's number. Assuming that a decrease in anion–cation interaction energy on changing the size of the quaternary cation lowers the free energy of activation of reaction (4) by that amount, the relative catalytic activities shown in Table III were quantitatively evaluated.[8] The relation between a rate constant k and the free energy of activation $\Delta G^{\neq}$ is generally represented by

TABLE III. Second-Order Rate Constants for Reaction (2) with Different Catalysts

Catalyst No.	k^a ($mol^{-1}\cdot cm^3\cdot s^{-1}$)		
	X=Cl	X=Br	X=I
1	—[b]	1.0	2.5
2	—	2.0	—
4	1.4	3.1	5.9
5	0.5	2.3	4.8
6	2.8	5.4	6.5
7	5.6	7.9	9.1
8	6.0	9.4	9.4

a) The second-order rate constant *k* is defined in the experimental section.
b) The value was less than 0.5.
Reaction conditions
Initial concentration of *n*-octyl methanesulfonate, $0.3\times 10^{-3}\,mol\cdot cm^{-3}$; solvent, toluene; initial concentration of potassium halide, $3.6\times 10^{-3}\,mol\cdot cm^{-3}$.
Volume: org. phase, $1\,cm^3$; aq. phase, $2\,cm^3$.
Amount of catalyst: 5 mg.
Reaction temperature: 90 °C.

TABLE IV. Relative Catalytic Activity for Reaction (2):[a] (A) Calculated Value Based on Eq. 7; (B) Experimental Value Obtained from Table III

Cation	Radius[b] (Å)	(A)[c]		
		X=Cl	X=Br	X=I
N^+Me_4	2.85	0.33	0.35	0.38
N^+Et_4	3.48	0.57	0.58	0.60
N^+Pr_4	3.98	0.80	0.80	0.82
N^+Bu_4	4.37	(1.0)	(1.0)	(1.0)

Catalyst No.	Structure of cation	(B)		
		X=Cl	X=Br	X=I
1	$-N^+(Me)_2Et$	—[d]	0.12	0.27
5	$-N^+Et_3$	0.1	0.28	0.53
6	$-N^+Pr_3$	0.50	0.68	0.71
7	$-N^+Bu_3$	(1.0)	(1.0)	(1.0)

a) Relative to N^+Bu_4 for (A) and relative to catalyst 7 for (B).
b) From ref. 10.
c) Anion radii were taken from ref. 9: Cl^-, 1.81; Br^-, 1.95; I^-, 2.16 (Å).
d) The value was less than 0.1.

$$k=(\boldsymbol{k}_B\cdot T/\boldsymbol{h})\cdot\exp(-\Delta G^{\neq}/\boldsymbol{R}\cdot T) \qquad (6)$$

where $\boldsymbol{k}_B$ is Boltzmann's constant, T the reaction temperature, $\boldsymbol{h}$ Planck's constant, $\Delta G^{\neq}$ the free energy of activation, and $\boldsymbol{R}$ the gas constant. Based on Eqs. 5 and 6, the ratio of rate constants with two different quaternary salts (k_{Q1}/k_{Q2}) can be represented by

$$k_{Q1}/k_{Q2}=\exp\{(-33.18/\varepsilon\cdot\boldsymbol{R}\cdot T)\cdot(1/r_{Q1}-1/r_{Q2})\} \qquad (7)$$

On the basis of Eq. 7, the relative catalytic activities of several symmetrical quaternary cations, whose radii were available in the literature,[10] were calculated. A dielectric constant of 2.2 was used for the calculation, since the dielectric constant of toluene is given as 2.38 (25 °C) and 2.15 (127 °C) in the literature.[11] The calculated relative catalytic activity with respect to the tetra-*n*-butylammonium cation is shown in Table IV. The quaternary cations of catalysts 5, 6, and 7 correspond to tetraethyl-, tetra-*n*-propyl-, and tetra-*n*-butylammonium cations, respectively, and that of catalyst 1 approximately corresponds to the tetramethylammonium cation. The observed relative catalytic activities of these catalysts with respect to catalyst 7 are also shown in Table IV.

When the nucleophile was iodide ion, a good agreement was observed between the calculated and experimental values. This confirmed that the difference in catalytic activity of these different catalysts can be attributed to the difference in anion–cation interaction energy. On the other hand, in the case of chloride or bromide the agreement was not good, and the range of the observed catalytic activity was considerably larger than the calculated values. This result suggests that another effect, in addition to the change of anion–cation interaction energy, was imposed by changing the structure of the quaternary cation supported on the catalyst.

Reaction Environment around the Active Site

It is well known that the relative reactivity of halide ions in *S*N2 reactions is affected by the nature of the solvent and is in the order of Cl > Br > I in an aprotic solvent or in the order of I > Br > Cl in a protic solvent. It has also been reported that the reactivity of chloride or bromide ion is reduced by hydration under liquid–liquid phase transfer conditions, whereas that of iodide ion is hardly affected by hydration under the same conditions and, therefore, the relative reactivity of halide ions under typical phase transfer conditions (catalyst: $C_{16}H_{33}P^+(C_4H_9)_3$, chlorobenzene–water system) is in the order of Br ∼ I > Cl.[12]

The relative reactivity of chloride or bromide ion relative to iodide ion observed in this work is shown for each catalyst in Table V. These values can be considered to reflect the reaction environment around the active site of the catalyst, since the reactivity of iodide ion is hardly affected by hydration. As shown in Table V, these values become smaller as the size of the immobilized cation becomes smaller, that is, as the cation becomes more hydrophilic in nature. The same tendency has been observed for reaction (1), as shown in Table II. On the basis of these results, it is concluded that the reaction environment around the active site is converted to a protic state with decrease in the size of the immobilized quaternary cation. Thus, the combination of this structural effect of the supported quaternary cation on the reaction environment and the nature of the nucleophile can be considered to account for the results shown in Table IV.

TABLE V. Relative Reactivities of Halide Ions for Reaction (2) with Different Catalysts

Catalyst No.	Catalyst Structure of cation	Relative reactivity[a] Cl	Br	I
1	$-N^+(Me)_2Et$	—[b]	0.39	(1.0)
5	$-N^+Et_3$	0.10	0.44	(1.0)
6	$-N^+Pr_3$	0.43	0.83	(1.0)
7	$-N^+Bu_3$	0.62	0.87	(1.0)

a) Relative to iodide. The values were obtained from Table III.
b) The value was less than 0.1.

TABLE VI. Relative Reactivities of Halide Ions in Some Reactions with Catalyst 8 or the Corresponding Nonimmobilized Catalyst

Substrate	Catalyst	Relative reactivity[a]		
		Cl	Br	I
n-Octyl methanesulfonate[b]	Catalyst 8[f]	0.64	1.0	(1.0)
n-Octyl methanesulfonate[c]	$C_{16}H_{33}P^+(C_4H_9)_3$	0.64	1.1	(1.0)
Benzyl bromide[d]	Catalyst 8	0.41	—	(1.0)
Benzyl chloride[d]	Catalyst 8	—	0.53	(1.0)
n-Octyl bromide[e]	Catalyst 8	0.36	—	(1.0)

a) Relative to iodide. *b*) From Table III. *c*) From ref. 12*b*. *d*) From ref. 1.
e) The reaction conditions were similar to those described in Table III. The second-order rate constants ($mol^{-1} \cdot cm^3 \cdot s^{-1}$) were 2.9 for Cl and 8.0 for I.
f) [Resin]-$CH_2P^+(C_4H_9)_3$.

It was also interesting to compare the relative reactivity of halide ions in triphase catalysis with that observed under liquid–liquid phase transfer catalytic conditions. As shown in Table VI, the value for catalyst 8 was similar to that observed under corresponding phase transfer conditions. This similarity suggests that the reaction environment around the active site of catalyst 8 is nearly the same as that around the corresponding nonimmobilized phase transfer catalyst under similar reaction conditions.

Contrary to the above conclusion, we had reported[1] that the reaction environment of catalyst 8 was more protic than that around the corresponding nonimmobilized phase transfer catalyst on the basis of the relative reactivity of halide ions for the reaction of benzyl bromide or benzyl chloride (see Table VI). The disagreement may be resolved by the concept that the reactivity of a nucleophile depends on the nature of the leaving group of the substrate.[13] This concept was experimentally confirmed by the result that the reactivity of chloride ion relative to iodide ion for the reaction of *n*-octyl bromide was identical to that for the reaction of benzyl bromide as shown in Table VI. Therefore, we now propose that the reaction environment of catalyst 8 is almost the same as that of the organic phase under liquid–liquid phase transfer catalytic conditions.

Conclusion

An important influence of the structure of the quaternary cation anchored to a support on the triphase catalytic activity was observed when the effect of mass transfer resistance on the rate of reaction was negligible. The structure affected not only the anion–cation interaction energy but also the reaction environment. As the size of the quaternary cation increases the reaction environment approaches a more aprotic state. The reaction environment around the active site of catalyst 8 ([resin]-$CH_2P^+(C_4H_9)_3$) was cosidered to be nearly the same as that of the corresponding nonimmobilized catalyst under liquid–liquid phase transfer conditions.

A dimethylhexadecyl-type catalyst was expected to show anomalous features because the corresponding trimethylhexadecylammonium salt tends to form a stable emulsion or micelles under liquid–liquid phase transfer catalytic conditions. However, the observed kinetic features (reaction order and relative catalytic activity for several anions) were normal for the simple displacement reaction.

Little effect of the central atom of the quaternary cation on the catalytic activity was observed in any reaction tested in this work.

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