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Phase-Transfer Catalysis by Polymer-Supported Crown Ethers and Soluble Crown Ether Analogues

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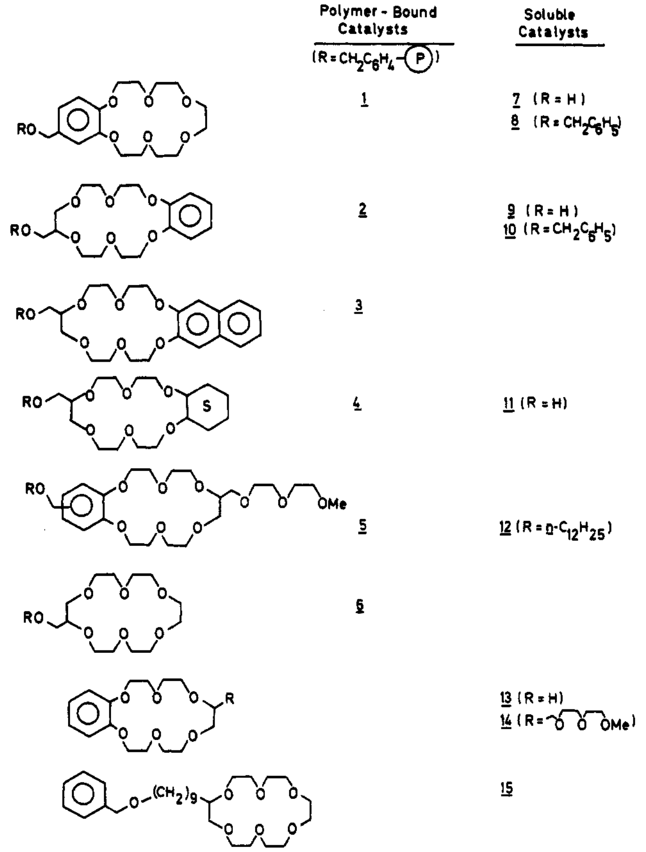
Six polymer-supported crown ethers are prepared by reactions of 2% cross-linked, chloromethylated polystyrene with hydroxymethyl group substituted crown ethers. Triphase catalytic activities of these materials are assessed in reactions of 1-bromooctane in toluene with aqueous potassium cyanide. The results provide important insight into the influence of structural variation within the crown ether upon catalytic activity. Closely related soluble ethers are examined as biphase catalysts for the same substitution reaction. For three different comparisons of structurally similar polymer-supported and soluble catalysts the former are more efficient by factors of 4.5–29.

Macrocyclic polyethers (crown ethers), cryptands, and quaternary ammonium and phosphonium salts have been attached to polymer supports[1] and utilized as triphase catalysts in a special type of phase-transfer catalytic reactions which was introduced by Regen in 1975.[2] In such systems the catalyst is an insoluble third phase which resides at the interface between immiscible organic and aqueous phases.[3] Compared with soluble phase-transfer catalysts, the polymer-supported catalysts have the important advantage of facile recovery for reuse.[3]

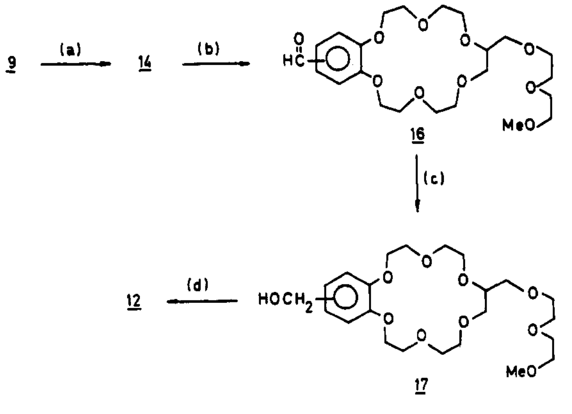
For polymer bound crown ethers, van Zon[4] and Tomoi[5] observed that enhanced levels of crown ether loading on cross-linked polystyrene produced catalysts with higher activity. Montanari[6–8] discovered that insertion of a long hydrocarbon spacer group between the polystyrene backbone and the crown ether unit gave increased catalytic activity for displacement reactions which involve soft nucleophilic anions, such as I^- and SCN^-. For harder anions like Br^- and CN^-, the addition of a spacer group had little effect. In general, polymer-supported crown ether catalysts have been found to be less efficient than soluble crown ether catalysts in stirred multiphase reaction systems.

For triphase catalysis by polystyrene-bound crown ethers, effects of stirring, catalyst amount, percent of ring substitution, and spacer group insertion upon catalyst efficiency have been probed.[1–8] Variation of the crown ether unit has received much less attention with only pendant 18-crown-6, benzo-18-crown-6, monoaza-15-crown-5, and monoaza-18-crown-6 being examined. We now report the preparation of the six polystyrene-supported 18-crown-6 derivatives **1–6** and their efficiencies as triphase catalysts in the reaction of 1-bromooctane in toluene with aqueous potassium cyanide. For comparison, the catalytic efficiencies of closely related soluble crown catalysts **7–15** have also been determined.

Chart I



Scheme I[a]



[a] (a) NaH, $TsOCH_2CH_2OCH_2CH_2OMe$, THF; (b) hexamethylenetetramine, CF_3CO_2H; (c) $NaBH_4$, *i*-PrOH; (d) NaH, *n*-$C_{12}H_{25}Br$, THF.

Results and Discussion

Synthesis. Soluble crown ether catalysts **14** and **12** and hydroxymethyl crown ether **17**, the precursor to polymer-supported catalyst **5**, were prepared by the reaction sequence outlined in Scheme I. Thus reaction of hydroxymethyl-substituted benzo-18-crown-6 **9**[9] with NaH and the tosylate of monomethyl diethylene glycol[10] formed

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Table I. Analytical Data for Polymer-Supported Crown Ethers and Pseudo-First-Order Rate Constants for the Triphase Reaction of Aqueous Potassium Cyanide with 1-Bromooctane in Toluene[a]

	titer (mequiv of crown ether/g)				
catalyst[b]	by weight increase	by elemental anal. (% O in parenthesis)	% ring substitn[c]	% yield of binding	$10^5 k_{obs}$ (s^{-1})[d]
1	1.86	1.89 (21.16)	65.1	97.3	1.7
2	1.56	1.79 (20.06)	61.7	92.2	4.4
3	1.78	1.87 (20.99)	65.4	97.8	5.3
4	1.40	1.53 (17.11)	58.0	86.7	16.5
5	1.10	1.32 (21.06)	57.3	85.7	1.5
6	1.94	2.08 (23.31)	65.1	97.3	1.8

[a] At 90.0 °C and 1300 rpm with 10% molar equiv of catalyst. [b] From (chloromethyl)polystyrene 2% cross-linked with divinylbenzene, 4.91 mequiv of Cl/g, 66.9% ring substitution. [c] Calculated from the oxygen elemental analysis. [d] Reproducibility was ±5% of the listed rate constant.

a C-pivot lariat crown[11] **14** in 80% yield. Formylation of **14** with hexamethylenetetramine in trifluoroacetic acid[12] provided a 72% yield of **16**. Sodium borohydride in 2-propanol reduced **16** to the hydroxymethyl-substituted C-pivot lariat crown **17** in 96% yield. Attachment of a lipophilic dodecyl group to **17** was accomplished by reaction with NaH and 1-bromododecane to afford a 67% yield of **12**.

The previously, reported, hydroxymethyl-substituted benzo-18-crown-6 **7**,[4] a structural isomer of **9**, was obtained from the corresponding formylated crown ether in a markedly improved 92% yield by reduction with sodium borohydride in 2-propanol. Crown ether **8** was prepared in 95% yield by reaction of **7** with NaH and benzyl bromide. An isomeric mixture of hydroxymethyl-substituted cyclohexano-18-crown-6 compounds **11** was obtained in 50% yield by hydrogenation of **9** with 5% ruthenium on carbon catalyst in ethanol at 100 °C and 1200 psi of hydrogen.

Polymer-supported catalysts **1**–**6** were prepared by reactions of the appropriate hydroxymethyl-substituted crown ethers with NaH and then with commercially available, 2% cross-linked, chloromethylated polystyrene (4.91 mmol Cl/g) in refluxing THF.[7,8] The percent of ring substitution (57–65%) was accurately determined by oxygen elemental analysis[8] (Table I). The comparable percentages of ring substition for **1**–**6** make these polymer-bound crown ethers suitable for structure–reactivity studies.

Kinetic Investigations of Triphase Reactions. Activities of polymer-bound crown ether and soluble crown ether catalysts were assessed with the standard nucleophilic substitution of cyanide from a concentrated aqueous KCN phase on 1-bromooctane in toluene[4,6,7] at 90 °C. Rates were measured by GLC analysis and pseudo-first-order kinetic behavior was observed for at least two reaction half-lives.

The effect of stirring rate variation upon pseudo-first-order rate constants for the triphase catalytic activity of polymer-bound crown ether **1** is shown in Figure 1. Similar dependency of reaction rate upon stirring speed has been observed in previous studies of triphase catalysis by other polymer-bound crown ethers.[5,7,8] To minimize the influence of diffusion,[7,8] a stirring speed of 1300 rpm was utilized for subsequent studies of reactions catalyzed by polymer-supported crown ethers **1**–**6**.

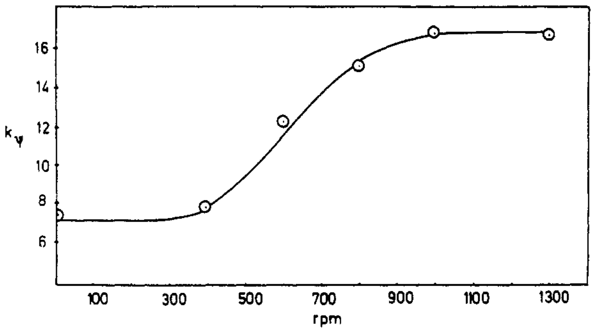

Figure 1. Pseudo-first-order rate constants in s^{-1} ($\times 10^6$) vs. stirring rate for triphase reactions of aqueous KCN with 1-bromooctane in toluene catalyzed by polymer-bound crown ether **1** at 90 °C.

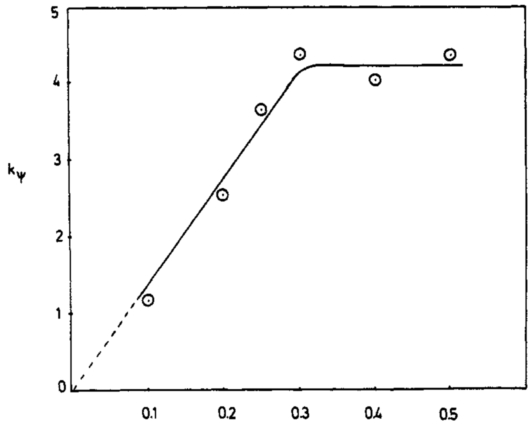

Figure 2. Pseudo-first-order rate constants in s^{-1} ($\times 10^5$) vs. molar equivalents of polymer-bound crown ether **2** for triphase reactions of aqueous KCN with 1-bromooctane in toluene at 90 °C.

Dependence of reaction rate upon the amount of polymer-supported crown ether **2** present is illustrated in Figure 2. Enhancing the proportion of catalyst produces a linear increase in the pseudo-first-order rate constant until a 10% molar equiv is reached. For subsequent increases in the amount of catalyst present, there is no effect upon the rate. Other workers have reported linear relationships between the pseudo-first-order constants and 10% or lower molar equivalents of triphase catalyst, but apparently did not conduct investigations at higher catalyst levels.[7,13,14] Presumably the plateau observed in Figure 2 results from a saturation of the aqueous–organic phase interface with the polymeric catalyst. For the structure–reactivity studies of polymer-supported crown ethers **1**–**6**, a uniform 10% molar equiv of catalyst was employed.

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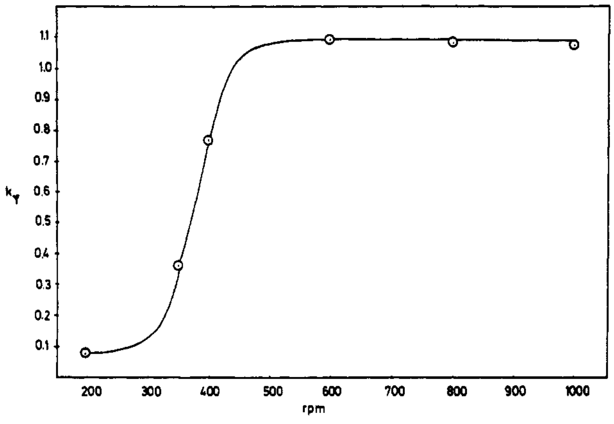

Figure 3. Pseudo-first-order rate constants in s^{-1} ($\times 10^6$) vs. stirring rate for biphase reactions of aqueous KCN with 1-bromooctane in toluene catalyzed by soluble crown ether **13** at 90 °C.

Pseudo-first-order rate constants for the triphase reaction of aqueous KCN with 1-bromooctane in toluene as effected by 10% molar equiv of polymer-supported crown ethers **1**-**6** with stirring at 1300 rpm at 90 °C are recorded in Table I. Modification of the polymer-supported benzo-18-crown-6 catalyst **1** by deletion of the benzo group (in catalyst **6**) or incorporation of a C-pivot lariat arm[11] (in catalyst **5**) has essentially no influence upon the catalyst efficiency. On the other hand, structural isomer **2** in which the crown ether ring is positioned between the polymer backbone and the lipophilic benzo group exhibits a 2.6-fold rate enhancement. This enhancement becomes 3.1-fold when the benzo group in catalyst **2** is replaced by a naphtho group in catalyst **3** and increases to 9.7-fold when the lipophilic group is changed to a saturated cyclohexano unit in catalyst **4**. These results clearly establish an unexpected enhancement of catalyst efficiency when the crown ether ring is positioned between the polymer backbone and a lipophilic hydrocarbon unit. Thus the positioning of lipophilic groups is demonstrated to have an important influence upon the triphase catalytic activity of polymer-supported crown ethers.

Kinetic Investigations of Biphase Reactions. To compliment the studies of phase-transfer catalysis by polymer-supported crown ethers in triphase systems, investigations were also conducted with soluble crown ether catalysts in biphase systems. For ready comparison with the triphase reaction results, a 10% molar equiv of the soluble crown ether catalyst was employed. The influence of stirring speed upon the pseudo-first-order rate constants for reactions of aqueous KCN with 1-bromooctane in toluene in the presence of benzo-18-crown-6 (**13**) is shown in Figure 3. Thus the rate constant is initially enhanced as the stirring speed increases but reaches a plateau above approximately 500 rpm. A stirring rate of 600 rpm was utilized for the structure–reactivity studies of the soluble crown ether catalysts.

From the pseudo-first-order rate constants listed in Table II, the relative catalytic efficiencies of crown ether catalysts **7**–**15** may be deduced. Employing benzo-18-crown-6 (**13**) as a standard, attachment of a hydroxymethyl group to the aromatic ring (catalyst **7**) decreases catalyst efficiency somewhat, whereas attachment of a (benzyloxy)methyl group (catalyst **8**) is modestly beneficial. On the other hand, when hydroxymethyl and (benzyloxy)methyl groups are attached to the polyether portion of benzo-18-crown-6 (catalysts **9** and **10**, respectively) modest efficiency enhancements are noted in both cases. However, further structural elaboration to provide a C-pivot lariat ether[11] **14** gives a catalyst with essentially the same activity as the parent benzo-18-crown-6. In light of this finding, it appears that the 3.3-fold increase in catalyst efficiency observed with **12** results from the lipophilic *n*-dodecyl group rather than the C-pivot lariat ether[11] portion. Of the soluble crown ether catalysts examined, the hydroxymethyl-substituted cyclohexano-18-crown-6 **11** is the most effective. If this increase arose simply from the more basic crown ether oxygens produced when a benzo group is replaced by a saturated cyclohexano unit, the efficiencies of catalyst **11** and the lipophilic 18-crown-6 derivative **15** would be expected to be quite similar. The additional efficiency of **11** probably results from enhanced interfacial activity due to the polar alcohol function.

Table II. Pseudo-First-Order Rate Constants for the Biphase Reaction of Aqueous Potassium Cyanide with 1-Bromooctane in Toluene[a]

catalyst	$10^6 k_{obs}$ (s^{-1})[b]	catalyst	$10^6 k_{obs}$ (s^{-1})[b]
7	0.6	**12**	3.3
8	1.8	**13**	1.0
9	2.1	**14**	0.9
10	1.5	**15**	7.2
11	23		

[a] At 90.0 °C and 600 rpm with 10% molar equiv of catalyst. [b] Reproducibility was ±5% of the listed rate constant.

Comparison of Polymer-Supported and Soluble Crown Ether Catalysts. Since both triphase and biphase reactions were studied at a common temperature and amount of catalyst, relative efficiencies of closely related polymer-supported and soluble crown ether catalysts may be compared. Division of the pseudo-first-order rate constant for the triphase catalyst by that for the structurally similar soluble catalyst provides: **1**/**8** = 9.4; **2**/**10** = 29; and **5**/**12** = 4.5. Thus the polymer-supported crown ethers are found to be more efficient in catalyzing the reaction of aqueous KCN with 1-bromooctane in toluene than closely related soluble catalysts by factors of 4.5–29. It is interesting to note the highest ratio is obtained for a polymer-supported catalyst in which the crown ether unit is positioned between the polymer backbone and a lipophilic group.

Experimental Section

IR spectra were obtained on neat samples with a Nicolet MX-S spectrometer and are recorded in reciprocal centimeters. ^1H NMR spectra were obtained with a Varian EM 360 spectrometer in deuteriochloroform and chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane. GLC analyses for kinetic runs were conducted with a Varian Model 3700 capillary, flame ionization instrument equipped with a 25 m × 0.20 mm WCOT SE-30 column and a Hewlett Packard Model 3390A integrating recorder. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

Unless specified otherwise reagent grade reagents and solvents were obtained from chemical suppliers and used as received. THF was purified by distillation from $LiAlH_4$ under nitrogen. Chloromethylated polystyrene, 200–400 mesh, cross-linked with 2% divinylbenzene with 5.0 mequiv of Cl/g was purchased from Fluka. Benzo-18-crown-6 (**13**),[15] 11-(hydroxymethyl)-2,3-benzo-18-crown-6 (**9**),[9] 11-[(benzyloxy)methyl]-2,3-benzo-18-crown-6 (**10**),[9] 4′-formyl-2,3-benzo-18-crown-6,[12] 11-(hydroxymethyl)-2,3-naphtho-18-crown-6,[16] hydroxymethyl-18-crown-6,[17] and 2-[9-(benzyloxy)nonyl]-18-crown-6 (**15**)[8] were prepared by literature methods. The tosylate of diethylene glycol monomethyl ether was prepared by the standard procedure.[10]

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Polymer-Supported Crown Ethers 1–6. A combination of literature procedures was utilized.[7,8] After mixture of the hydroxymethyl crown ether (1.0 mmol) and NaH (2.0 mmol) was stirred in THF at 50 °C under nitrogen for 2 h, 170 mg (0.85 mmol of chlorine) of the THF-swollen chloromethylated polystyrene was added. After the mixture was refluxed for 96 h, the insoluble material was filtered, washed sequentially with Et_2O, MeOH, CH_2Cl_2, and Et_2O, and then dried for 3 h at 65 °C and 0.02 torr. The amount of crown ether bonded to the polymer was determined by weight increase and elemental analysis for oxygen[8] (Table I).

4′-[(Benzyloxy)methyl]-2,3-benzo-18-crown-6 (8). NaH (0.12 g, 3.0 mmol, 60% dispersion in mineral oil) was washed with pentane and suspended in 5 mL of THF. Under nitrogen, a solution of 7 (0.68 g, 2.0 mmol) in THF (2.0 mL) was added dropwise and the mixture was stirred for 1 h at room temperature. Benzyl bromide (0.60 g, 3.5 mmol) in 3 mL of THF was added and the mixture was refluxed overnight. The solvent was removed in vacuo and the residue was chromatographed on alumina with EtOAc as eluent to provide 0.82 g (95%) of 8 as a colorless oil: IR 1134 (CO); ^1H NMR 3.5–4.3 (m, 20), 4.45 (s, 2), 4.50 (s, 2), 6.8–7.0 (m, 3), 7.31 (s, 5). Anal. Calcd for $C_{24}H_{32}O_7$: C, 66.65; H, 7.46. Found: C, 66.45; H, 7.49.

11-(Hydroxymethyl)-2,3-cyclohexano-18-crown-6 (11). To a solution of 9 (4.00 g, 11.7 mmol) in absolute EtOH (100 mL) was added 5% Ru on carbon. Hydrogenation was performed at 100 °C with 1200 psi of hydrogen for 15 h. The catalyst was filtered and the solvent was evaporated in vacuo. The residue was subjected to chromatography on alumina with EtOAc–MeOH as eluent to give 2.03 g (50%) of 11 as a colorless, extremely hygroscopic oil: IR 3400 (OH), 1101 (CO); ^1H NMR 1.0–2.1 (m, 8), 2.85 (s, 1), 3.25–4.1 (m, 23). Anal. Calcd for $C_{17}H_{32}O_7 \cdot 0.25H_2O$: C, 57.85; H, 9.28. Found: C, 57.82; H, 9.21.

4′(5′)-[(*n*-Decyloxy)methyl]-11-(2,5,8-trioxanonyl)-2,3-benzo-18-crown-6 (12). Sodium hydride (0.07 g, 1.65 mmol, 60% dispersion in mineral oil) was suspended in THF (10 mL) and a solution of 17 (0.68 g, 1.41 mmol) in 10 mL of THF was added dropwise under nitrogen. After the mixture was stirred for 1 h at 50 °C, a solution of 1-bromododecane (0.42 g, 1.7 mmol) in THF (10 mL) was added and the mixture was stirred and refluxed for 3 days. The solvent was evaporated in vacuo and the residue was purified by chromatography on alumina with EtOAc–petroleum ether (30–60 °C) (1:1) as eluent to afford 0.62 g (67%) of 12 as a colorless oil: IR 1136 (CO); ^1H NMR 0.65–1.8 (m, 23), 3.1–4.5 (m, 36), 6.80 (br s, 3). Anal. Calcd for $C_{35}H_{62}O_{10}$: C, 65.39; H, 9.72. Found: C, 65.12; H, 9.88.

11-(2,5,8-Trioxanonyl)-2,3-benzo-18-crown-6 (14). Under nitrogen, NaH (0.32 g, 8.0 mmol, 60% dispersion in mineral oil) was washed with pentane and suspended in 15 mL of THF. A solution of 9 (2.50 g, 7.3 mmol) in THF (15 mL) was added dropwise and the resultant mixture was stirred for 1 h at room temperature. The tosylate of diethylene glycol monomethyl ether (2.14 g, 7.8 mmol) in 15 mL of THF was added and the reaction mixture was stirred and refluxed for 3 days. The solvent was evaporated in vacuo and the residue was dissolved in $CHCl_3$, washed with water, and dried over $MgSO_4$. After evaporation of the solvent in vacuo, the residue was purified by chromatography on alumina with EtOAc as eluent to afford 2.58 g (80%) of 14 as a colorless oil: IR 1126 (CO); ^1H NMR 3.35 (s, 3), 3.2–4.3 (m, 29), 6.85 (s, 4). Anal. Calcd for $C_{22}H_{36}O_9$: C, 59.44; H, 8.16. Found: C, 59.20; H, 8.05.

4′(5′)-Formyl-11-(2,5,8-trioxanonyl)-2,3-benzo-18-crown-6 (16). A mixture of 14 (1.85 g, 4.2 mmol), trifluoroacetic acid (3 mL), and hexamethylenetetramine (0.58 g, 4.2 mmol) was stirred at 90 °C under nitrogen for 24 h. The reaction mixture was cooled and concentrated in vacuo. Ice water (33 mL) was added and the mixture was stirred for 1 h. After extraction with $CHCl_3$ (3 × 10 mL), the combined extracts were dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by chromatography on alumina with EtOAc as eluent to provide 1.43 g (72%) of 16 as a hygroscopic colorless oil: IR 1687 (C=O), 1132 (CO); ^1H NMR 3.2–4.4 (m, 32), 6.8–7.6 (m, 3), 9.83 (s, 1). Anal. Calcd for $C_{23}H_{36}O_{10} \cdot 0.5H_2O$: C, 57.36; H, 7.74. Found: C, 57.05; H, 7.34.

4′(5′)-(Hydroxymethyl)-11-(2,5,8-trioxanonyl)-2,3-benzo-18-crown-6 (17). The formyl crown 16 (1.22 g, 2.6 mmol) was dissolved in 2-propanol (23 mL) and $NaBH_4$ (0.14 g, 3.7 mmol) was added. The mixture was stirred at room temperature for 36 h after which 30 mL of H_2O was added and the resultant solution was neutralized with HOAc and extracted with $CHCl_3$. The extract was washed with H_2O, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by column chromatography on alumina with EtOAc–MeOH (25:1) as eluent to give 1.18 g (96%) of 17 as a hygroscopic colorless oil: IR 3448 (OH), 1130 (CO); ^1H NMR 2.65 (br s, 1), 3.40 (s, 3), 3.3–4.35 (m, 32), 4.55 (d, 2), 6.85 (br s, 3). Anal. Calcd for $C_{23}H_{38}O_{10} \cdot 0.5H_2O$: C, 57.13; H, 8.12. Found: C, 56.79; H, 7.87.

Kinetic Measurements. Into a 50-mL (25 mm × 150 mm) screw-cap glass culture tube[14] were placed 5.0 mL of HPLC grade toluene, 5.0 mL of 7.5 M aqueous KCN, 3.0 mmol of dodecane (internal standard), and a Teflon-coated stirring bar. The tube was placed in a 90.0 ± 0.1 °C constant temperature bath and the contents were magnetically stirred at the desired rate. A Caframo Model RZR1 variable speed stirring motor was utilized and stirring rates were determined with a Power Instrument Model C-891 strobe light tachometer. The appropriate amount of polymer-bound crown ether or soluble crown ether catalyst (usually 0.30 mmol) was added and conditioned by stirring for 12 h at 1000 rpm for the former and for 1 h at 600 rpm for the latter. At zero time, 3.0 mmol of 1-bromooctane was added. Samples (10 μL) were removed at desired time intervals (at least 8 samples per run which covered at least 2 half-lives) and analyzed by GLC for the relative concentrations of 1-bromooctane and dodecane. For runs with soluble catalysts, the reaction samples were eluted through a small column of silica gel in disposable pipet to remove the catalyst prior to GLC analysis. Plots of log $[OctBr]_t/[OctBr]_0$ were linear and rate constants were calculated from the slopes using a linear regression program.

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Registry No. 7, 71015-62-8; 8, 102615-68-9; 9, 85725-88-8; 10, 85725-87-7; 11, 102615-69-0; 12, 102576-23-8; 13, 14098-24-9; 14, 102615-70-3; 15, 88106-64-3; 16, 102539-20-8; 17, 102539-21-9; diethyleneglycol monomethyl ether tosylate, 50586-80-6; 1-bromododecane, 143-15-7; 1-bromooctane, 111-83-1; KCN, 151-50-8.