

고분자 물질로 지지된 크라운 에테르류: 6. Lariat Azacrown Ether의 상간이동촉매 활성

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Polymer-Supported Crown Ethers: 6. Phase-transfer Catalytic Activities of Lariat Azacrown Ethers

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요약: 삼상계 조건하에서 halogen 교환반응에 대한 고정화 lariat azacrown ether의 상간이동 촉매 활성을 환치환율, 기질의 구조, 시약의 종류, 용매, 촉매구조를 중심으로 평가하였다. 측쇄에 여분의 산소 donor를 갖는 lariat촉매는 donor를 갖지않는 대응하는 고정화 촉매에 비해 고효성을 나타내었다. 1-bromooctane과 KI와의 반응에 대한 monoaza-15-crown-5 unit와 두개의 여분 donor를 갖는 촉매의 활성 증대는 crown unit donor와 측쇄 donor와의 협동작용에 의해 K^+ 이온과의 착체 형성의 촉진에 의한 것으로 결론되었다. 회수한 촉매는 활성의 감소없이 재사용이 가능하였다.

Abstract: The phase-transfer catalytic activity of the immobilized lariat azacrowns for halogen exchange reactions under tri-phase conditions has been studied as a function of loading, substrate structure, reagent structure, solvent, and catalyst structure. The lariat catalysts with extra oxygen donors in the spacer chain exhibited higher activity than the corresponding immobilized catalysts without the donors in the spacer. The increased activity of the catalyst containing monoaza-15-crown-5 unit and two extra donors for the reaction of 1-bromooctane with KI was concluded to result from the enhanced complexation with the K^+ ion, induced by the cooperative coordination of the crown unit donors and the donors in the spacer chain. The recovered catalysts could be re-used without decrease in activity.

INTRODUCTION

Polymer-supported phase-transfer catalysts can be used, in principle, for any reaction that is catal-

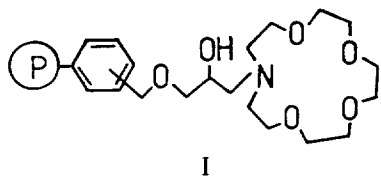
ized by a soluble phase-transfer catalyst. The activity of polymer-supported phase-transfer catalysts is dependent on many experimental parameters.¹⁻³ Some of them are related to the catalysts themself-

ves : active site structure, cross-linking level, loading, distance between active sites and supports, morphology of supports, particle size, etc.

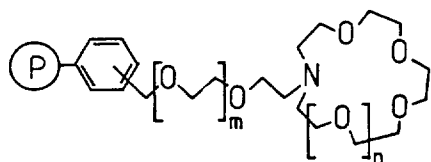
Others belong to reaction conditions : stirring speed, substrate structure, solvent, reagent concentration, etc.

In many known examples, polymer-supported phase transfer catalysts are less active than their soluble analogues.^{4,5} This disadvantage is improved to some extent by adjusting these parameters properly.

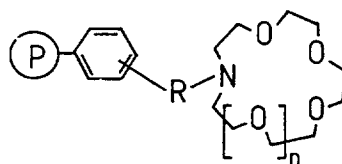
In a previous paper polystyrene resins(I) containing crown ether moieties and hydroxyl groups adjacent to the crown rings have been reported to exhibit high catalytic activity for halogen exchange reaction with aqueous alkali iodide under triphase conditions,⁶ due to the cooperative coordination of crown ring donors and the hydroxyl group in the side arm.



This paper reports on the phase-transfer catalytic activity of crown ethers attached on polystyrene supports by oxyethylene spacers, presented in a previous paper.⁷ Such immobilized lariat azacrown ethers (II, III) are expected to have high binding ability of alkali cations and thereby high catalytic activity for tri-phase reactions, compared with immobilized simple azacrown ethers IV, V. Actually IIa, prepared by the reaction of chloromethylated polystyrene with N-(2-hydroxyethyl)monoaza-15-crown-5, have been reported to be effective catalysts for tri-phase reactions.⁸



IIa : m=0, n=1 IIIa : m=1, n=1
 IIb : m=0, n=2 IIIb : m=1, n=2



IVa : R = (CH₂)₄, n=1 IVb : R = (CH₂)₄, n=2
 Va : R = (CH₂)₇, n=1 Vb : R = (CH₂)₇, n=2

EXPERIMENTAL

Materials

Polystyrene-supported lariat crown ethers were prepared by the procedure described.⁷ Polystyrene-supported monoazacrown ethers with tetra- or heptamethylene spacers were prepared by the method described previously.^{6,7} Other reagents and solvents obtained commercially were used as received.

Measurement

Phase-transfer reactions were followed by GLC on a Shimadzu 4C-PT thermal conductivity instrument with a 2 m glass column of Silicone GE SF-96 on Chromosorb W AW DMCS at 170°C.

Phase-transfer Reactions

The halogen exchange reaction of 1-bromo- or 1-chlorooctane with aqueous NaI or KI was carried out under tri-phase conditions according to the procedure previously described.⁶

Catalysts used were recovered using a fritted glass funnel and washed with water, dioxane/water(1 : 1 v/v), THF/water(1 : 1 v/v), THF, methanol and acetone, and dried under reduced pressure at 60°C.

RESULTS AND DISCUSSION

The phase-transfer catalytic activity of II and III was examined using the conversion of 1-haloocane to iodoctane under tri-phase conditions as a typical reaction, and was evaluated by using pseudo-first-order rate constants(*k*_{obsd}).

It has been already revealed that rates of tri-phase reactions carried out at stirring speeds of

500-600 rpm are not limited by mass transfer of reactants.^{2,9-11} This fact was also confirmed in this case with the immobilized lariat azacrown catalysts.

Figure 1 shows the effect of stirring speed on k_{obsd} with catalyst IIa on the reaction of 1-bromooctane with NaI. Rate constants increased when the stirring speed rose to 450 rpm but were constant above that value. The other experiment was carried out by stirring at about 500-550 rpm.

Table 1 shows the activity of catalysts IIa and IIIa for the reaction of 1-chlorooctane with NaI or KI. It has been reported that the reaction of 1-chlorooctane catalyzed by polymer-supported phase-transfer catalysts, crosslinked with 1-2 mol% of DVB, is controlled only by the intrinsic reactivity of active sites of the catalysts, and the rates do not depend on the catalyst particle size.^{9,11,12} Rates with IIIa hardly depended on the catalyst size (see Table 1). This indicates that this halogen exchange with the lariat catalysts is also controlled only by the intrinsic activity, and is not affected by the diffusion of the reactants.

The activity of IIa and IIIa increased with decreasing ring substitution (RS) (Table 1). This result concludes that the intrinsic activity of the immobilized lariat azacrowns increases as the RS de-

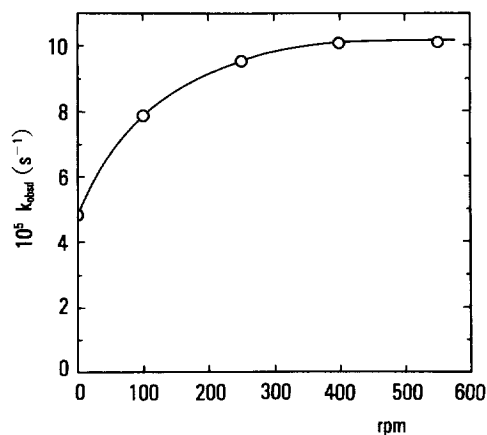


Fig. 1. Effect of stirring speed on k_{obsd} at 90°C in the reaction of 1-bromooctane with sodium iodide catalyzed by IIa(RS 22%).

creases. Similar RS dependences of activity have been observed for the reaction of 1-chlorooctane in the presence of polymer-supported phosphonium salts or crown ethers.^{9,11-13} The reduced RS results in the decreased hydrophilicity and the increased lipophilicity of the catalysts, as shown in Fig. 1.⁷ The high activity of the low ring-substituted catalysts, therefore, can be explained by the decreased hydration of the active site with high nucleophilicity.

The activity of IIIa with two extra donors was a little larger than that of IIa with one extra donor for the reaction with NaI. However, a considerable difference in the activity between IIIa and IIa was observed for the reaction with KI. This result suggests that catalyst IIa can not sufficiently bind the K^+ ion because of the deficiency of donor atoms (see later).

The activity (k_{obsd}) of the lariat catalyst for the reaction of 1-bromooctane was depended on the particle size of the catalyst : for example, $10^5 k_{\text{obsd}} \text{ (s}^{-1}\text{)} = 6.9$ for 60-100 mesh catalyst IIa with 42% RS and 8.9 for the 100-200 mesh one in the reaction with KI. This result supports the idea that the reaction of 1-bromooctane is limited by both the

Table 1. Reaction of 1-Chlorooctane with NaI or KI in the Presence of Polymer-supported Lariat Crown Ethers^{a)}

Polymer-supported lariat crown	Ring substitution(%)	$10^7 k_{\text{obsd}} \text{ (s}^{-1}\text{)}$	
		NaI	KI
IIa	8	10.8	6.1
	14	9.3	5.6
	22	7.8	5.5
	29	5.8	5.2
IIIa	12	12.5(12.7) ^{b)}	11.3
	22	9.1	10.0
	31	7.0	8.5
	42	4.4	6.4(6.6) ^{b)}

^{a)} Reaction conditions : 1-Chlorooctane, 20 mmol ; Reagent, 100 mmol ; Crown unit, 0.40 mmol ; Catalyst particle size, 60-100 mesh ; H_2O (15 ml)-toluene (20 ml) ; 90°C ; stirring speed, 500-550 rpm.

^{b)} Catalyst particle size, 100-200 mesh.

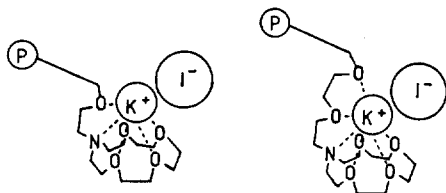
Table 2. Reaction of 1-Bromooctane with NaI or KI in the Presence of Polymer-supported Crown Ethers^{a)}

Polymer-supported crown ether	Spacer	Monoazacrown unit	Ring substitution (%)	10 ⁵ k _{obsd} (s ⁻¹)	
				NaI	KI
IVa	(CH ₂) ₄	15-crown-5	22	4.0	0.96
IIa	CH ₂ OCH ₂ CH ₂		22	10.2	5.1
Va	(CH ₂) ₇		20	4.1	0.44
IIIa	CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂		22	10.7	12.3
IVb	(CH ₂) ₄	18-crown-6	23	6.0	11.0
IIb	CH ₂ OCH ₂ CH ₂		23	11.1	15.4
Vb	(CH ₂) ₇		22	6.0	12.1
IIIb	CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂		23	8.7	16.3

^{a)} Reaction conditions are the same as in Table 1, except for the use of 1-Bromooctane as a substrate.

intrinsic reactivity of active site of the catalyst and the intraparticle diffusion of the reactants, as reported previously for the reaction with other supported phase-transfer catalysts.^{2,9-11,13}

Table 2 reports the effect of the structure of spacer chains and active sites on the activity of the lariat catalysts (20-23%RS ; 60-100 mesh) for the reaction of 1-bromooctane. Lariat catalysts IIa and IIIa with the extra oxygen donor in the spacer chains exhibited higher activity than corresponding catalysts IVa and Va. A particularly large difference in activity was observed for the reaction with KI. This result suggests that in the case of IIa the cooperative coordination of the crown ether unit and the oxygen donor in the side arm with the K⁺ ion increases the binding ability for the cation, and thereby the catalytic activity, although such a coordination is not yet enough to bind K⁺ tightly (see Scheme 1). In practice, KI complexing with N-(2-methoxyethyl)monoaza-15-crown-5 has an X-ray crystal structure in which the K⁺ ion is located above the crown donor group plane and is also coordinated with the oxygen donor in the side arm.¹⁴

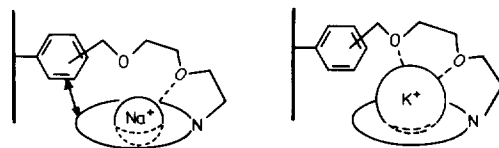


Scheme 1

Catalyst IIIa with additional two oxygen donors had higher activity than catalyst IIa with one donor for the reaction with KI. The additional donors must facilitate the cooperative binding of K⁺ larger than Na⁺, because only the 15-membered crown structure has rather low binding ability for K⁺^{15,16} (see Scheme 1).

The binding constant for N-[(2-methoxyethoxy)ethyl]monoaza-15-crown-5 with Na⁺ in methanol has been reported to be larger than that for N-(2-methoxyethyl)monoaza-15-crown-5.¹⁷

However, corresponding immobilized catalysts IIa and IIIa had the similar activity for the reaction with NaI (see Table 2). The Na⁺ ion smaller than K⁺ must nestle in the crown ring and give rise to possible repulsions between the macroring and the benzene ring attached to the polymer backbone and the side arm, and the oxygen donor located far from the crown ring could not effectively coordinate with the Na⁺ ion, as shown in Scheme 2.¹⁵ Such repulsions will be minimized for the non-immobilized crown ethers with two oxygen donors and the terminal methyl group.



Scheme 2

In the case of the complexation with K^+ such repulsions must not take place because the cation is located above the 15-crown-5 ring (see Scheme 2).

The introduction of the oxygen donor into the spacer chain of the catalyst with 18-crown-6 structure increased the catalytic activity for the halogen exchange reaction. An increment in the activity, however, was smaller than that in the case of the catalyst with 15-crown-5 structure (Table 2). This behavior can be accounted for by the idea that the 18-membered structure containing six donor atoms is able to bind alkali cations without the extra coordination of the donor in the spacer, whereas the 15-membered structure with five donors needs the additional coordination to bind the cations effectively.

The effect of the percentage of RS on the activity of catalysts II and III for the reaction of 1-bromo-octane is shown in Figures 2-5. The catalysts with ca. 20-30% RS exhibited maximal activity for the halogen exchange reaction. Similar RS dependences have been reported for other supported phase-transfer catalysts.^{9,11~13,18~20}

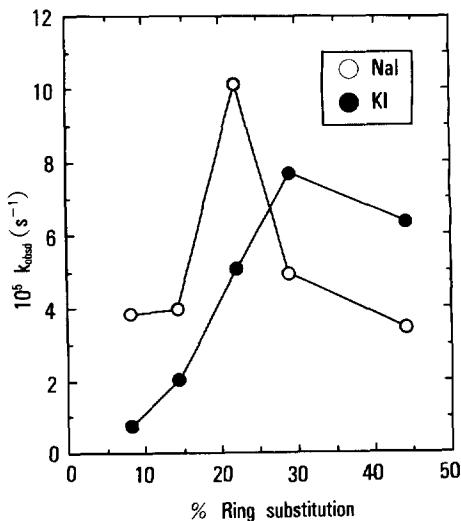


Fig. 2. Dependence of activity of catalyst IIa with monoaza-15-crown-5 unit for the reaction of 1-bromo-octane with NaI or KI on % ring substitution. Reaction conditions are the same as in Table 2.

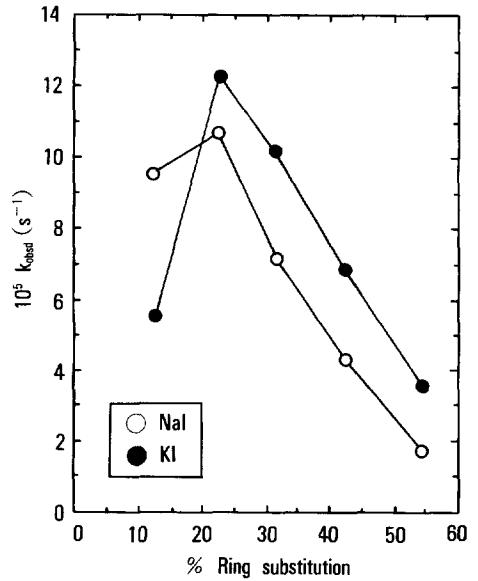


Fig. 3. Dependence of activity of catalyst IIIa with monoaza-15-crown-5 unit for the reaction of 1-bromo-octane with NaI or KI on % ring substitution. Reaction conditions are the same as in Table 2.

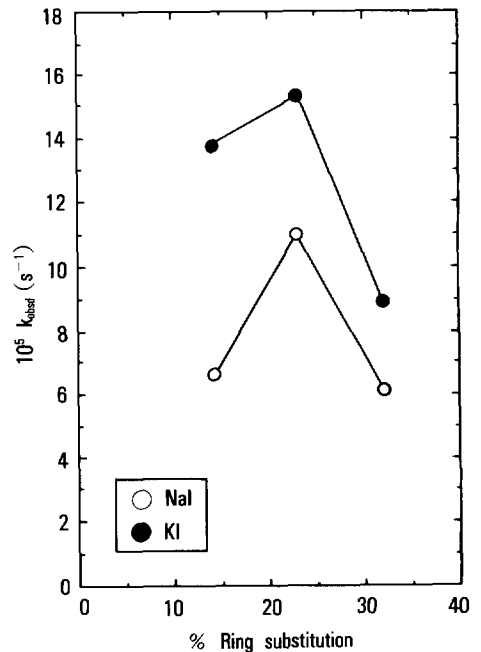


Fig. 4. Dependence of activity of catalyst IIb with monoaza-18-crown-6 unit for the reaction of 1-bromo-octane with NaI or KI on % ring substitution. Reaction conditions are the same as in Table 2.

The low activity of the catalysts with ca. 10% RS is due to the low hydrophilicity or high lipophilicity of the catalysts (see Fig. 1 and 2⁷). The reduced hydrophilicity must result in slow intraparticle diffusion of the reagent KI or NaI and hence the depressed formation of the active site which should be less hydrated species with high intrinsic reactivity. In practice, it has been reported by Montanari et al. that the complexation of supported crown ethers with KI is retarded with decreasing RS.^{19,20} The low activity of the high ring-substituted (42-54%) catalysts is attributed to the low reactivity of the more hydrated iodide anion in the catalyst with high hydrophilicity and the reduced intraparticle diffusion of the substrate. The catalysts having a proper hydrophile-lipophile balance, which results from RS of ca. 20-30% in this case, have eventually maximal apparent activity.

The activity of IIIb with 18-crown-6 structure and one oxygen donor in the spacer was similar to that

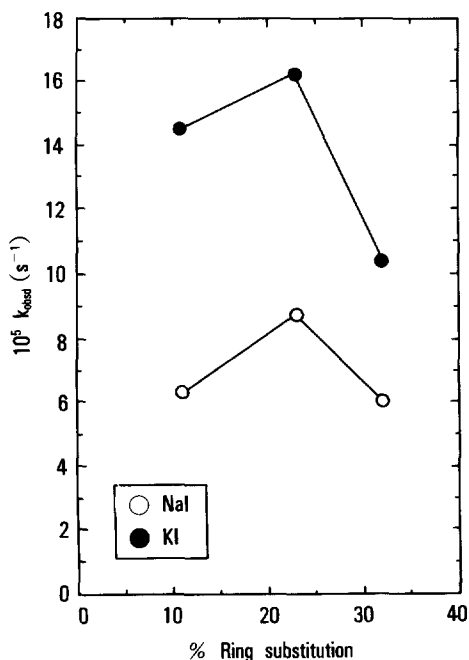


Fig. 5. Dependence of activity of catalyst IIIb with monoaza-18-crown-6 unit for the reaction of 1-bromo-octane with NaI or KI on % ring substitution. Reaction conditions are the same as in Table 2.

of IIIb with the same crown unit and two extra donors. Lariat catalysts IIb and IIIb as well as IVb and Vb were more effective for the reaction with KI than for the reaction with NaI (Fig. 4 and 5). This corresponds to the well-known fact that the 18-membered crown binds K⁺ tightly, but Na⁺ a little loosely.²¹

Figure 6 reports on the effect of organic solvent on the activity of catalyst IIb for the reaction with KI. The activity increased with the increasing swelling power of the solvent in the order heptane < toluene < chlorobenzene.^{10,12} The polar solvent, chlorobenzene induces the facilitated intraparticle diffusion of reactants and also enhances intrinsic reactivity, as reported previously for other supported phase-transfer catalysts.¹²

The lariat catalysts recovered from the reaction system could be re-used without significant decrease in activity, as shown in Table 3. A slight increase in the activity of the re-used catalysts may be due to the decreased particle size induced by

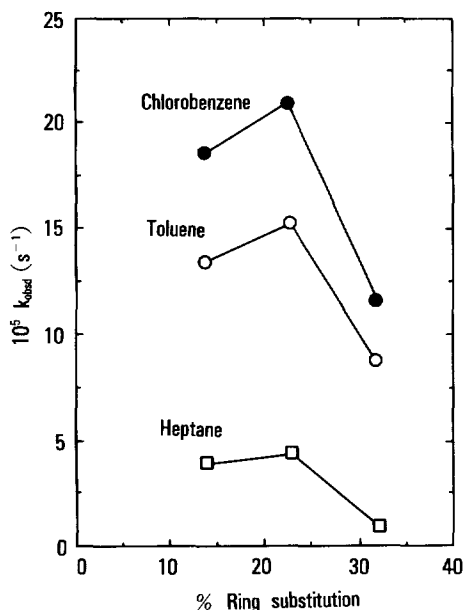


Fig. 6. Solvent effect on activity of catalyst IIb with monoaza-18-crown-6 unit for the reaction of 1-bromo-octane with KI. Reaction conditions are the same as in Table 2.

Table 3. Reusability of Polymer-supported Lariat Crown Catalysts for Halogen Exchange Reaction^{a)}

Polymer-supported lariat crown	Ring substitution(%)	10 ⁵ k _{obsd} (s ⁻¹)					
		1st		2nd		3rd	
		NaI	KI	NaI	KI	NaI	KI
IIa	22	10.2	5.1	10.8	5.2	10.5	—
IIIa	31	7.1	10.2	7.6	12.0	7.4	—
IIb	23	11.1	15.4	10.8	14.5	—	14.3
IIIb	32	6.2	10.4	6.7	10.8	—	10.5

^{a)} Reaction conditions are the same as in Table 2.

mechanical stirring in the reaction system.

In conclusion the lariat catalyst with monoaza-15-crown-5 unit and two extra oxygen donors in the spacer chain exhibited extremely higher activity for the reaction of 1-bromooctane with KI, compared with the corresponding catalyst without oxygen donors in the spacer.

Such a high activity is due to the increased complexation with the K⁺ ion, induced by the cooperative coordination of the crown donors and the additional oxygen donors in the spacer. An increment in the activity of the catalysts with monoaza-18-crown-6 unit, induced by the introduction of oxygen donors in the spacer, is smaller than that in the case of the catalysts with monoaza-15-crown-5 unit, because the 18-membered ring can bind K⁺ or Na⁺ without the extra coordination of the donors in the spacer.

The most important factor that determines the catalytic activity of the lariat catalyst is the hydrophilic/lipophilic balance of the catalyst ; the catalyst with ca. 20-30% ring substitution has the best balance for the reaction of 1-bromooctane.

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