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The Use of Silica Gel-Supported Ionenes as Reagents and Catalysts for Several Substitution Reactions in Toluene[1)]

Noritaka OHTANI,* Kosaku CHIDA, Hajime SERITA,† Toshiaki MATSUNAGA,† and Chikai KIMURA††
Department of Chemical Engineering for Resources, Mining College, Akita University, Tegata-Gakuencho, Akita 010
†Department of Fuel Chemistry, Mining College, Akita University, Tegata-Gakuencho, Akita 010

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Several ionene bromides were used as reagents for the displacement of decyl methanesulfonate into 1-bromodecane. They were very reactive when adsorbed by silica gel. The enhanced activities of the ionenes were hardly dependent on their structures and molecular weights but decreased gradually with increasing the amount of ionene adsorbed by silica gel. Ionene chlorides exhibited a similar enhancement of reactivity when adsorbed by silica gel. However, unlike the ionenes, a large increase in activity due to adsorption was not observed with pendant-type polycations such as poly(4-vinylpyridinium bromide) and poly[(4-vinylbenzyl)tributylammonium chloride]. The silica gel-supported ionenes also exhibited excellent catalytic activities for solid-liquid-solid triphase substitution reactions, particularly for the reactions between 1-bromodecane and such inorganic salts as consisted of relatively hard-basic nucleophilic anions.

It is well-known that lipophilic quaternary ammonium salts are not only good nucleophilic reagents in nonpolar media but also excellent phase-transfer catalysts.[2)] In order to simplify salt recovery and product isolation, the salts have been covalently attached as a pendant group, either to the matrix of swellable cross-linked polymer or to the surface of porous inorganic materials.[3–6)] To those insoluble materials, the salts have been introduced usually at random, which leads to an ambiguous distribution of active sites and an unavoidable assumption about the microenvironment around the active sites. Furthermore, immobilization of the salts gives rise, in most cases, to the reduction of overall activities of the salts, which has been explained in terms of diffusional limitation.[5)]

On the other hand, few reports except two studies[7,8)] have been concerned with reaction and catalysis of the quaternary salts which are adsorbed by inorganic materials. If the quaternary salts are lipophilic, however, this reaction system is likely of little value because the salts are in dynamic equilibrium between adsorbed and desorbed states.[7)] This equilibrium makes it difficult to evaluate the influence of adsorbent unless the adsorption induces a drastic change in activities of the salts. The equilibrium also makes it difficult to accomplish a complete recovery of the salts.

Ionenes are a specific kind of polycations having a definite chemical structure in which quaternary ammonium groups are spaced regularly along the polymer backbone.[9)] Generally, they are quite hydrophilic and easily soluble in water but most of them are neither soluble nor swellable in nonpolar organic solvents. This nature of the ionenes has restricted their use only to aqueous reaction systems. Thus, we have successfully utilized them as catalysts for aqueous interionic reactions[10)] and as flocculants of aqueous kaolin suspension.[11)]

This work demonstrates the applicability of some hydrophilic ionenes, which are shown in Fig. 1(a)—(d), to excellent reagents and catalysts of various substitution reactions in toluene under the conditions where the ionenes are deposited on the surface of silica gel or other inorganic supports. The method is quite simple. After silica gel and a methanol solution of the ionenes (x—y, X) were mixed and equilibrated, the mixture was evaporated to dryness. The obtained silica gel-ionenes complexes (x—y, X/silica gel) were used as reagents of the liquid-solid biphase reactions (Eq. 1) or as catalysts for the solid-liquid-solid triphase catalytic reactions (Eq. 2).

$$\begin{gathered} n\text{-}\mathrm{C_{10}H_{21}OMs} + x\text{-}y,\ \mathrm{X/silica\ gel} \\ \longrightarrow n\text{-}\mathrm{C_{10}H_{21}X} + x\text{-}y,\ \mathrm{OMs/silica\ gel} \qquad (1) \\ \mathrm{X = Cl\ or\ Br,\ OMs = CH_3SO_3} \end{gathered}$$

$$\begin{gathered} n\text{-}\mathrm{C_{10}H_{21}X + KY(solid)} \\ \xrightarrow{x\text{-}y,\ \mathrm{Br/silica\ gel}} n\text{-}\mathrm{C_{10}H_{21}Y + KX(solid)} \qquad (2) \\ \mathrm{X = OMs\ or\ Br,\ Y = I,\ CN,\ Br,\ OPh,\ or\ OAc} \end{gathered}$$

The rate enhancement through adsorption has been examined for the ionenes as well as some pendant-type polycations as shown in Fig. 1(e)—(g).

Experimental

Materials. Commercial α,ω-alkanediamines and piperazine were converted to the corresponding α,ω-bis(dimethylamino)alkanes and N,N'-dimethylpiperazine using formalin-formic acid. α,ω-Dihaloalkanes and α,α'-dichloro-p-xylene were purchased and distilled.

Ionene polymers (x—y, X) were prepared from the reaction of the N-methylated diamines with the equimolar dihalides under the conditions previously reported.[11)] 2-Hydroxy-3-ionene chloride, 3-OH, Cl was prepared according to the literature.[12)] The intrinsic viscosities of the ionenes were measured. The data are summarized as follows: x-y, X, $[\eta]$/dl g^{-1} (25 °C, aq 0.4 mol dm^{-3} KBr unless otherwise stated); 2-5, Br, 0.12; 3-3, Br, 0.07; 3-4, Br(I), 0.22; 3-4, Br(II), 0.15; 3-4, Br(III), 0.10; 3-6, Br, 0.15; 4-4, Br, 0.05; 6-2, Br,

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[††] Present address: Tokyo Kasei University, Kaga, Itabashi-ku, Tokyo 173.

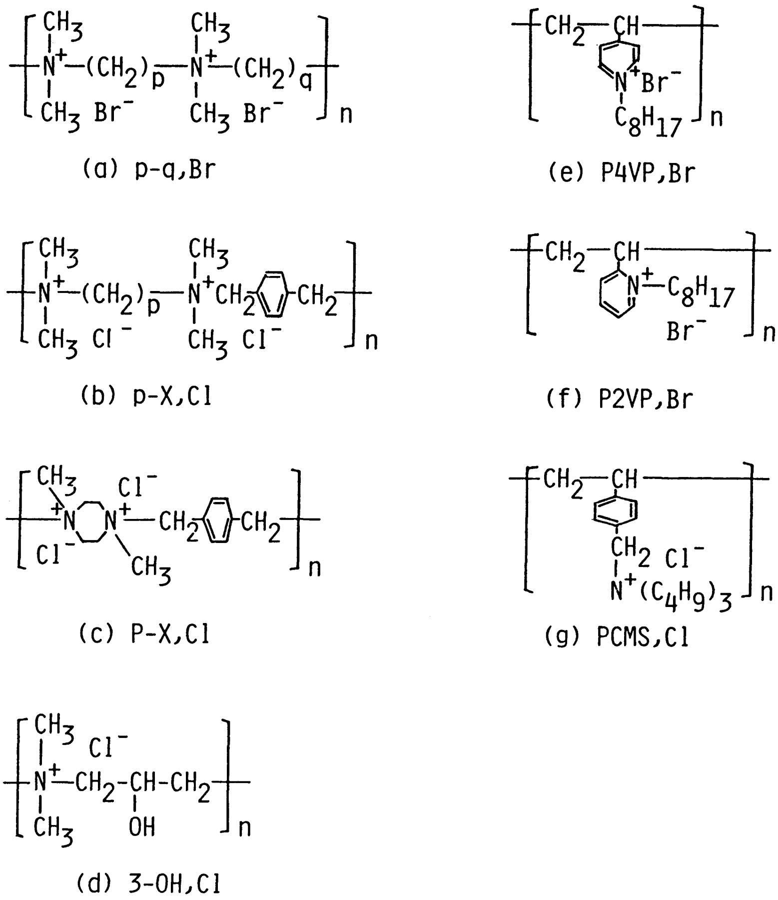
(a) p-q,Br
(b) p-X,Cl
(c) P-X,Cl
(d) 3-OH,Cl
(e) P4VP,Br
(f) P2VP,Br
(g) PCMS,Cl

Fig. 1. Ionenes and pendant-type polycations used.

0.09; 6-6, Br, 0.19; 2-X, Cl, 0.18 (0.3 mol dm^{-3} KBr); 3-X, Cl, 0.21; 6-X, Cl, 0.23 (0.3 mol dm^{-3} KBr); P-X, Cl, 0.18 (0.2 mol dm^{-3} KBr); 3-OH, Cl, 0.08. The viscosity-molecular weight relationships for ionenes are available only for 3-4, Br and 6-6, Br.[13] The molecular weights of 3-4, Br(I), 3-4, Br(II), 3-4, Br(III), and 6-6, Br were 40000, 27000, 15000, and 20000, respectively.

Freshly distilled 2- and 4-vinylpyridines were polymerized and then quaternized by 1-bromooctane,[14] to give P2VP, Br and P4VP, Br. Poly[4-(chloromethyl)styrene] was prepared by suspension polymerization of distilled 4-(chloromethyl)-styrene using benzoyl peroxide for 7 h at 80 °C and was purified to remove insoluble crosslinked resins through several reprecipitations using dioxane-methanol. The linear poly[4-(chloromethyl)styrene] was reacted with tributylamine in *N*,*N*-dimethylformamide [14 d, 50 °C] to give the corresponding ammonio-attaching polystyrene, PCMS, Cl. The molecular weight and the degree of quaternization of P2VP, Br, P4VP, Br, and PCMS, Cl were measured according to the literature:[14] Polycation, molecular weight, degree of quaternization; P2VP, Br, 450000, 37.4%; P4VP, Br, 74000, 79.7%; PCMS, Cl, —, 60.0%.

Silica gel (Wakogel C-200, 100—200 mesh), activated alumina (Wako, abt. 200 mesh), neutral alumina (Wako, W-200), and activated carbon powder (Wako, —200 mesh) were dried in vacuo prior to use [3 h, 110 °C]. Molecular Sieves (Wako, 4A 1/16) was ground to a powder and was dried prior to use. The specific surface area of the inorganic supports was measured on Yanagimoto Surface Area Analyzer GSA-10.

Potassium phenoxide, prepared from neutralization of phenol with aqueous potassium hydroxide, and all other commercial solid inorganic reagents were also dried [3 h, 110 °C in vacuo]. Decyl methanesulfonate (abbreviated as decyl mesylate hereinafter) was prepared by the reaction of 1-decanol with methanesulfonyl chloride,[15] and was purified by vacuum distillation.

Silica Gel-Supported Ionenes. A given amount of the pre-dried silica gel was added in one portion to a stirred solution of an ionene in 30 ml of methanol or ethanol. The mixture was stirred for 1 h at room temperature. The solvent was then evaporated and the resulting ionene-silica gel complex (abbreviated as complex hereinafter) was dried in vacuo at 110 °C for 3 h. Other supported polycations were also prepared by the same procedure. Ion content, the ammonium content per gram of the complex, was adjusted to be 0.25 mmol g^{-1} unless stated otherwise. For comparison with the ionenes, potassium bromide and sodium chloride were also supported on silica gel in a manner similar to the literature.[16]

Ionene Halide as a Reagent for Nucleophilic Substitution Reactions. A 25 ml culture tube with a Teflon-lined screw cap was charged with 0.073 mmol of ionene supported or nonsupported plus 1.0 ml of toluene containing pentadecane as an internal standard. The tube was placed in an oil bath maintained at 90 °C and the mixture was stirred for 20 min with a Teflon-coated magnetic stirring bar, followed by injection of 0.073 mmol of decyl mesylate via a syringe.

The disappearance of the mesylate and the appearance of 1-halodecane in the toluene phase were followed by GLC (Hitachi 163 Gas Chromatograph).

Ionene Halides as Solid-Liquid-Solid Triphase Catalysts. To a 25 ml culture tube with a Teflon-lined screw cap was added 5 mmol of solid reagent salt (KBr, NaI, NaCN, KOPh, or KOAc), 0.05 mmol of a polycation supported or nonsupported, and 4.0 ml of toluene containing pentadecane as an internal standard. The mixture was stirred for 1 h at 90 °C, followed by injection of decyl mesylate (0.8 mmol) or 1-bromodecane (0.7 mmol). The substrates and the products were quantitatively analyzed by GLC.

Results and Discussion

Ionene Halide as a Reagent. Nonsupported ionene bromides were all insoluble in toluene. They were very slow to react with the eqimolar amount of decyl mesylate. The results of typical ionene bromides are shown in Fig. 2. The reactions did not follow second-order kinetics. Even after several days, the substantial parts of the bromides were found to remain unreacted.

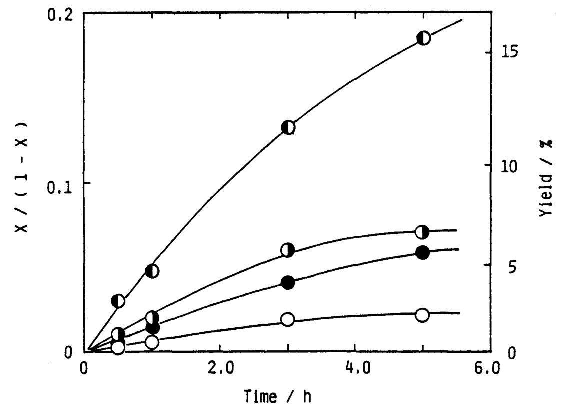

Fig. 2. Reaction of nonsupported ionene bromides with decyl mesylate.
x; yield 1-bromodecane.
●, 3-3, Br; ○, 3-4, Br(I); ◑, 4-4, Br; ◐, 6-6, Br.

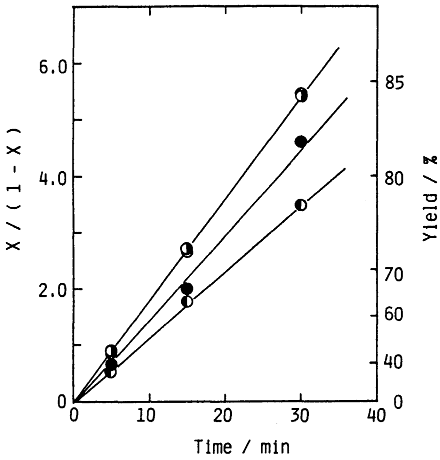

Fig. 3. Reaction of silica gel-supported ionene bromides with decyl mesylate.
●, 3-3, Br; ○, 3-4, Br(I); ◑, 4-4, Br; ◐, 6-6, Br.

When the ionene bromides were supported on silica gel, however, the rates of the substitution were dramatically increased as shown in Fig. 3. The reactions were completed in a few hours. A plot of $x/(1-x)$ vs. reaction time was almost linear for all the supported ionenes, indicating that the reactions were of second order, that is, first order with respect to both decyl mesylate and ammonium bromide. This also indicates that all the ammonium bromides of one ionene have an equal reactivity. The desorption of the ionenes during the reactions was neglected because the weight loss of 3-4, Br complex was not observed after the complex was soaked in toluene for 1 h at 90 °C, separated by filtration, and dried in vacuo. The second-order rate constants calculated from the slopes of the plots are in the narrow range of 2.7×10^{-3} to 4.3×10^{-3} $mol^{-1}\,dm^3\,s^{-1}$, which are comparable to the reported data for organic-soluble quaternary onium salts.[17] Despite of a polar nature of silica gel surface, the high reactivities observed for the adsorbed ionenes are striking. The results of silica gel-supported and nonsupported ionene bromides are summarized in Table 1 together with the results of P4VP, Br, P2VP, Br, and KBr. It should be noted again that the reactivity of silica gel-supported ionene bromides was hardly dependent on the ionene structure and that the reactivity was much higher than that of nonsupported ionene bromides.

These results clearly indicate that, being adsorbed on silica gel, the ionenes allow decyl mesylate to diffuse easily to active sites and provide an increased number of the active sites. Ionene bromides are crystalline polymers.[9] They have crystalline regions under the nonsupported state. The ammonium bromides in the crystalline region are likely difficult to react. It is therefore assumed that the difference in reactivity of the nonsupported ionenes is attributable partly to the difference in the morphological structure aside from the influence of the powder size.

Table 1. Substitutions of Decyl Mesylate into 1-Bromodecane Using Nonsupported and Silica Gel-Supported Ionene Bromides[a)]

Ionene bromide	Yield/%	
	Nonsupported	Supported
2-5, Br	1.4	94.4
3-3, Br	4.0	97.0
3-4, Br(I)	1.7	97.9
3-6, Br	0.1	99.2
4-4, Br	5.6	98.0
6-2, Br	2.2	96.1
6-6, Br	11.9	95.9
P4VP, Br	64.2	86.0
P2VP, Br	3.5	44.2
KBr	1.0[b)]	28.9[b)]

a) Reactions were carried out in toluene at 90 °C for 3 h: n-$C_{10}H_{21}OMs$, 0.0734 mmol; ammonium bromide, 0.0734 mmol; toluene, 1.0 ml. b) Yield after 20 h.

The adsorption to silica gel possibly induces the destruction of the crystalline region and also weakens the electrostatic interaction among the ammonium bromide ion pairs, so that the formation of aggregates of the ion pairs becomes difficult.

As shown in Fig. 4 (solid line), silica gel-supported 3-4, Br gave an identical reactivity irrespective of molecular weight of the ionene. This fact and the equal reactivity of the ammonium bromides in one ionene strongly suggest uniform and monolayer coverage of ionene over the silica gel surface. The result shown in Fig. 5 supports the validity of the assumption. At low levels of loading on silica gel, 3-4, Br exhibited a constant reactivity. But, beyond 0.5 mmol g^{-1} of ion content, the reactivity of the 3-4, Br complex decreased with increasing loading. The specific surface area of the silica gel was ca. 270 m^2 g^{-1} obtained from BET measurement. Since the maximum cross section per mmol of ammonium unit, estimated from CPK model, is ca. 200 m^2 when 3-4, Br molecule is fully extended, it seems reasonable to assume monolayer adsorption in the case of low ion content.

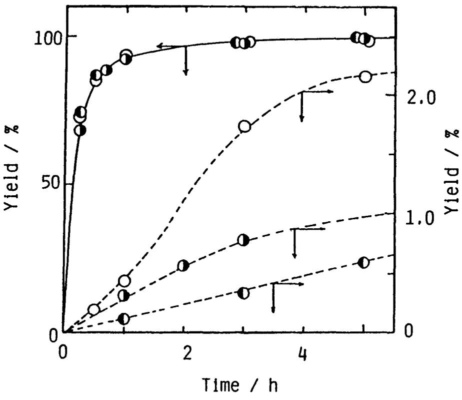

Fig. 4. Effect of molecular weight on the activities of nonsupported and silica gel-supported 3-4, Br toward decyl mesylate.
○, 40000; ◐, 27000; ◑, 15000.——,supported. ----,nonsupported.

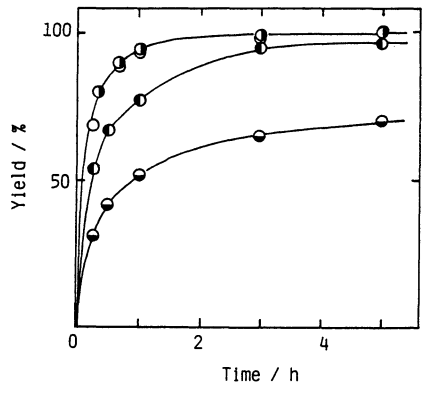

Fig. 5. Effect of ion content on the activity of silica gel-supported 3-4, Br toward decyl mesylate.
○, 0.25; ◑, 0.50; ◐, 1.00; ◒, 2.00 mmol g^{-1}.

P4VP, Br was relatively active without any carrier, whereas P2VP, Br was as poorly active as ionene bromides (Table 1). P4VP, Br swells well in toluene. The high reactivity and swellability imply the absence of the extensive aggregation among the ion pairs of P4VP, Br. Therefore, an increase in activity due to adsorption was not significant for P4VP, Br, while P2VP, Br exhibited a moderate improvement. It is noted that, under the adsorbed state, these pendant-type polycations are not so reactive as ionene bromides. This implies either the relatively weak interaction of the pendant ammonio groups with the silica gel surface or the presence of a dynamic equilibrium of the ammonio groups between adsorbed and desorbed states to form a sort of looped structure of the polymer chains over the silica gel surface. The looped structure is often assumed in the case of the adsorptions of linear polyelectrolytes from aqueous solutions.[18]

As mentioned above, the state of adsorption may be a primary factor to determine the effectiveness of this reaction system. An additional factor to influence the reaction rate is the local concentration of decyl mesylate. Since 0.3 g of uncoated silica gel adsorbs 54% of decyl mesylate from the reaction mixture, decyl mesylate is undoubtly concentrated around the active sites, whereas the adsorption of the product, 1-bromodecane, is as small as 1%.

Figure 6 shows the effect of carriers upon the reactivity of 6-6, Br supported on them. The yield of 1-bromodecane increased in the order of silica gel>activated carbon>Molecular Sieves 4A>activated alumina. This order did not correlate to an ability of carrier to adsorb decyl mesylate from the reaction mixture; silica gel (54%)>activated alumina (34%)>active carbon (8%)>Molecular Sieves 4A (6%). These facts suggest that the interaction between support surface and ammonium bromides is important and that silica gel may attract preferentially ammonium ions to make bromide counter ions somewhat free from the electrostatic restraint of the ammonium ions.

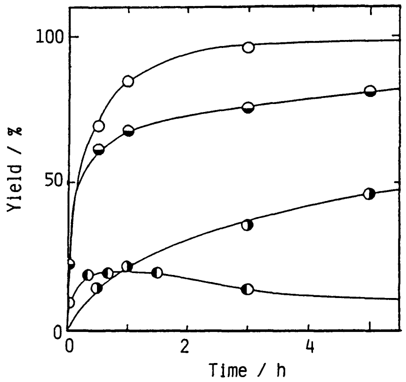

Fig. 6. Effect of carrier on the activity of supported 6-6, Br toward decyl mesylate.
○, silica gel; ◐, activated alumina; ◒, active carbon; ◑, Molecular Sieves 4A.

Table 2. Substitution of Decyl Mesylate into 1-Chlorodecane Using Nonsupported and Silica Gel-Supported Ionene Chlorides[a)]

Ionene Chloride	Yield/%	
	Nonsupported	Supported
2-X, Cl	1.3	74.6
3-X, Cl	0.5	72.0
6-X, Cl	4.1	75.9
P-X, Cl	1.9	79.8
3-OH, Cl	0.0	71.9
PCMS, Cl	66.6	89.2
NaCl	0.0[b)]	16.0[b)]

a) Reactions were carried out in toluene at 90 °C for 3 h: n-$C_{10}H_{21}OMs$, 0.0734 mmol; ammonium chloride, 0.0734 mmol; toluene, 1.0 ml. b) Yield after 20 h.

Contrary to expectation,[7,16,19)] alumina was not only ineffective in this system but also promotive of the hydrolysis of both decyl mesylate and 1-bromodecane. The hydrolysis takes place possibly due to the presence of an irremovable water adsorbed by the alumina. The use of neutral alumina instead of activated alumina brought about any improvement neither on reaction rate nor on product composition. Active carbon also gave the hydrolysis product, 1-decanol, as a by-product, whose yield had reached ca. 25% when the mesylate completely disappeared.

Similarly, ionene chlorides were found to be much more reactive toward decyl mesylate when they were supported on silica gel. The results are summarized in Table 2 together with the results of PCMS, Cl, and NaCl. The reaction rates enhanced by adsorption were very similar for all ionene chrolides, while the rates of nonsupported ionenes differed from each other. PCMS, Cl, which contains pendant ammonio groups, is active without any carrier probably due to its high swellability. Its adsorption onto silica gel, therefore, did not induce a significant increase in activity. This tendency was quite similar to that of P4VP, Br.

Silica Gel-Supported Ionenes as Solid–Liquid–Solid Triphase Catalysts. Silica gel-supported ionenes were found to enhance some substitution reactions between liquid substrates and solid inorganic reagents. Figure 7 shows the results of the reaction between decyl mesylate and potassium bromide. The reaction hardly proceeded either in the absence of catalysts or even in the presence of nonsupported 3-4, Br. The two rates were almost identical. This indicates that the nonsupported 3-4, Br has no catalytic activity.

However silica gel-supported 3-4, Br largely accelerated the reaction. Although uncoated silica gel also promoted the reaction, it was less catalytically active than the 3-4, Br complex. This is consistent with the result that, as reagents, the supported 3-4, Br was much more reactive than the supported KBr (Table 1). Contrary to the lack of catalytic activity of the nonsupported 3-4, Br, the supported 3-4, Br contributes substantially to the rate enhancement. The contribution of the supported 3-4, Br tends to be amplified with decreasing ion content of the complex (Fig. 7).

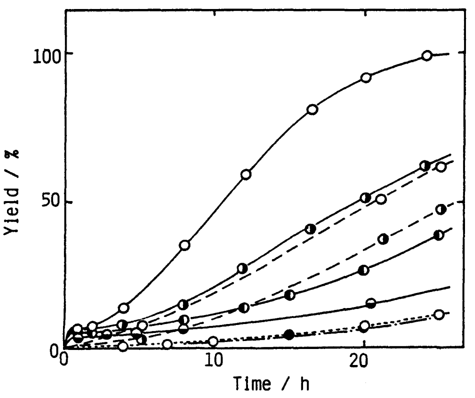

Fig. 7. Catalytic effects of silica gel and 3-4, Br on the solid–liquid–solid triphase reactions between decyl mesylate and potassium bromide.
——, supported 3-4, Br; ion content; ○, 0.25; ◑, 0.50; ◐, 1.00; ◒, 2.00. - - -, silica gel; weight/mg; ○, 200; ◑, 100. ------, nonsupported 3-4, Br. — - —, none of catalysts.

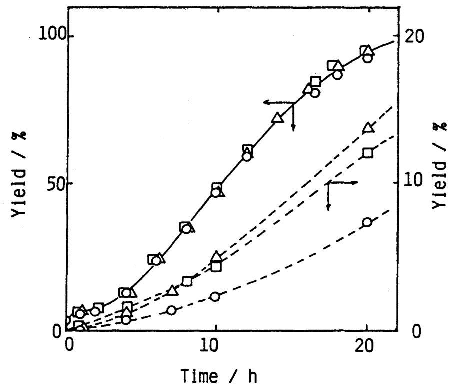

Fig. 8. Solid–liquid–solid triphase catalytic reaction between decyl mesylate and potassium bromide.
○, 3-4, Br; △, 4-4, Br; □, 6-6, Br. ——, supported; - - -, nonsupported.

Figure 8 shows the effect of ionene structure on the catalysis. Unlike 3-4, Br, nonsupported 6-6, Br and 4-4, Br, which had relatively high reactivities toward decyl mesylate (Table 1), had minimal catalytic activities. When adsorbed on silica gel, every ionene afforded much higher catalytic efficiency. The enhanced rates were very similar from one ionene to another.

A specific feature of the catalysis of the complexes is the large reaction rates at the initial stage, which is hardly observed either for uncoated silica gel or for nonsupported ionenes. The amount of 1-bromodecane formed within the first one hour approximately corresponded to that of ammonium bromides of the ionene added (Figs. 7 and 8). After the initial stage of the rapid reaction, a rather slow increase in the yield was observed and the time-yield curve presents somewhat autocatalytic feature. These phenomena can be

Table 3. Solid-Liquid-Solid Triphase Reactions Catalyzed by Silica Gel and Silica Gel-Supported 3-4, Br[a]

Substrate	Solid reagent	Yield/%		
		None	Uncoated silica gel	Supported 3-4, Br[b]
n-$C_{10}H_{21}OMs$	NaI[c]	23	23	20
	KCN	65		74
	KOPh[d]	21	88	87
	KOAc	16	100	96
n-$C_{10}H_{21}Br$	NaI	tr.	5	21
	KCN	0	0	tr.
	KOPh	0	17	48
	KOAc	0	9	35

a) Reactions were carried out in toluene at 90 °C for 25 h: n-$C_{10}H_{21}OMs$, 0.81 mmol ; n-$C_{10}H_{21}Br$, 0.72 mmol; solid reagents, 5.0 mmol; silica gel, 0.2 g. b) Ion content, 0.25 mmol g^{-1}; complex weight, 0.2 g. c) Yield after 1.0 h. d) Yield after 15 min.

accounted for in terms of high reactivity of active sites and slow regeneration of the active sites. Namely, the adsorbed ammonium salts in the form of bromide, which are the active sites in this system, can react immediately with decyl mesylate but ion exchange, which restores the ionene to the original bromide form, is slow compared to the chemical reaction. A clear account has not been given of the mechanism of this sort of ion exchange. There are many possible ways in which the counter ions of the ammonio groups are displaced: exchange by direct contact with the solid KBr, indirect exchange via contact with silica gel-adsorbed KBr, exchange by the trace amounts of KBr salt dissolved in the organic phase, and exchange by the KBr salt dissolved in the minimal amounts of irremovable water. Some discussion on this matter will be done later in this paper.

Table 3 shows the results of other substitution reactions catalyzed by the 3-4, Br complex. Generally, in S_N2 reactions, mesylate is a good leaving group compared to bromide. Hence decyl mesylate underwent rather facile substitutions, particularly with sodium iodide and with potassium phenoxide even in the absence of any catalyst. It was found, however, that the catalytic efficiencies of the complex as well as the uncoated silica gel had no relation to the substrate reactivity, but the efficiencies were determined by the combination of leaving group and attacking nucleophile.

Neither the complex nor the uncoated silica gel facilitated the displacements of decyl mesylate attacked by soft-basic ions, such as iodide and cyanide. In contrast, the displacements of the mesylate by hard-basic ions, acetate and phenoxide, were enhanced both by the complex and by the uncoated silica gel. The catalysis of the complex in these reactions, however, has nothing to do with the supported ionene because the catalytic efficiency of the complex coincides with that of the uncoated silica gel. Interestingly, it is only with bromide ion, a medium-basic nucleophile, that the substitution of decyl mesylate was really catalyzed by the ionene adsorbed on silica gel.

When bromide was a leaving group, the distinct catalytic action of the 3-4, Br complex was observed except for the reaction with sodium cyanide (Table 3), while the nonsupported 3-4, Br hardly catalyzed either reaction. The complex was catalytically more active than the uncoated silica gel, indicating that the adsorbed ionene played a key role in the catalysis. Furthermore, the reaction of 1-bromodecane was fast with hard acetate or phenoxide rather than with soft iodide, though the rates were considerably leveled among these reactions compared to the reactions of decyl mesylate. This fact is consistent with the observations that acetate[8] and phenoxide[20] are relatively reactive under anhydrous phase-transfer conditions.

On the basis of all the results, the catalysis of the complex may be summarized as follows. Silica gel undoubtly assists the catalysis through activating the ammonium salts of the ionene. However, the overall rates of the catalytic reactions were controlled by ion-exchange process. Taking into consideration that the uncoated silica gel accelerates the substitutions with hard-basic nucleophiles, silica gel likely facilitates the ion exchange rather selectively of hard-basic anions.

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