[Chem. Pharm. Bull.
32(2) 409—417 (1984)]

Polymer-Supported Phase Transfer Catalysis: Kinetics of a Bromide Ion Displacement Reaction and the Effect of Mass Transfer on the Global Rate of Reaction

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(Received May 20, 1983)

The bromide ion displacement reaction of *n*-octyl methanesulfonate catalyzed by polymer-bound phosphonium ion was studied and the effects of the phosphonium ion content and the degree of cross-linking on the intrinsic activity and the intraparticle diffusion were examined. The catalysts were prepared by quaternization of chloromethylated polystyrene with tri-*n*-butylphosphine. All experiments were carried out in a stirred tank reactor in the temperature range from 60 to 90 °C and at ambient pressure.

The intrinsic rate of reaction was proportional to the concentration of *n*-octyl methanesulfonate, and gradually increased with the concentration of potassium bromide in the aqueous phase. The intrinsic activity decreased with increases in the phosphonium ion content and the degree of cross-linking. The liquid-to-solid mass transfer resistance was insignificant at stirring speeds above 400 rpm under the present conditions. The intraparticle diffusion of *n*-octyl methanesulfonate was found to be an important factor controlling the global rate of reaction. The effective diffusivity of *n*-octyl methanesulfonate in polymer resin decreased remarkably with increase in the degree of cross-linking.

Keywords——phase transfer catalyst; immobilization; polystyrene resin; anion displacement; *n*-octyl methanesulfonate; reaction kinetics; intraparticle diffusion

Polymer-supported catalysts have recently found widespread applications in organic syntheses and related fields.[1,2] The important advantages in using immobilized catalysts are the simplification of product work-up and the easiness of catalyst recovery. In addition, the catalysts can be used in flow reactors.

One interesting and important example is the immobilization of phase transfer catalysts.[3] Since this technique was first proposed by Regen,[4a] many phase transfer catalysts, such as onium salts,[4] crown ethers,[4i,j,5] cryptands,[4j,5b,c,6] and cosolvents,[6] have been immobilized on polymer supports. Though kinetic studies on this reaction system have been done,[4b,d,k,m] the mechanism has not been clarified in detail.

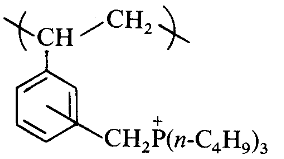
The disadvantages of the immobilization of soluble catalysts may be the reduction in catalytic activity associated with diffusion limitation and the decrease in reactivity of active components. In the case of immobilization of phase transfer catalysts, the catalytic activity decreases with increase in the content of onium groups in the polymer matrix and in the degree of cross-linking.[4f,m] The decrease is considered to be partly due to the changes in the active-site mobility and the microenvironment in the polymer resin.[4g,h] Montanari *et al.*[4j,k] reported that the catalytic activity was enhanced by interposing a long spacer chain between the onium group and the polymer backbone, resulting in an increase in the active-site mobility. Inter- and intraparticle mass transfer resistances are also important factors affecting the catalytic activity.[4d,l,m] Therefore, it is necessary to discuss the intrinsic activity and the effects of mass transfer resistances separately.

Previously, we investigated the kinetic features of anion displacement, the reactivities of anions[7] and the relation between the activity and the structure of onium groups.[8] In the present work, we have investigated the effect of intraparticle diffusion on the global rate of reaction and examined the effects of the content of onium group and the degree of cross-linking on the intrinsic activity and the intraparticle diffusion. The bromide ion displacement reaction of *n*-octyl methanesulfonate, Eq. (1), was chosen as a model reaction, because (i) the rate of reaction is appropriate to study the effects of mass transfer resistances, (ii) the reverse reaction is negligible, and (iii) no reaction occurs in the absence of catalyst.

$$n\text{-}C_8H_{17}OSO_2CH_3 \text{ (org. phase)} + KBr \text{ (aq. phase)} \longrightarrow$$

$$n\text{-}C_8H_{17}Br \text{ (org. phase)} + CH_3SO_3K \text{ (aq. phase)} \qquad (1)$$

catalyst;



The catalyst was prepared by quaternization of chloromethylated polystyrene with tri-*n*-butylphosphine. In order to change the particle size, the degree of cross-linking and the phosphonium ion content, the chloromethylated copolymers were synthesized by suspension copolymerization of styrene, chloromethylstyrene and divinylbenzene.

Experimental

Materials——Unless otherwise stated, all reagents were obtained commercially and used without further purification. *n*-Octyl methanesulfonate was prepared by the procedure reported by Williams *et al.*[9] Bio-Beads S-Xl (1.34 meq chlorine/g, 200—400 mesh) was obtained from Bio-Rad Laboratories. Other copolymers used were prepared by the usual copolymerization of styrene, chloromethylstyrene and divinylbenzene.[4f,m,10]

Catalyst Preparation——A 50 ml culture tube equipped with a Teflon-lined screw cap was charged with 5.0 g of chloromethylated polystyrene and 20 ml of toluene. After tri-*n*-butylphosphine (5.0 g) had been added, the tube was sealed, placed in an oil bath (90 °C) for 70 h, and then cooled to room temperature. The polymer was filtered off and washed with methanol and benzene in a Soxhlet extractor for 24 h. After drying under reduced pressure, the catalyst particles were sieved into the required mesh sizes. The sieving process was repeated several times, and only spherical particles were selected by rolling the catalyst particles on an inclined plane. The sizes of dried and swollen (by the reaction mixture) particles were measured with a microscope. The phosphonium ion content, estimated by elemental analysis, and the degree of cross-linking of the catalysts used are presented in Table II. Since the observed phosphonium ion content did not depend on the catalyst particle size, the phosphonium ion is considered to be homogeneously dispersed in the polymer resin.

Apparatus and Operating Procedure——All kinetic experiments were carried out in a stirred tank reactor (glass, 7.0 cm i.d. and 9.2 cm height) placed in a thermostated bath. Four evenly spaced vertical baffles (9.0 cm high and 0.7 cm wide) were fitted to the wall of the reactor. A six-bladed turbine impeller (3.0 cm in diameter) was used for agitation.

In a typical run, the reactor was charged with 49 ml of toluene, 1 ml of *n*-tridecane (internal standard for gas-liquid chromatography (GLC)), 100 ml of 4.0 M aqueous solution of KBr, and 0.5 g of catalyst. The reaction mixture was stirred at 200 rpm for 1 h to condition the catalyst. The stirring speed was increased to 600—800 rpm, and the reaction was started by adding 0.01 mol of *n*-octyl methanesulfonate. Samples of 0.3 ml of organic phase were taken at intervals of 10—20 min and analyzed by GLC (Shimadzu GC-3BT) with a 2 m × 3 mm column of 2% silicone GE SE-30 on Chromosorb W (AW-DMCS, 80—100 mesh) at 150 °C. The reaction conditions are shown in Table I. Under these conditions, *n*-octyl bromide was produced selectively and the reverse reaction was negligible. No reaction occurred in the absence of catalyst, as shown in Fig. 2.

Results

Kinetics

To investigate the intrinsic kinetics, the rate of reaction was measured by using

Table I. Experimental Conditions

Reaction temperature, °C	60—90
Catalyst loading, g/cm^3	0—1.5×10^{-2}
Concentration of *n*-octyl methanesulfonate in organic phase, mol/cm^3	0.5×10^{-4}—4.0×10^{-4}
Concentration of potassium bromide in aqueous phase, mol/cm^3	0.2×10^{-3}—6.0×10^{-3}
Stirring speed, rpm	0—1000
Volume of organic phase, cm^3	25—50
Volume of aqueous phase, cm^3	50—100

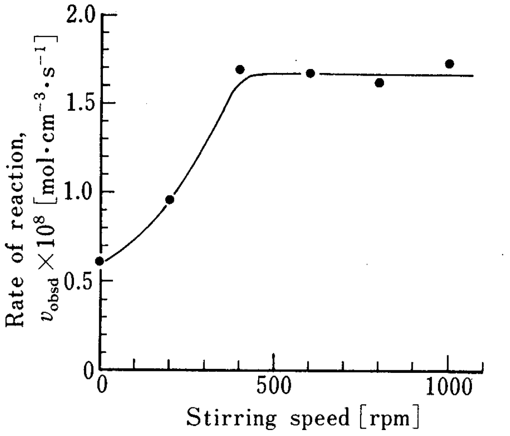


Fig. 1. Effect of Stirring Speed on the Rate of Reaction

Catalyst No. 1: temperature, 85 °C; $C_A=2.0\times10^{-4}$ [mol·cm^{-3}]; $C_B=4.0\times10^{-3}$ [mol·cm^{-3}]; $m=1.0\times10^{-2}$ [g·cm^{-3}].

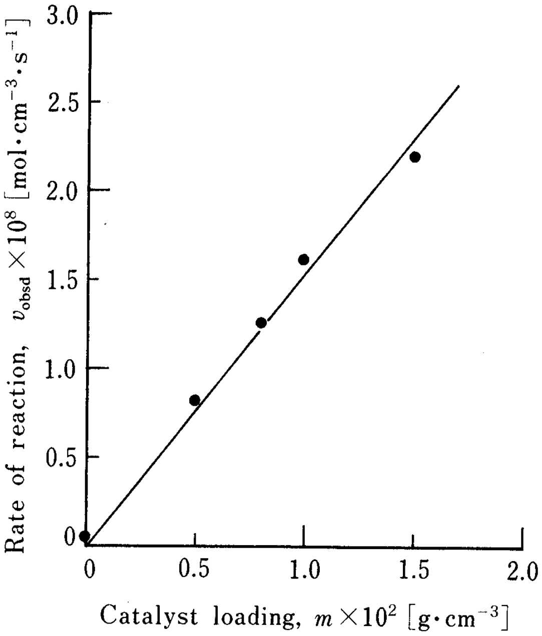


Fig. 2. Effect of Catalyst Loading on the Rate of Reaction

Catalyst No. 1: temperature, 85 °C; stirring speed, 600 rpm; $C_A=2.0\times10^{-4}$ [mol·cm^{-3}]; $C_B=4.0\times10^{-3}$ [mol·cm^{-3}].

sufficiently small particles (catalyst No. 1). First, the effects of mass transfer resistances were examined. The observed rate of reaction, v_{obsd} [mol·cm^{-3}·s^{-1}], is independent of the stirring speed above 400 rpm and is proportional to the catalyst loading, m [g·cm^{-3}] (mass of catalyst per unit volume of organic phase), as shown in Figs. 1 and 2. Here, C_A and C_B are the concentrations of *n*-octyl methanesulfonate in the organic phase and potassium bromide in the aqueous phase, respectively. Tomoi *et al.*[4m] reported that the rates of reaction were almost independent of the stirring speed above 400 rpm, though their rates were larger than those in this work. From these results, it can be concluded that the liquid-to-solid mass transfer resistance is insignificant at stirring speeds above 400 rpm. In the following description, the rate of reaction is represented as gram moles of *n*-octyl methanesulfonate reacted per gram of catalyst per second, v [mol·g^{-1}·s^{-1}].

By the procedure discussed in detail in the following section, the effectiveness factor, η [−], for catalyst No. 1 was calculated to be greater than 0.96,[15] indicating that the intraparticle diffusion resistance can be neglected. The activation energy of this reaction was calculated to be 22.7 [kcal·mol^{-1}] from an Arrhenius plot (Fig. 3).

The reaction is first order with respect to *n*-octyl methanesulfonate in the concentration

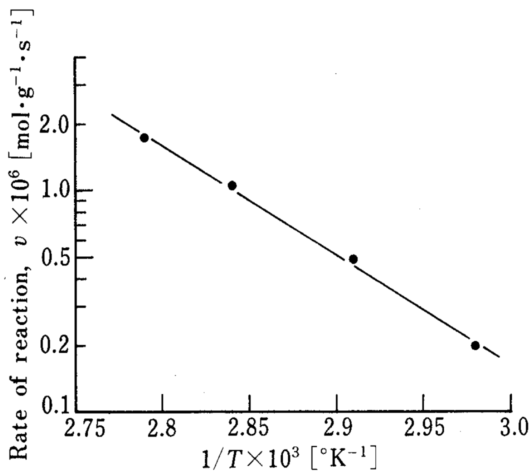


Fig. 3. Arrhenius Plot

Catalyst No. 1: stirring speed, 600 rpm; $C_A = 2.0 \times 10^{-3}$ [mol·cm^{-3}]; $C_B = 4.0 \times 10^{-3}$ [mol·cm^{-3}]; $m = 1.0 \times 10^{-2}$ [g·cm^{-3}].

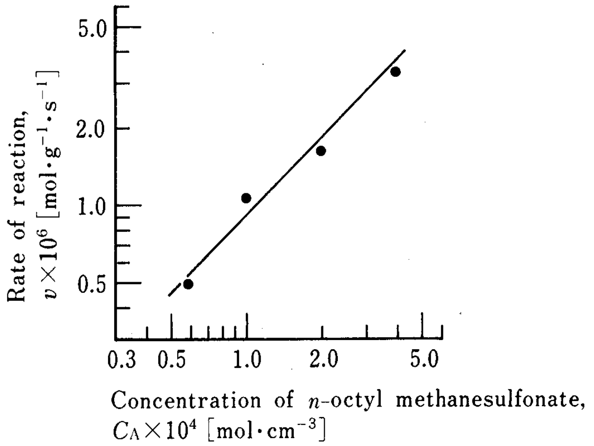


Fig. 4. Dependence of the Rate of Reaction on the Concentration of n-Octyl Methanesulfonate

Catalyst No. 1: temperature, 85 °C; stirring speed, 600 rpm; $C_B = 4.0 \times 10^{-3}$ [mol·cm^{-3}]; $m = 1.0 \times 10^{-2}$ [g·cm^{-3}].

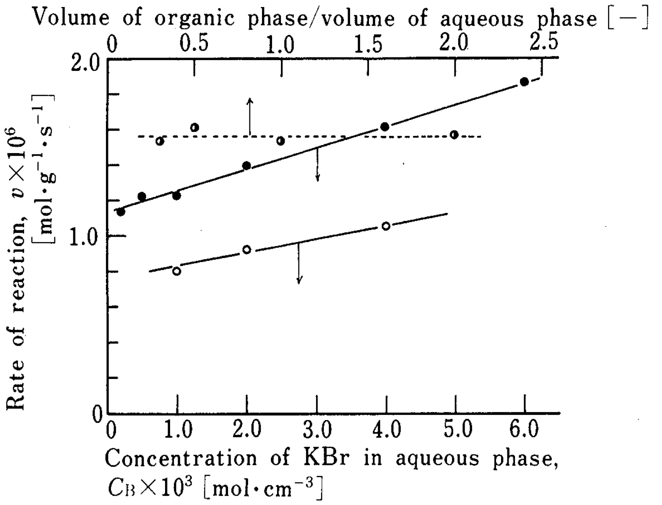


Fig. 5. Dependence of the Rate of Reaction on the Concentration of Potassium Bromide and the Volume Ratio of Organic to Aqueous Phase

●, catalyst No. 1; ○, catalyst No. 4. Temperature, 85 °C; stirring speed, 600 rpm; $C_A = 2.0 \times 10^{-4}$ [mol·cm^{-3}]; $m = 1.0 \times 10^{-2}$ [g·cm^{-3}].

range from 0.6×10^{-4} to 4.0×10^{-4} [mol·cm^{-3}], as shown in Fig. 4.

The effects of the concentration of potassium bromide in aqueous phase and the volume ratio of organic to aqueous phase are shown in Fig. 5. The rate of reaction is independent of the volume ratio, whereas it gradually increases with the concentration of potassium bromide, even near the saturated concentration (*ca.* 6.0×10^{-3} [mol·cm^{-3}]). For catalyst No. 1, a linear relationship existed between v and C_B in the range from 0.25×10^{-3} to 6.0×10^{-3} [mol·cm^{-3}]. A similar relationship was obtained with the small particles of catalyst No. 4 (smaller than 200 mesh). This catalyst contains about half as much phosphonium ion as catalyst No. 1. Thus, the rate of reaction is well expressed by Eq. (2).

$$v = k^* (1 + \alpha C_B) C_A \qquad (2)$$

where the parameters, k^* and α, were estimated as follows:

$\alpha = 1.10 \times 10^2$ [cm^3·mol^{-1}] for both catalysts

$k^* = 5.63 \times 10^{-3}$ [cm^3·g^{-1}·s^{-1}] for catalyst No. 1

$k^* = 3.67 \times 10^{-3}$ [cm^3·g^{-1}·s^{-1}] for catalyst No. 4

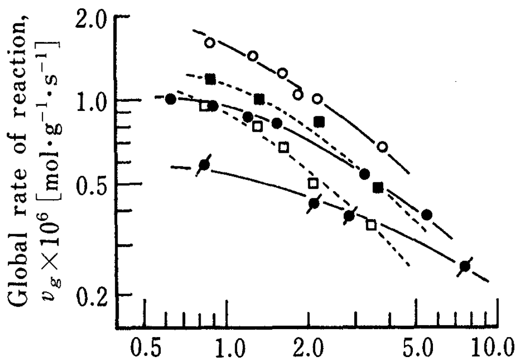


Fig. 6. Dependence of the Global Rate of Reaction on the Radius of Catalyst Particles

—●—, catalyst No. 3; —●—, catalyst No. 4; ---■---, catalyst No. 6; ---□---, catalyst No. 7; —○—, catalyst No. 8.

Temperature, 85 °C; stirring speed, 600 rpm; $C_A = 2.0 \times 10^{-4}$ [mol·cm^{-3}]; $C_B = 4.0 \times 10^{-3}$ [mol·cm^{-3}]; $m = 1.0 \times 10^{-2}$ [g·cm^{-3}].

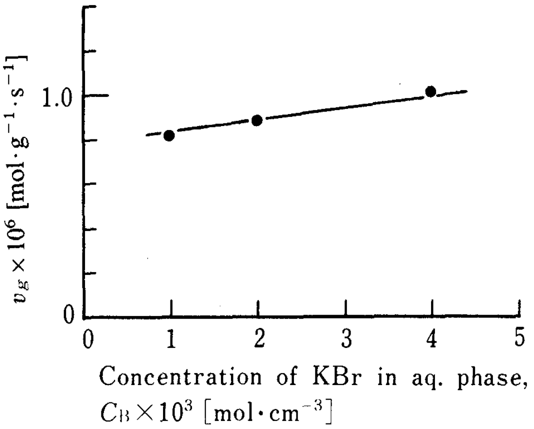


Fig. 7. Dependence of the Global Rate of Reaction on the Concentration of Potassium Bromide

Catalyst No. 8 ($r_s = 0.0235$ cm): temperature, 85 °C; stirring speed, 600 rpm; $C_A = 2.0 \times 10^{-4}$ [mol·cm^{-3}]; $m = 1.0 \times 10^{-3}$ [g·cm^{-3}].

The Effect of Intraparticle Diffusion

The effect of intraparticle diffusion on the global rate of reaction, v_g [mol·g^{-1}·s^{-1}], was investigated with various catalysts (catalyst Nos. 3—8). In Fig. 6, the rates of reaction are plotted against the radius, r_s [cm], for each catalyst. r_s is the mean radius of swollen particles. Since an excess of potassium bromide was used, the concentration could be assumed to be constant throughout the course of reaction.

In all cases, the rate of reaction decreases with the particle radius, indicating that the intraparticle diffusion controls the rate of reaction. The dependence of the rate of reaction on particle radius increases with both the phosphonium ion content, a [mol·g^{-1}], and the degree of cross-linking.

The relation between v_g and C_B observed for the larger particles (catalyst No. 8: $r_s = 0.0235$ [cm]) is shown in Fig. 7. The rate of reaction increases slightly with the concentration of potassium bromide.

Discussion

Kinetic Analysis

The mechanism of liquid–liquid phase transfer catalysis with onium salts is well established.[11] Regen *et al.*[4b,d] and Montanari *et al.*[4k] reported that the phase transfer catalysis with onium salts immobilized on a polymer support proceeds by a mechanism similar to that of liquid–liquid phase transfer catalysis. We also reached the same conclusion in the previous paper.[7] Thus, the following reaction model can be assumed for the bromide ion displacement reaction of *n*-octyl methanesulfonate.

$$\text{P-OSO}_2\text{CH}_3 + \text{KBr (aq. phase)} \overset{K}{\rightleftharpoons} \text{P-Br} + \text{CH}_3\text{SO}_3\text{K (aq. phase)} \quad (3)$$

$$n\text{-C}_8\text{H}_{17}\text{OSO}_2\text{CH}_3 \text{ (org. phase)} + \text{P-Br} \xrightarrow{k} n\text{-C}_8\text{H}_{17}\text{Br (org. phase)} + \text{P-OSO}_2\text{CH}_3 \quad (4)$$

where "P-" represents the phosphonium ion supported on the polymer matrix. The ion exchange between methanesulfonate and bromide forms of resin (Eq. (3)) is assumed to be in equilibrium. If the bromide ion displacement of *n*-octyl methanesulfonate with polymer-bound phosphonium bromide (Eq. (4)) is the rate-determining step, v can be expressed as

$$v = kC_{\mathrm{A}}\frac{KC_{\mathrm{B}}}{C_{\mathrm{X}}+KC_{\mathrm{B}}} \tag{5}$$

where C_{X} is the concentration of potassium methanesulfonate in the aqueous phase, and k and K are the rate and equilibrium constants, respectively.

As shown in Fig. 4, this reaction is actually first order with respect to *n*-octyl methanesulfonate. However, the rate of reaction increases with the concentration of potassium bromide (Fig. 5). Since an excess of potassium bromide was used under our experimental conditions and K is considered to be sufficiently large,[11b)] ($C_{\mathrm{X}} \ll KC_{\mathrm{B}}$), Eq. (5) can be simplified to

$$v = kC_{\mathrm{A}} \tag{6}$$

Thus, the increase in the rate of reaction with the concentration of potassium bromide cannot be explained by this model. This increase is considered to be mainly due to changes of the microenvironment in the polymer resin. An increase in the salt concentration reduces the amount of imbibed water in the polymer resin and alters the microenvironment to a more aprotic one.[4g,h)] As a result, the anion reactivity increases with the concentration of potassium bromide. More detailed investigations are necessary for a clear understanding to this phenomenon.

Under our experimental conditions, the rate of reaction was well approximated by Eq. (2), and only k^* depends on the phosphonium ion content.

The Effect of Intraparticle Diffusion

In this section, the intraparticle diffusion effects (Fig. 6) are analyzed, and the effects of the phosphonium ion content and the degree of cross linking on the global rate of reaction are considered. Since an excess of potassium bromide was used under our experimental conditions, the dependence of the reaction rate on the particle radius is assumed to be due to the intraparticle mass transfer resistance of *n*-octyl methanesulfonate.

According to the theory of reaction engineering kinetics,[12)] the global rate of reaction can be expressed as

$$v_g = \eta v_o \tag{7}$$

where v_o is the intrinsic rate of reaction, and η [$-$] is the effectiveness factor. As described in the previous section, the reaction is first order with respect to *n*-octyl methanesulfonate. For a first order reaction, η can be expressed in terms of the Thiele modulus, ϕ_1 [$-$].

$$\eta = \frac{3}{\phi_1}\left\{\frac{1}{\tanh\phi_1} - \frac{1}{\phi_1}\right\} \tag{8}$$

$$\phi_1 = r_s\sqrt{\frac{k_1\rho_p}{D_e}} \tag{9}$$

where ρ_p [$\mathrm{g\cdot cm^{-3}}$] is the particle density, k_1 [$\mathrm{cm^3\cdot g^{-1}\cdot s^{-1}}$] is the first order rate constant per unit mass of catalyst, and D_e [$\mathrm{cm^2\cdot s^{-1}}$] is the effective diffusivity in the polymer matrix. Based on these equations and the relations of v_g to r_s (Fig. 6), the values of k_1 and D_e for each catalyst can be estimated by the regression method (Table II). As shown in Fig. 8, the calculated global rates, $(v_g)_{\mathrm{cal}}$, agree well with the observed data, $(v_g)_{\mathrm{obsd}}$.

The relation between v_g and C_{B} in Fig. 7 was obtained for larger particles of catalyst No. 8. The line calculated from Eqs. (7)—(9) and by use of the values for catalyst No. 8 in Table II agrees well with the experimental data. If the intraparticle mass transfer resistance of

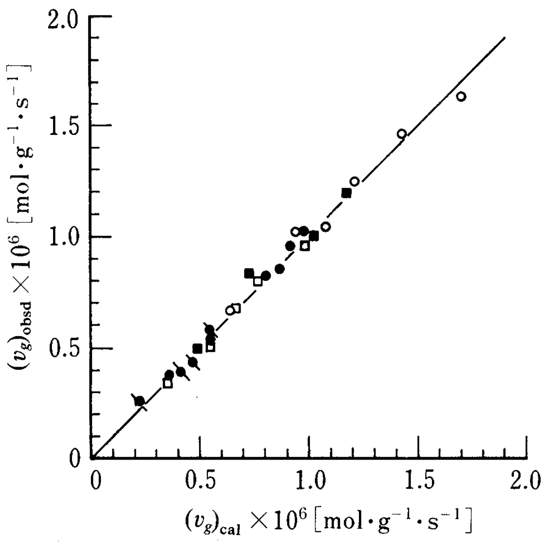


Fig. 8. Comparison of Observed v_g with Calculated v_g

Symbols are the same as in Fig. 6.

TABLE II. Properties of Catalysts and Calculated Parameter Values

Cat. No.	Phosphonium ion content, $a \times 10^3$ [mol·g^{-1}]	Cross-linking [%]	Volume swelling, s [−]	$k_1 \times 10^3$ [cm^3·g^{-1}·s^{-1}]	$D_e \times 10^7$ [cm^2·s^{-1}]	k_1/a [cm^3·mol^{-1}·s^{-1}]
1[a]	0.95	1	—	8.05	—	8.47
2	0.14	1	—	1.54	—	11.0
3	0.28	1	3.40	2.81	1.25	10.0
4	0.57	1	3.05	4.98	1.13	8.74
5	1.03	1	2.55	8.64	1.11	8.39
6	1.03	3	2.10	7.10	0.870	6.89
7	1.03	5	1.90	6.80	0.422	6.60
8	1.54	1	1.86	11.0	1.07	7.14

[a] Bio-Beeds S-X1 was used as chloromethylated polystyrene.

potassium bromide is significant, the global rate of reaction should decrease more with decrease in the concentration of potassium bromide. Based on these results, it is concluded that the intraparticle mass transfer resistance of *n*-octyl methanesulfonate is the important factor limiting the rate of reaction under our experimental conditions.

It is interesting to compare the obtained values of k_1 and D_e with the properties of the catalyst, such as the phosphonium ion content and the degree of cross-linking. In Table II, k_1/a is the intrinsic rate constant per unit mole of phosphonium ion in the polymer resin, corresponding to the intrinsic activity per unit mole of phosphonium ion, and the extent of swelling, s [−], is defined as the volume ratio of swollen to dried particles. $k_1/a, D_e$ and s are plotted *versus* the phosphonium ion content and the degree of cross-linking in Figs. 9 and 10. The intrinsic activity and the extent of swelling decrease in the same pattern with increase in the phosphonium ion content and the degree of cross-linking, whereas the effective diffusivity is more sensitive to the degree of cross-linking than to the phosphonium ion content.

It is considered that the intrinsic activity (k_1/a) depends on both the mobility and hydration state of pendant phosphonium groups, and these factors are controlled by the nature of the microenvironment and by the flexibility of the polymer resin.[4g,h,13] As the phosphonium ion content increases, the polymer catalyst becomes more hydrophilic, so that high mobility of pendant phosphonium groups is maintained only in an aqueous-like environment.[4g] When the salt concentration in the aqueous phase is very high, as under the

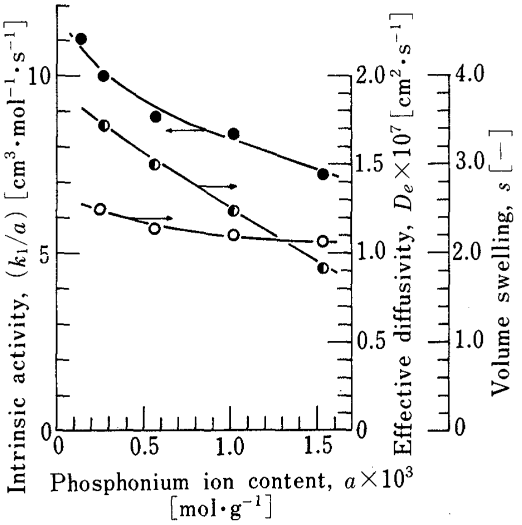


Fig. 9. Intrinsic Activity and Effective Diffusivity *vs.* the Phosphonium Ion Content

●, (k_1/a); ○, D_e; ◐, s.

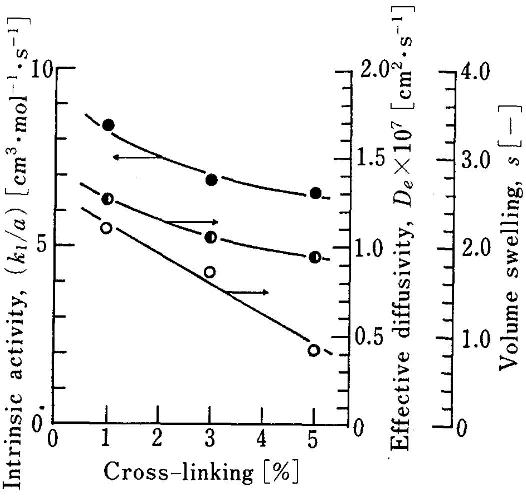


Fig. 10. Intrinsic Activity and Effective Diffusivity *vs.* the Degree of Cross-Linking

●, (k_1/a); ○, D_e; ◐, s.

present conditions, the phosphonium group is more hydrated with increase in the phosphonium ion content, but the required amount of water to maintain high mobility of the pendant groups is not imbibed in the polymer resin. Therefore, the decrease in k_1/a as shown in Fig. 9 is ascribed to the higher hydration state and to the decrease in the mobility of phosphonium groups. The decrease in the activity at higher degrees of cross-linking (Fig. 10) can be also ascribed to the decrease in mobility, because the cross-linking reduces the flexibility of the polymer resin.

The effective diffusivity in polymer matrix is influenced by many factors, such as the extent of swelling, the degree of cross-linking, the nature of the microenvironment and the interaction of the diffusing substance with the polymer.[14] Tomoi *et al.*[4l,m] reported that the rate of diffusion decreased with increase in the degree of cross-linking and that this decrease could be ascribed to the decrease in the extent of swelling. In the present work, a similar result was observed (Fig. 10), but the effective diffusivity decreased slightly with the content in spite of the substantial decrease in the extent of swelling (Fig. 9). Usually, the rate of diffusion is proportional to the porosity of the catalyst particle and inversely proportional to the complexity of the diffusion path. Accordingly, it may be concluded that the increase in phosphonium ion content reduces the porosity along with the decrease in the extent of swelling, and that the cross-linking increases the complexity of the diffusion path in addition to the decrease in porosity. However, it may be necessary to take into account many other factors.

Conclusions

Results obtained from this study indicate that the efficiencies of phase transfer catalysts immobilized on polymer resin are influenced by the environment inside and outside the polymer resin, and by the liquid-to-solid and intraparticle mass transfer resistances.

The bromide ion displacement reaction of *n*-octyl methanesulfonate proceeds by a mechanism (Eqs. (3) and (4)) similar to that of liquid–liquid phase transfer catalysis. Under our experimental conditions, the ion exchange between methanesulfonate and bromide forms of the resin (Eq. (4)) is in equilibrium and the rate-determining step is the bromide ion displacement of *n*-octyl methanesulfonate with polymer-bound phosphonium bromide. The intrinsic activity decreases as the concentration of potassium bromide decreases. Moreover, the increases in both the phosphonium ion content and the degree of cross-linking decrease the intrinsic activity. These effects are considered to be due to changes in the nature of the microenvironment and the flexibility of the polymer resin.

The liquid-to-solid mass transfer resistance is negligible at stirring speeds above 400 rpm, but the intraparticle diffusion of *n*-octyl methanesulfonate is an important factor limiting the overall activity of the catalyst. The effective diffusivity of *n*-octyl methanesulfonate in polymer resin is sensitive to the degree of cross-linking rather than to the phosphonium ion content, because of the increase in the complexity of the diffusion path with the degree of cross-linking. Also, the rate of diffusion may depend on the amount of water imbibed in the polymer resin.

A better understanding of the relation of the microenvironment in the polymer matrix to the properties of the polymer resin and the reaction conditions is needed to develop more effective catalysts.

Acknowledgement We are grateful to Mr. Tenshoku Kyo for his assistance in this work.

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15) Since the properties of catalyst No. 1 (the activity and the degree of cross-linking) are almost the same as those of catalyst No. 5, the effectiveness factor for catalyst No. 1 was calculated from Eqs. (8) and (9) and by using the values for catalyst No. 5 in Table II.