Crown Ethers as Phase-transfer Catalysts. A Comparison of Anionic Activation in Aqueous–Organic Two-phase Systems and in Low Polarity Anhydrous Solutions by Perhydrodibenzo-18-Crown-6, Lipophilic Quaternary Salts, and Cryptands

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Anion-promoted nucleophilic substitutions carried out in aqueous–organic two-phase systems in the presence of catalytic amounts of perhydrodibenzo-18-crown-6 follow the classic mechanism of phase-transfer catalysis. The observed pseudo-first-order rate constants are linearly related to the concentration of complexed crown ether in the organic phase. The narrow reactivity range and the sequence found in the reaction between *n*-octyl methanesulphonate and a homogeneous series of anions in the PhCl–H_2O two-phase system ($N_3^- > I^- \sim Br^- > CN^- > Cl^- > SCN^-$) remain largely unaltered in anhydrous PhCl. From this point of view complexed crown ethers differ substantially from lipophilic quaternary salts and cryptates. Indeed, removal of the hydration sphere of the anions in going from two-phase to anhydrous conditions is balanced by a larger cation–anion interaction, resulting in a very small variation of anion reactivity. This indicates that, unlike cryptates, complexed crown ethers can hardly be considered as a source of ' naked anions.' A comparison is also reported among lipophilic crown ethers, quaternary salts, and cryptands as phase-transfer catalysts.

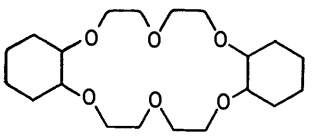
ANIONIC activation by crown ethers in homogeneous solution has been widely studied in the last ten years,[1] but the use of these systems as liquid-to-liquid [2] and solid-to-liquid [3] phase-transfer catalysts is relatively recent. Phase-transfer catalysis (p.t.c.) is classically performed in the presence of liphophilic quaternary salts Q^+Y^-,[4] and its mechanism has been fully clarified.[4-6] The same mechanism is at work [7] when liphophilic [2.2.2] cryptands are used as phase-transfer catalysts and also the relative anion reactivity under comparable reaction conditions is identical.

In quaternary salts and especially in cryptates, anions are largely separated from the cationic centre and are thus very reactive. The reactivity is further increased by the low polarity of the organic medium in which the quaternary salt or cryptate is dissolved and in which the reaction occurs. In the case of crown ethers the situation differs for at least two reasons. (i) In 18-crown-6 and its derivatives the anion can directly approach the complexed cation from a direction perpendicular to the plane of the polyether system. (ii) Complexation constants depend not only on the cation but also on the nature of the anion. Moreover, average dissociation rates of complexed crown ethers are several orders of magnitude faster than those of comparable bicyclic cryptands.[8]

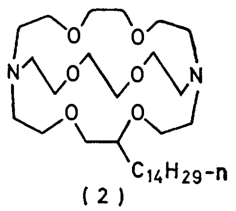
These factors suggested that anion-promoted reactions catalysed by lipophilic crown ethers in aqueous–organic two-phase systems would not necessarily follow a mechanism identical with that found for quaternary salts and cryptates. In particular, it seemed possible that reactions occur at least partially at the liquid–liquid interface.† Moreover, the enhanced cation–anion interaction in complexed crown ethers may lead to a different degree of anion activation than the other two catalytic systems, under similar reaction conditions.

Only a few kinetic parameters of solid-to-liquid [9] and liquid-to-liquid [10] phase-transfer reactions catalysed by crown ethers are available, and, to the best of our knowledge, no systematic kinetic study has been published on the reaction mechanism of crown ethers under liquid–liquid two-phase conditions.

We report here a study of reaction mechanism and anion reactivity in nucleophilic aliphatic substitutions catalysed by perhydro-18-crown-6 (PHDB) (1) in aqueous–organic two-phase systems. A study of catalysis by the complexed crown ether (1) of nucleophilic substitutions in low polarity organic solvents and a comparison of catalytic activity of crown ether (1), the cryptand (2) (2.2.2, C_{14}) and tributylhexadecylphosphonium salts (3) under phase-transfer conditions are also included.



(1)



(2)

n-$C_{16}H_{33}\overset{+}{P}Bu_3$ Y^-

(3)

RESULTS

Rates of displacement of the methanesulphonate group in n-octyl methanesulphonate (4) by a homogeneous series of anions (Cl^-, Br^-, I^-, SCN^-, N_3^-, CN^-) were measured at 70° in a water–chlorobenzene two-phase system in the presence of catalytic amounts of PHDB (1) (0.003—

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† Crown ethers can easily approach a crystal lattice and abstract cations, so that they are probably the catalysts of choice for many solid-to-liquid phase-transfer reactions.[1]

0.05 mol per mol of substrate) and with a 5 : 1 molar ratio of inorganic salt to substrate [reaction (1)].

$$n\text{-}C_8H_{17}OSO_2Me + KY \xrightarrow[\text{PhCl-H}_2\text{O}]{\text{PHDB}} n\text{-}C_8H_{17}Y + MeSO_3K \quad (1)$$

$$Y = Cl, Br, I, SCN, N_3, CN$$

Reactions were carried out with stirring at 1 000 r.p.m. to ensure that the rates were independent of the ion diffusion rates at the interface. Indeed, as observed for quaternary salts,[6] reaction rates increased with increases in the stirring speed up to 400 r.p.m., and were then constant above this value. Reaction rates were measured by n.m.r. analysis, following the disappearance of the methanesulphonate, with phenyl benzyl ether as internal standard. They followed the kinetic equation (2) up to at least three half-lives.

$$\text{rate} = k_{\text{obs.}}[\text{substrate}] \qquad (2)$$

By using liquid membranes [5] it was shown that under the reaction conditions all the crown ether is in the organic phase, in free or complexed form. In the absence of crown ether no reaction was observed up to at least 20 half-lives of the slowest catalysed reaction; therefore significant amounts of substrate could not be present in the aqueous phase. Finally, titrimetric and atomic absorption measurements detected no potassium methanesulphonate complexed by the crown ether in the organic phase, so equilibrium (3) is shifted fully to the right.

$$([K^+ (PHDB)]MeSO_3^-)_{\text{org.}} + (KY)_{\text{aq}} \rightleftharpoons ([K^+ (PHDB)]Y^-)_{\text{org.}} + (MeSO_3K)_{\text{aq}} \quad (3)$$

In the range examined (0.5—5 × 10^{-2}M), the observed rate constants are linearly related to the concentration of the [K$^+$ (PHDB)]Y$^-$ complex in the organic phase. Figures 1 and 2 show two such correlations, for a high (KI) and low (KBr) complexation constant respectively. The extent of complexation, which remains constant during the reaction, was determined by potentiometric titration of the anion in the organic phase and ranged from 2% for KCl to 93% for KI. The values are reported in Table 1, together with the second-order rate constants ($k_{\text{obs.}}$/[complexed PHDB]).

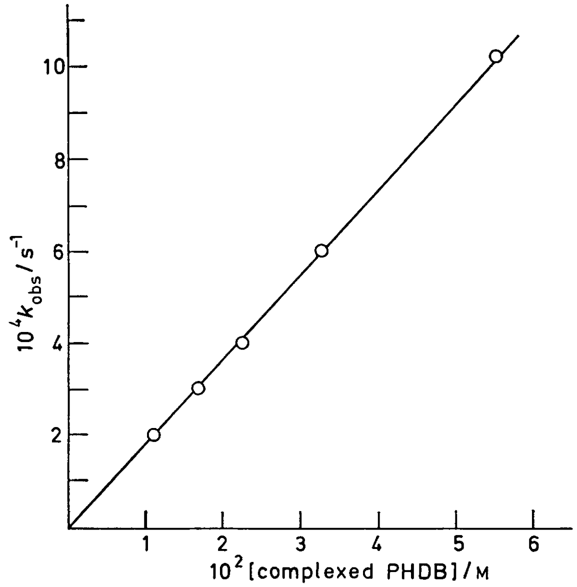

FIGURE 1 Dependence of the observed rate constants ($k_{\text{obs.}}/\text{s}^{-1}$) on the [K$^+$ (PHDB)]I$^-$ concentration for the reaction of n-octyl methanesulphonate with iodide ion in PhCl-H$_2$O two-phase system at 70°. For reaction conditions see footnote *a* of Table 1

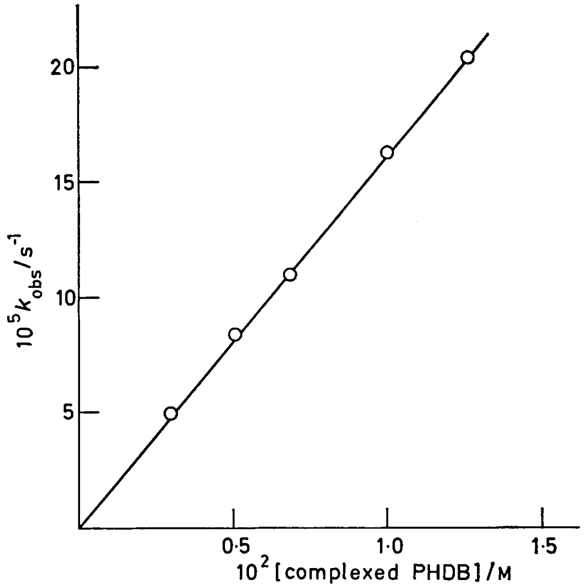

FIGURE 2 Dependence of the observed rate constants ($k_{\text{obs.}}/\text{s}^{-1}$) on the [K$^+$ (PHDB)]Br$^-$ concentration for the reaction of n-octyl methanesulphonate with bromide ion in PhCl-H$_2$O two-phase system at 70°. For reaction conditions see footnote *a* of Table 1

Karl Fischer analyses showed that, under these reaction conditions and in the presence of non-complexable [8a] lithium salts, the crown ether as such is associated with 2 mol. equiv. of water. In the presence of potassium salts, additional water (1—5 mol equiv., depending on the anion) is transferred into the organic phase (Table 1).

The anion reactivities were also measured in anhydrous chlorobenzene, in the presence of catalytic amounts of crown ether and of an excess of inorganic salt, as solid phase, to ensure a constant complexation. The extent of complexation depends on the anion, and ranges from 1% for Cl$^-$ to 95% for SCN$^-$. The reactions follow the kinetic equation (2) (Table 1).

In the case of [K$^+$ (PHDB)]Br$^-$, kinetics were repeated in the absence of KBr, using a homogeneous solution of the pre-formed complex (0.5—2 × 10^{-2}M) and a comparable concentration of substrate (4) (1—5 × 10^{-2}M). The reactions follow the kinetic equation (4), and the rate constants were identical with those obtained in the presence of the solid phase (Table 1).

$$\text{rate} = k[\text{substrate}][\text{complexed PHDB}] \qquad (4)$$

In comparison, Table 2 also includes the second-order rate constants measured, under identical conditions, in

TABLE 1

Second-order rate constants for nucleophilic substitutions of methanesulphonate by anions (Y^-) in n-octylmethanesulphonate in the presence of perhydrodibenzo-18-crown-6, at 70°

	Phase-transfer conditions [a]			Anhydrous conditions [b]	
Y	10^2k/l mol^{-1} s^{-1} [c,d]	% Complexation	Hydration state n of $[K^+ (PHDB)]Y^- \cdot nH_2O$ [e]	10^2k/l mol^{-1} s^{-1} [c,d]	% Complexation
N_3	5.1 (2.8)	12.3	5.3 ± 0.3	9.7 (6.1)	12.8
CN	0.72 (0.4)	12.2	7.3 ± 0.4	4.9 (3.0)	5.7
Cl	0.38 (0.2)	2.0	5.4 ± 0.4	0.86 (0.5)	1.0
Br	1.6 (0.9)	16.8	4.0 ± 0.2	2.0 [f] (1.2)	12.0
I	1.8 (1.0)	92.8	3.3 ± 0.3	1.6 (1.0)	87.6
SCN	0.20 (0.1)	83.0	4.0 ± 0.2	0.26 (0.2)	95.4

[a] A chlorobenzene solution (20 ml) of substrate (6.0×10^{-1}M) and of $[K^+ (PHDB)]Y^-$ (0.2—3.0×10^{-2}M), and a water solution (15 ml) of potassium salt (4.2M). [b] Same amounts of PhCl, substrate, and complexed crown as in *a*. in the presence of anhydrous KY (24 mmol). [c] k is defined as $k = k_{obs.}/[\text{complexed PHDB}]$. [d] Relative rates in parentheses. [e] For the uncomplexed crown ether $n = 2.0 \pm 0.2$. [f] $k = 2.2 \times 10^{-2}$ l mol^{-1} s^{-1} by using a homogeneous solution of the pre-formed complex: [PHDB,KBr] 0.5—2.0×10^{-2}M, [substrate] 1.0—5.0×10^{-2}M.

the presence of hexadecyltributylphosphonium salts (3) in PhCl–H_2O and anhydrous PhCl.

TABLE 2

Second-order rate constants for nucleophilic substitutions of methanesulphonate by anions (Y^-) in n-octyl methanesulphonate in the presence of $C_{16}H_{33}P^+Bu_3Y^-$, at 70°

	Phase-transfer conditions (PhCl–H_2O) [a]		Anhydrous PhCl [b]	
Y	10^2k/ l mol^{-1} s^{-1} [c]	k_{rel}	10^2k/ l mol^{-1} s^{-1} [c]	k_{rel}
N_3	4.7	6.8	15.0	19.0
CN	3.0	4.4	19.6	24.8
Cl	0.44	0.6	5.2	6.6
Br	0.74	1.1	2.3	2.9
I	0.69	1.0	0.79	1.0
SCN	0.13	0.19	0.19	0.24

[a] A chlorobenzene solution (20 ml) of substrate (6.0×10^{-1}M) and of $C_{16}H_{33}P^+Bu_3Y^-$ (1—10×10^{-2}M), and an aqueous solution (15 ml) of KY (4.2M). [b] [Substrate] 2—8×10^{-2}M, $[C_{16}H_{33}P^+Bu_3Y^-]$ 3—4×10^{-2}M. [c] k is defined as $k = k_{obs.}/[C_{16}H_{33}P^+Bu_3Y^-]$.

DISCUSSION

Reaction Mechanism.—The kinetic behaviour observed in nucleophilic aliphatic substitutions under two-phase conditions in the presence of catalytic amounts of PHDB is identical with that for reactions under similar conditions in the presence of lipophilic quaternary salts [6] and cryptates.[7] In particular: (i) reactions follow regular pseudo-first-order kinetics, and $k_{obs.}$ is linearly related to the concentration of complexed crown ether in the organic phase (Figures 1 and 2); (ii) the presence of the substrate and of all the crown ether in the organic phase excludes the possibility that reaction occurs, even in part, in the aqueous phase; and (iii) reactions cannot proceed at the interface since $k_{obs.}$ is independent of the stirring rate above 400 r.p.m.[11] This result is particularly significant in view of the importance of interfacial phenomena in the case of crown ethers.[1] Thus the classic mechanism of phase-transfer catalysis [4-6] is also at work in the case of lipophilic crown ethers: attack by the anionic reagent on the substrate occurs in the organic phase and is rate determining, while transfer of anions through the interface is a relatively fast step and does not require the concomitant transfer of cationic counterparts.

These conclusions may be summarized in equation (5), which is similar to those proposed [6,7] for phase-transfer reactions catalysed by quaternary salts and cryptands completely insoluble in water.

$$\begin{tikzcd} \mathrm{RX} + [\mathrm{K}^+ (\mathrm{PHDB})]\mathrm{Y}^- \arrow[rr] & & \mathrm{RY} + [\mathrm{K}^+ (\mathrm{PHDB})]\mathrm{X}^- \arrow[d] & \text{(organic phase)} \\ \mathrm{Y}^- \arrow[u] & + \ \mathrm{K}^+ \ + & \mathrm{X}^- & \text{(aqueous phase)} \end{tikzcd} \qquad (5)$$

Anion Reactivity.—The range of reactivity of the homogeneous series of anions in the PhCl–H_2O system under p.t.c. conditions is very narrow, and the observed sequence ($N_3^- > I^- \sim Br^- > CN^- > Cl^- > SCN^-$) differs from the well known anion reactivity scales in protic and dipolar aprotic solvents.[12] This sequence is similar to that found with quaternary salts [6] and cryptates [7] under p.t.c. conditions.

It had been demonstrated for the last two systems [6,7] that this reactivity sequence results from specific solvation of anion and substrate by a limited number of water molecules, since almost identical rate constants were determined by adding to the homogeneous solution of catalyst and substrate in anhydrous chlorobenzene the amount of water associated with both species in the organic phase under p.t.c. conditions. This experiment could not be repeated in the case of crown ethers, because of the low complexation constants and the necessity of working in the presence of an excess of inorganic salt as solid phase.

However, the hydration number of each anion under p.t.c. conditions is identical with that found for quaternary salts [6] and for cryptates [7] $[K^+ (2.2.2, C_{14})]Y^-$, so that for crown ethers also the anomalous reactivity scale in the two-phase system derives from the few molecules of water associated with the catalyst and with the substrate in the organic phase.

On the other hand, the behaviour of complexed crown ethers substantially differs from that of quaternary salts and cryptates when reactivities measured under two-phase conditions are compared with those found in low polarity anhydrous organic solvents (*e.g.* chlorobenzene). For crown ethers the second-order rate constants are the same for SCN^-, I^-, and Br^-, increase by a factor of two for Cl^- and N_3^-, and only for CN^- increase sevenfold. Although the reactivity range is slightly expanded, the relative order is identical in the two systems: this sharply contrasts with the behaviour of quaternary salts and cryptates, where anion reactivity increases up to one order of magnitude, and where the reactivity scale ($CN^- > N_3^- > Cl^- > Br^- > I^- > SCN^-$) is identical to the well known sequence found in dipolar aprotic solvents.

A striking example is given by $[K^+ (PHDB)]Cl^-$: its reaction rate is only twice as high in anhydrous *versus* p.t.c. conditions, whereas increases of 11 and 14.5 fold are found in the case of quaternary salts [6] and cryptates,[7] respectively. Reaction rates of complexed crown ethers (1) and quaternary salts (3) in anhydrous chlorobenzene and in chlorobenzene–water are compared in Figure 3.

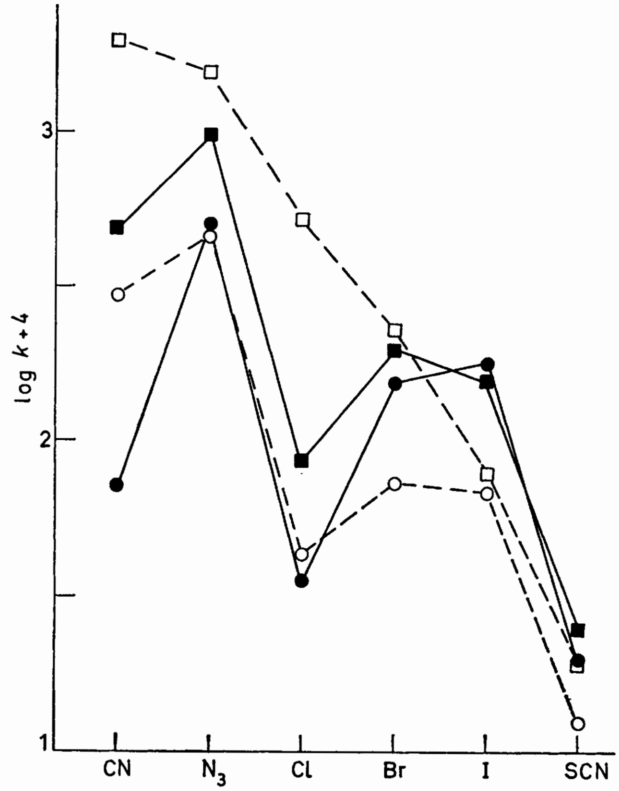

FIGURE 3 Comparison of the second-order rate constants (k/l mol^{-1} s^{-1}) for the reaction of n-octyl methanesulphonate with various nucleophiles Y^- associated with $[K^+ (PHDB)]$ and $C_{16}H_{33}P^+Bu_3$ in anhydrous PhCl and in the PhCl–H_2O two-phase system at 70°: $[K^+ (PHDB)]Y^-$–PhCl (■); –PhCl–H_2O (●); $C_{16}H_{33}P^+Bu_3Y^-$–PhCl (□); –PhCl–H_2O (○)

The reason for this behaviour evidently lies in the different topology of the three systems. In cryptates and in bulky quaternary salts [6,7] cation–anion interactions are minimized, independently of the medium. Therefore, in the absence of solvation, the anion is highly reactive, as in non-polar solvents. On the other hand, in PHDB (1) the anion can always interact with the complexed cation from a direction perpendicular to the plane of the ring. Depending on the nature of the anion and the solvent, crown ether can give rise to a wide spectrum of ionic species, contact ion-pairs, solvent separated ion-pairs, and dissociated ions.[8b,12d,13] *X*-Ray structural measurements [14] and n.m.r. studies in solution [15] have supplied much information on this subject.

In particular, all the data indicate that the ion-pair tends to become progressively more intimate as the solvent polarity decreases. Under these conditions interaction between the anion and the solvent becomes much less favourable, especially for small anions with high charge density and low polarizability.[13b-d] Thus, going from two-phase conditions to anhydrous non-polar solvents, removal of the hydration sphere of the anion must be balanced by a larger interaction between anion and cation within the ion-pair. The result is the very small variation of anion reactivity, and the compression of the reactivity range.* A parallel effect, particularly clear in the case of electronegative and less polarizable anions, is the decrease of the complexation constant.

The conclusion is that complexed crown ethers can hardly be considered as a source of 'naked ions',[3,9b] even in anhydrous, non-polar solvents. This may apply more correctly to quaternary salts, and especially to cryptates derived from lipophilic cryptands such as (2). Indeed, in the latter system, cation–anion separation is more complete, with no aggregation even in low polarity solvents.[7] Thus the reactivity of the unsolvated anion associated with the cryptate is probably the highest actually obtainable in solution.[7]

Choice of Phase-transfer Catalysts.—In the case of quaternary salts it was widely demonstrated that the observed rate constants depend on the anion concentration in the organic phase and the lipophilicity of quaternary cation, with other structural factors much less important.[5,6] Similar considerations can be applied to cryptands fully soluble in the organic phase, such as (2), since their catalytic activity depends directly on the degree of complexation. This is always very high, even for electronegative or slightly polarizable anions, such as Cl^-.[7]

TABLE 3

Comparison of catalytic efficiency of perhydrodibenzo-18-crown-6 and $C_{16}H_{33}P^+Bu_3Y^-$ in the reaction of n-octyl methanesulphonate with various nucleophiles (Y^-) under p.t.c. conditions in PhCl–H_2O

	$10^5k_{obs.}/s^{-1}$ [a]		
Y	PHDB	Q^+ [b]	$k_{obs.}^{PHDB}/k_{obs.}^{Q^+}$ [b]
N_3	25.1	188.0	0.13
CN	3.5	120.0	0.03
Cl	0.3	17.6	0.02
Br	10.7	29.6	0.4
I	66.8	27.6	2.4
SCN	6.6	5.2	1.3

[a] At 70°, with catalyst concentration 4×10^{-2}M; for the other reaction conditions see footnote *a* of Tables 1 and 2. [b] $Q^+ = C_{16}H_{33}P^+Bu_3$.

The case of crown ethers is completely different, since

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* The very narrow reactivity range found in nucleophilic aliphatic substitutions in acetonitrile in the presence of crown ethers [9b] can easily be explained on the same basis.

complexes of macrocyclic polyethers are up to five times less stable than their macrobicyclic counterparts.[8] The stability constants of crown ether complexes, even with the more favourable cations, are markedly low in the case of electronegative or slightly polarizable anions. Thus, $k_{\text{obs.}}$ values under p.t.c. conditions decrease dramatically compared with those of quaternary salts (Table 3) and cryptates.[7]

It may be deduced that crown ether (1) certainly cannot be chosen as catalyst for reactions promoted by anions such as Cl^- or CN^- under p.t.c. conditions, while for dispersed charge and/or polarizable anions lipophilic crown ethers, quaternary salts, and cryptands may all be used.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on a Varian A 60 spectrometer with tetramethylsilane as internal standard, potentiometric titrations were obtained with a Metrohm potentiograph type E 576 using silver and calomel electrodes, the latter isolated with potassium sulphate bridge, and molecular weight measurements were carried out with a Hitachi–Perkin-Elmer model 115 apparatus.

Materials and Solvents.—Perhydrodibenzo-18-crown-6 (1) was an AnalaR grade commercial product used without further purification. n-Octyl methanesulphonate, b.p. 112—114° at 2 mmHg, n_{D}^{20} 1.439 8, was prepared according to the literature (lit.,[16] b.p. 110—114° at 2 mmHg, n_{D}^{20} 1.439 2).

All inorganic salts were AnalaR grade commercial products; potassium azide was prepared according to the literature.[17] They were used without further purification, except for the experiments in anhydrous conditions in which they were carefully dried and stored in a desiccator.

Chlorobenzene was AnalaR grade chemical solvent used without further purification in the reactions carried out under phase-transfer conditions. For the experiments performed under anhydrous conditions, it was carefully purified and dried as previously reported.[6] Karl Fischer titrations showed a water content $\leqslant$ 50 p.p.m.

Extent of Complexation and Distribution Coefficients.—The extent of complexation of PHDB (1) under phase-transfer conditions was determined by stirring a standardized chlorobenzene solution (20 ml) of (1) (2—8 × 10^{-2}M) with an aqueous solution (15 ml) of potassium salt (4.2M) in a flask thermostatted at 70°. The system was stirred for 1 h, then kept without stirring for an additional 2—3 h to allow good separation of the two phases. Portions of the organic phase were withdrawn, and titrated with 0.01N-silver nitrate (potentiometric titration). Ancillary experiments showed that in all cases stirring times of *ca.* 60 min were sufficient to obtain a constant value of complexation.

Equilibrium (3) was studied under the conditions described above, with the addition to the system of potassium methanesulphonate (12 mmol) corresponding to the amount formed in reaction (1) at 100% conversion.

The extent of complexation under anhydrous conditions was determined by stirring a standardized chlorobenzene solution (20 ml) of PHDB (1) (2—8 × 10^{-2}M), thermostatted at 70°, with anhydrous potassium salt (24 mmol) as solid phase. Samples of the solution were withdrawn at various times by stopping the stirrer for 2—3 h and titrated potentiometrically with 0.01N-silver nitrate. This procedure was repeated until a constant value was obtained (1—3 h).

Hydration State of Complexed Crowns.—The hydration state of complexed crowns was determined by stirring for 1 h a standardized chlorobenzene solution (20 ml) of PHDB (1) (2—8 × 10^{-2}M) with an aqueous solution (15 ml) of the corresponding potassium salt (4.2M) in a flask thermostatted at 70°. Stirring was stopped and portions of the organic phase were withdrawn at intervals until a constant content of water was measured (Karl Fischer analysis; 3—6 h). The concentration of complexed KY in the organic layer was measured in parallel by potentiometric titration. The hydration state of PHDB (1) was determined as described above, using an aqueous solution of lithium chloride instead of potassium salts. Potentiometric titration of the organic layer did not detect Cl^-.

Kinetic Measurements.—The apparatus used for kinetic measurements under phase-transfer conditions has been previously described.[6] In a typical procedure, the reaction flask was thermostatted at 70 ± 0.1° and charged with an aqueous solution (15 ml) of potassium salt (4.2M) and a standardized chlorobenzene solution (20 ml) of PHDB (1) (2—10 × 10^{-2}M). The mixture was stirred for 1 h, then two portions (5 ml) of the organic phase were withdrawn, and the percentage complexation was determined by potentiometric titration. A chlorobenzene solution (10 ml) of n-octyl methenesulphonate (1.2M) and benzyl phenyl ether (0.8M) as internal standard, already at 70 ± 0.1°, was added to the flask, and stirring and timing were started. Portions of the organic phase were withdrawn at various times by stopping the stirrer for 40—60 s to allow adequate separation. These were quenched by cooling in an ice-bath and analysed by ^{1}H n.m.r. Reactions rates were determined by following the disappearance of the triplet ($\text{C}H_2\text{OSO}_2\text{Me}$) centred at δ 4.05 and using the singlet at δ 4.80 ($\text{OC}H_2\text{Ph}$) as standard. The pseudo-first-order rate constants ($k_{\text{obs.}}$) were obtained by plotting log [substrate] *versus* time and determining the slope of the straight lines. The second-order rate constants k were evaluated by dividing $k_{\text{obs.}}$ by the complexed crown concentration.

In the kinetic measurements under anhydrous solid-to-liquid conditions a standardized chlorobenzene solution (20 ml) of PHDB (1) (2—10 × 10^{-2}M) was added to previously dried potassium salt (24 mmol), in a reaction flask thermostatted at 70 ± 0.1°. This mixture was stirred for 3 h, then two portions (5 ml) of solution were withdrawn after stopping the stirrer for 3 h, and the percentage complexation was determined (potentiometric titration). A chlorobenzene solution (10 ml) of n-octyl methanesulphonate (1.2M) and benzyl phenyl ether (0.8M) as internal standard, already at 70 ± 0.1°, was added to the flask, and stirring and timing were started. The progress of the reaction was evaluated as described for the kinetic runs in the PhCl–H_2O system.

In the kinetic measurements under anhydrous homogeneous conditions standardized chlorobenzene solutions (10 ml) of n-octyl methanesulphonate (5—20 × 10^{-2}M) were added to a standardized solution (40 ml) of $[\text{K}^+ (\text{PHDB})]\text{Br}^-$ (0.6—2 × 10^{-2}M) in a 100 ml flask thermostatted at 70 ± 0.1°. The solution of $[\text{K}^+ (\text{PHDB})]\text{Br}^-$ was prepared as described above. Samples (5 ml), withdrawn periodically, were quenched in ice-cold MeOH (50 ml) and the unchanged nucleophile was determined using 0.01N-silver nitrate (potentiometric titration). The second-order rate constants were evaluated using a least-squares computer program, as previously described.[6] Kinetics measurements with hexadecyltributylphosphonium salts (3) have been previously reported.[6]

Liquid Membranes.—In a U shaped system, thermostatted at 70 ± 0.1°, standardized solutions (A) (30 ml) of [K$^+$ (PHDB)]Y$^-$ (2—3 × 10^{-2}M) and chlorobenzene (B) (30 ml) were connected through an aqueous solution (90 ml) of the corresponding inorganic salt KY (4.2M). The system was stirred and samples of organic phases (A) and (B) were independently withdrawn at various times by stopping the stirrer for 20 min to allow adequate separation, and titrated with 0.01N-silver nitrate (potentiometric titration). These measurements showed that no transfer of [K$^+$ (PHDB)]Y$^-$ from (A) to (B) could be detected even after several days. The runs with free crown ether (1) were performed as described above, using an aqueous solution of lithium chloride (4.2M) instead of potassium salts. The concentration of (1) in solutions (A) and (B) was checked by ^{1}H n.m.r. analysis, using benzyl phenyl ether as internal standard. In this case also no transfer of (1) from (A) to (B) was detected.

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REFERENCES

[1] G. W. Gokel and H. D. Durst, *Synthesis*, 1976, 168.

[2] (*a*) D. Landini, F. Montanari, and F. M. Pirisi, *J.C.S. Chem. Comm.*, 1974, 880; (*b*) D. Landini, A. Maia, F. Montanari, and F. M. Pirisi, *Gazzetta*, 1975, **105**, 863; (*c*) M. Makosza and M. Ludwikow, *Angew. Chem. Internat. Edn.*, 1974, **13**, 665; (*d*) M. Schlosser, B. Spakic, C. Zardini, and C. Van Chan, *ibid.*, 1975, **14**, 365; (*e*) A. W. Herriott and D. Picker, *J. Amer. Chem. Soc.*, 1975, **97**, 2345.

[3] (*a*) H. Dupont Durst, *Tetrahedron Letters*, 1974, 2421; (*b*) J. W. Zubrick, B. I. Dunbar, and H. Dupont Durst, *ibid.*, 1975, 71; (*c*) C. L. Liotta and H. Harris, *J. Amer. Chem. Soc.*, 1974, **95**, 2250; (*d*) C. L. Liotta, H. P. Harris, M. McDermott, T. Gonzales, and K. Smith, *Tetrahedron Letters*, 1974, 2417.

[4] (*a*) C. M. Starks, *J. Amer. Chem. Soc.*, 1971, **93**, 195; (*b*) C. M. Starks and R. M. Owens, *ibid.*, 1973, **95**, 3613.

[5] D. Landini, A. Maia, and F. Montanari, *J.C.S. Chem. Comm.*, 1977, 112.

[6] D. Landini, A. Maia, and F. Montanari, *J. Amer. Chem. Soc.*, 1978, **100**, 2796.

[7] D. Landini, A. Maia, F. Montanari, and P. Tundo, *J. Amer. Chem. Soc.*, 1979, **101**, 2526.

[8] (*a*) J. M. Lehn, *Structure and Bonding*, 1973, **16**, 1; (*b*) *Accounts Chem. Res.*, 1978, **11**, 49.

[9] (*a*) D. J. Sam and H. E. Simmons, *J. Amer. Chem. Soc.*, 1974, **96**, 2252; (*b*) C. L. Liotta, E. E. Grisdale, and H. P. Hopkins, jun., *Tetrahedron Letters*, 1975, 4205; (*c*) A. Knöchel, J. Oehler, and G. Rudolph, *ibid.*, p. 3167; (*d*) A. el Basyony, J. Klimes, A. Knöchel, J. Oehler, and G. Rudolph, *Z. Naturforsch.*, 1976, **31b**, 1193; (*e*) W. L. Dorn, A. Könchel, J. Oehler, and G. Rudolph, *ibid.*, 1977, **32b**, 776; (*f*) A. Knöchel, J. Oehler, and G. Rudolph, *ibid.*, p. 783.

[10] Kam-Ham Wong, *J.C.S. Chem. Comm.*, 1978, 282.

[11] F. M. Menger, *J. Amer. Chem. Soc.*, 1970, **92**, 5965.

[12] (*a*) A. J. Parker, *Chem. Rev.*, 1969, **69**, 1; (*b*) R. Fuchs and L. L. Cole, *J. Amer. Chem. Soc.*, 1973, **95**, 3194; (*c*) W. T. Ford, R. J. Hauri, and S. G. Smith, *ibid.*, 1974, **96**, 4319; (*d*) G. Illuminati, 'Chemistry,' ed. M. R. J. Dack, Wiley, New York, 1976, vol. 8/2, ch. 12.

[13] (*a*) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem. Internat. Edn.*, 1972, **11**, 16; (*b*) V. V. Litvak and S. M. Shein, *Zhur. org. Khim.*, 1976, **12**, 1723; (*c*) C. M. Thomassen, T. Ellingsen, and J. Ugelstad, *Acta Chem. Scand.*, 1971, **25**, 3024; (*d*) V. M. De Palma and E. M. Arnett, *J. Amer. Chem. Soc.*, 1978, **200**, 3514.

[14] (*a*) M. A. Bush and M. R. Truter, *Chem. Comm.*, 1970, 1439; (*b*) D. Bright and M. R. Truter, *J. Chem. Soc.* (*B*), 1970, 1544; (*c*) M. A. Bush and M. R. Truter, *ibid.*, 1971, 1440; (*d*) *ibid.*, 1972, 340; (*e*) *ibid.*, p. 345; (*f*) N. K. Dalley, D. L. Smith, R. M. Izatt, and J. J. Christensen, *J.C.S. Chem. Comm.*, 1972, 90; (*g*) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, 1974, **74**, 351.

[15] D. Live and S. I. Chan, *J. Amer. Chem. Soc.*, 1976, **98**, 3769.

[16] H. R. Williams and H. S. Mosher, *J. Amer. Chem. Soc.*, 1954, **76**, 2984.

[17] M. W. Miller and L. F. Andrieth, *Inorg. Synth.*, 1946, **2**, 140.