# Mechanism of solid-liquid phase transfer catalysis by polymer-supported linear polyethers

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Polystyrene resin-supported oligo-oxyethylenes have been used as catalysts in the reaction of solid potassium phenoxide with 1-bromobutane in toluene. Detailed kinetic analysis has established the rate law to be similar in form to that found for catalysis by a non-supported polyether, and activation energies also to be similar. In each case the rate controlling process appears to be the reaction of the catalyst/salt complex with the alkyl halide. The various possible mechanisms by which phase transfer of the salt into the resin-bound catalyst takes place are discussed, and collisional contact between the resin and the solid salt shown to be a prerequisite for efficient catalysis.

## INTRODUCTION

The use of phase transfer catalysts both in liquid–liquid and solid–liquid reactions is now a routine occurrence in organic synthesis[1,2] and a large number of polymer-supported analogues have also been shown to be effective catalysts[3,4]. Resin-bound linear polyethers readily catalyse displacement reactions of aqueous salts with alkyl halides[5–7]. However, the catalytic effect is relatively small compared with that observed when solid salts are used[8–10]. The apparent catalysis of a reaction between a solid and liquid by a second solid raises important questions about the molecular processes involved and we have now completed a detailed study of such a system. The reaction we have examined is that of solid alkali metal phenoxides with 1-bromobutane in toluene catalysed by polystyrene resin-supported oligo(oxyethylenes), the preliminary results of which have already been published[8,11].

## EXPERIMENTAL

### *Materials*

Analar toluene was used as supplied except for the 'anhydrous' reactions when it was dried over lithium aluminium hydride and then fractionated. 1-Bromobutane (Koch Light Ltd) was used as supplied. 2-[2-(2-Methoxy ethoxy)ethoxy]-ethanol (Fluorochem Ltd) was used as supplied except in the 'anhydrous' reactions when it was dried by passing down a column of molecular sieves.

In the vast majority of reactions the catalyst support employed was a 2% crosslinked gel-type resin with a particle size of 35–75 μm (Bio Beads SX2). When the role of the matrix was examined, a 2% crosslinked gel-type resin with particle size 250–500 μm and a 10% crosslinked macroporous species (toluene as diluent) with particle size 100–200 μm were prepared in-house using methods previously described[12]. In addition a macroreticular support of nominal crosslink ratio ~42% and particle size 15–20 μm (Polymer Laboratories Ltd) was also employed.

Potassium phenoxide was synthesized using the method reported by Kornblum and Lurie[13]. The white solid was thoroughly washed with acetone and petroleum ether and ground to a fine powder before drying at 60°C under vacuum. It was assayed by titration with hydrochloric acid using methyl red as indicator and had a purity greater than 99%. When required in the form of large crystals the phenoxide was dissolved in the minimum volume of boiling tetrahydrofuran with the aid of a few drops of water. The filtered hot solution was allowed to cool slowly to room temperature over a period of 3 h during which time crystallization in the form of plates of average dimensions 1 x 0.5 x 0.03 cm took place. These were collected carefully under gentle suction, washed with a little toluene, and dried under vacuum at 60°C.

### *Supported catalysts*

2-[2-(2-Methoxyethoxy)ethoxy]-ethanol (HOE3Me) was converted to its sodium salt and reacted with chloromethylated resins[14] as previously described[8]. In the case of this short-chain polyether, virtually quantitative conversion of chloromethyl groups was obtained in all catalyst preparations, though the exact conditions employed were varied somewhat (*Table 1*). The loadings of the polyether therefore correspond to the original degrees of chloromethylation of each resin. Each polymer-supported catalyst is designated ®XYE3Me where XY refers to the nominal crosslink ratio of the support, E3 indicates three ethylene oxide residues in the polyether, and Me is the methyl head group. When appropriate the catalyst loading on the support is indicated in brackets.

### *Catalysed Williamson ether syntheses*

$K^+OPh^-$ (solid) + n-BuBr (toluene) $\xrightarrow{\text{Catalyst}}$ PhOBu + $K^+Br^-$.

These were carried out on a small scale as previously described[8] and the reactions monitored by quantitative gas–liquid chromatographic (g.l.c.) methods using n-nonane as

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*Table 1* Preparation of polymer-supported oligo(oxyethylenes)[8]

| Polymer-supported catalyst[a] | Particle size (μm) | Molar ratio, polyether/ NaH/CMP[c] | Reaction Co-solvent | Reaction temperature (°C) | Reaction time (days) | % Functionalization[b] |
|---|---|---|---|---|---|---|
| Ⓟ X10E3Me | 100–200 | 20/10/1 | – | 110 | 2 | 71 |
| Ⓟ X2E3Me | 35–75 | 10/2/1 | Tetrahydrofuran | 80 | 3 | 61 |
| Ⓟ X2E3Me | 35–75 | 4/2/1 | Tetrahydrofuran | 80 | 3 | 37 |
| Ⓟ X2E3Me | 35–75 | 6/2/1 | Toluene | 110 | 3 | 10 |
| Ⓟ X2E3Me | 250–500 | 5/2/1 | Tetrahydrofuran | 80 | 3 | 70 |
| Ⓟ X42E3Me | 15–20 | 9/3/1 | Xylene | 120 | 3 | 29 |

[a] See text for explanation of symbolism
[b] % aromatic groups substituted with polyether residues
[c] CMP - Chloromethylated polymer

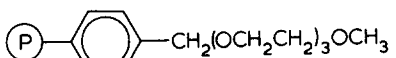
the internal standard. The stationary phase used in all g.l.c. analyses was 5% Apiezon and Chromosorb G. Reactions were carried out in 5 ml round-bottomed flasks fitted with a small but wide reflux condenser so that g.l.c. samples could easily be withdrawn via the condenser. Reactions were usually magnetically stirred at ~600 rpm using a Gallenkamp stirrer/hotplate and this was found to give reliable and reproducible agitation conditions.

### *Solubility of $K^+OPh^-$ in toluene*

The solubility of $K^+OPh^-$ in toluene was measured by flame absorption photometry utilizing a Perkin–Elmer 360 instrument. Calibration was achieved using solutions of pure potassium phenoxide in toluene containing a small quantity of HOE3Me. The solubility in toluene alone was conservatively estimated as $\leqslant 0.5$ ppm

## RESULTS

Preliminary investigations[8,11] indicated that while the catalytic activity of bound oligo(oxyethylene) species increased with increasing chain length of the polyether it was more difficult to achieve high loadings of these on resins and as a result this more detailed examination was pursued with the supported catalyst, I.



(I)

$HO(CH_2CH_2O)_3CH_3$

(II)

By appropriate choice of conditions, virtually quantitative yields of n-butyl phenyl ether could be achieved in Williamson syntheses[8] and the present results will dwell on the mechanistic details rather than the synthetic utility of these systems.

### *Experimental rate laws*

Kinetic studies were carried out with ⓅX2E3Me (61% loaded) and the non-supported species, II. The usual technique of varying the concentration of one component while keeping the other concentrations fixed was employed in order to deduce kinetic dependences. Initial rates were derived from the tangents at zero time to the decay curves of 1-bromobutane. *Figures 1* and *2* show such decay curves, over significant extents of reaction, to be virtually independent of the amount of solid potassium phenoxide employed, both in the case of the supported and non-supported catalyst.

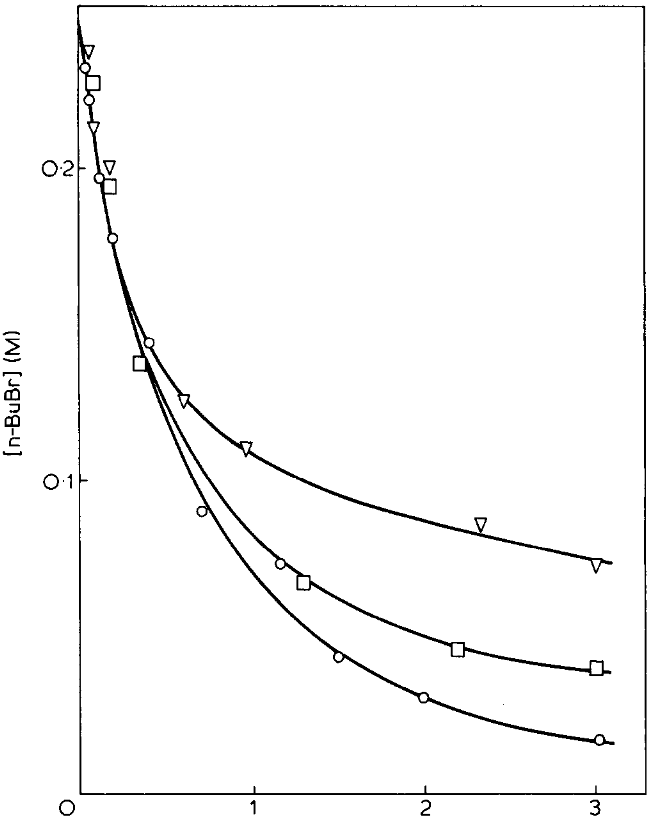


*Figure 1* Variation in decay curves with weight of $K^+OPh^-$ using ⓅX2E3Me as catalyst. [n-BuBr] = 0.24 M; catalyst = 1.16 mmol of ethereal oxygen (61% loaded); temperature = 105°C. $K^+OPh^-$ = ○, 2.0 mmol; □, 1.0 mmol; △, 0.5 mmol

A zero order rate dependence may be deduced in each case. Conventional log[rate] *versus* log[1-bromobutane] plots yielded good straight lines from which the kinetic exponent for 1-bromobutane was deduced to be ~1 for both catalysts. Similar analysis of the catalyst dependence (expressed as mmol of ethereal oxygen) also gave good straight line plots with kinetic exponents ~0.9 and ~1.2 for I and II, respectively. Thus the experimental rate laws for bound and unbound catalysts can be summarized as:

$$\frac{-\mathrm{d}[\mathrm{BuBr}]}{\mathrm{d}t} = k_1 [\mathrm{BuBr}]^{1.0} [\mathrm{KOPh}]^{0} [\mathrm{I}]^{0.9}$$

and

$$\frac{-\mathrm{d}[\mathrm{BuBr}]}{\mathrm{d}t} = k_2 [\mathrm{BuBr}]^{1.0} [\mathrm{KOPh}]^{0} [\mathrm{II}]^{1.2}$$

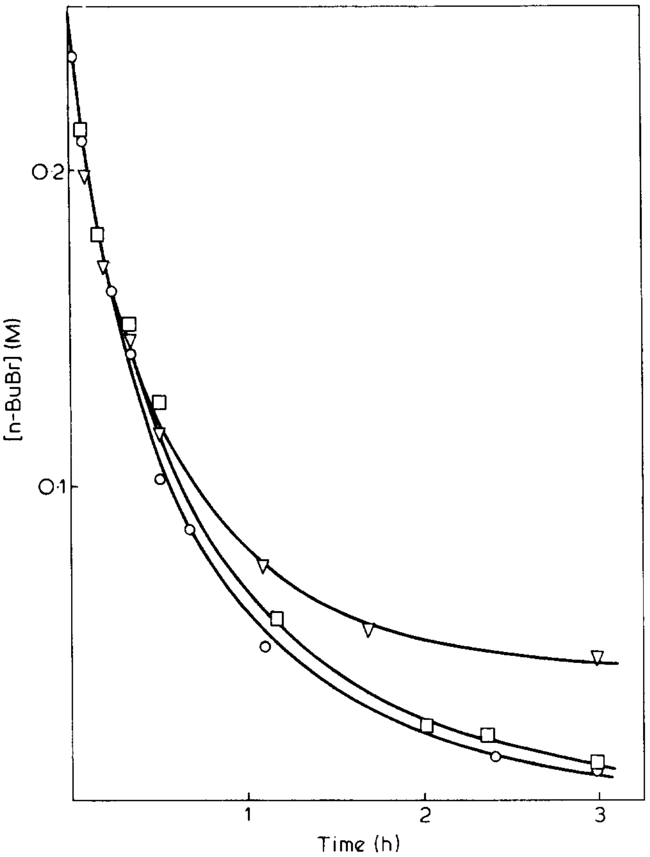


***Figure 2*** Variation in decay curves with weight of $K^+OPh^-$ using HOE3Me as catalyst. [n-BrBr] = 0.24 M; catalyst = 1.16 mmol of ethereal oxygen; temperature = 105°C. $K^+OPh^-$ = ⊙, 2.0 mmol; ⊡, 1.0 mmol; △, 0.5 mmol

where the terms in phenoxide salt and catalyst refer strictly to weights of each. The most important feature of these is the overall similarity in the dependences, strongly suggesting that the rate controlling process is the same for both catalysts I and II. This observation is confirmed by the results of experiments conducted in the temperature range 75°–105°C. *Figure 3* shows the Arrhenius plots for $k_1$ and $k_2$ from which the activation energies for reactions catalysed by I and II are 42 and 47 kJ $mol^{-1}$, respectively. No attempt was made to evaluate pre-exponentail factors because of the arbitary units of $k_1$ and $k_2$.

### *Structure of polymer support*

Further compelling evidence arises from experiments in which the structure of the resin support was varied over all of the types conveniently available. *Table 2* shows that for fixed reaction conditions the rate of reaction is independent of the particle size of the support, its crosslink ratio and also its morphology, i.e. whether it is a gel-type resin or a macroporous or macroreticular species[15].

### *Catalyst loading*

The loading of catalyst I was varied from 10 to 61% and the results appear in *Figure 4* where each experiment was carried out with a fixed total amount of catalyst. The variation in the rate of reaction is quite different to that observed for strong diffusion control by a resin matrix[12] and is discussed in detail later.

### *Effect of stirring, phenoxide salt crystal size and inhibition of resin salt contact*

A number of ancillary experiments were performed in order to differentiate between a number of possible molecular processes which might be involved in the catalyses using the bound catalyst I. *Figure 5* summarizes these. Using the normal powdered form of the phenoxide salt, but with no stirring, reduced the reaction rate by only a small amount, and the refluxing solvent appeared to provide sufficient agitation. The behaviour of polymer-supported onium salts used as catalysts in liquid–liquid reactions can be quite different, and reaction rates can be highly dependent on the efficiency of agitation of the phases[21]. This is particularly true when the amount of bound catalyst used is large compared with the area of the phase boundary in the unstirred state[18]. Using a form of the salt prepared as large platelets (~1 x 0.5 x 0.03 cm) without stirring, reduced the rate further. However, by far the most significant effect on the reaction was achieved by separating the resin catalyst and

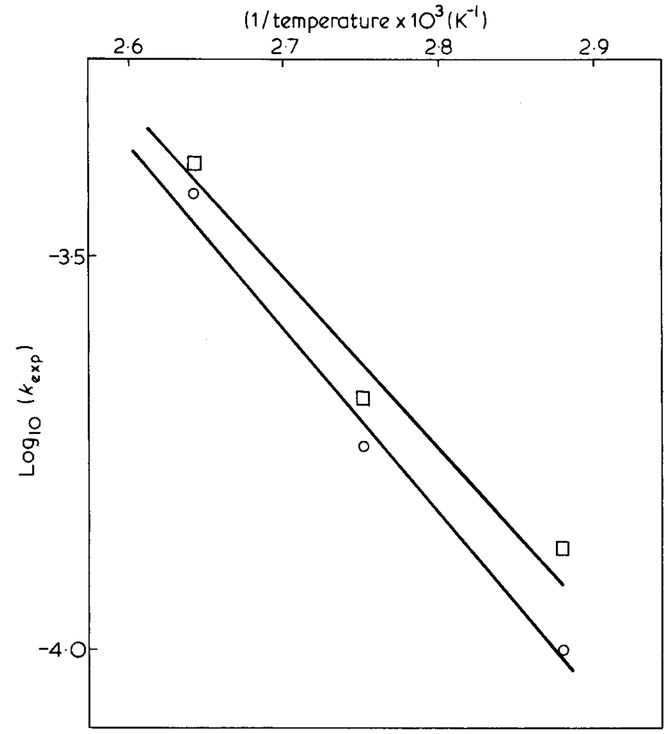


***Figure 3*** Temperature dependences of reactions catalysed by ®X2E3Me, ⊡; and HOE3Me, ⊙

***Table 2*** Effect of matrix type and particle size on rate of reaction[a]

| Catalyst[b] (loading) | Particle size (μm) | Initial rate x $10^5$ ($M^{-1}$ $s^{-1}$) | Loss of n-BuBr[c](%) |
|---|---|---|---|
| ® X2E3Me (61%) | 35–75 | 10.0 | 93 |
| ® X2E3Me (61%)[d] | ⩽ 35 | 10.5 | 98 (2.5 h) |
| ® X2E3Me (70%) | 250–500 | 10.0 | 99 (2.5 h) |
| ® X10E3Me (71%) | 100–200 | 11.0 | 92 |
| ® X42E3Me (29%) | 15–20 | 10.5 | 95 |
| HOE3Me (–) | – | 9.1 | 98 |

[a] $[n\text{-BuBr}]_{initial}$ = 0.24 M; $K^+OPh^-$ = 2.0 mmol; catalyst = 1.16 mmol of oxygen; temperature 105°C

[b] See Experimental for designation

[c] After 3 h unless specified

[d] Crushed sample of first catalyst

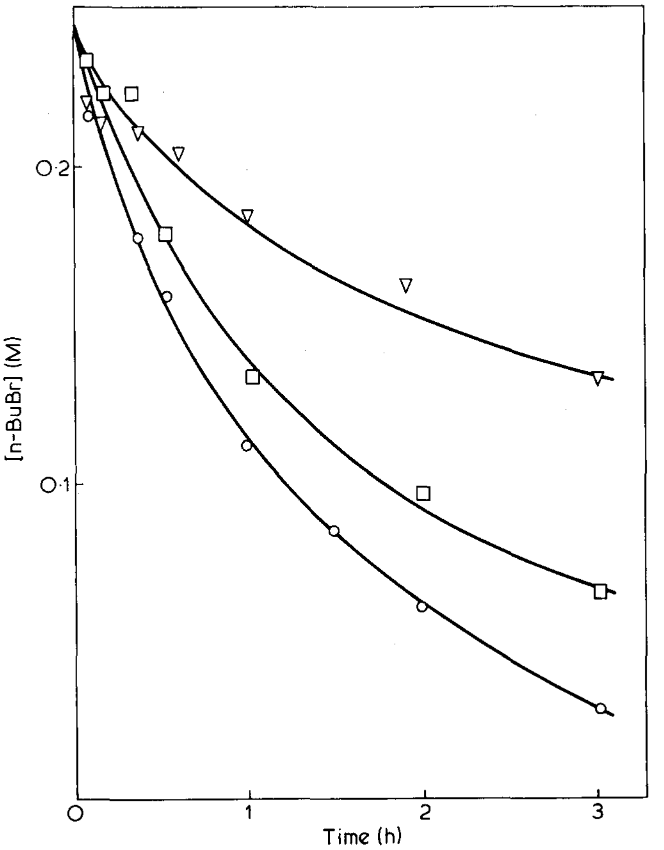


*Figure 4* Variation in decay curves with the loading of ⓅX2E3Me [n-BuBr] = 0.24 M; $K^+OPh^-$ = 2.0 mmol; total catalyst = 0.58 mmol of oxygen; temperature = 105°C. Loading = ⊙, 61%; ⊡, 37%; △, 10%

the solid salt using a small partitioned reactor (*Figure 6*) when, inhibition of resin/salt contact apparently reduced the rate of reaction to almost its uncatalysed value[8].

### *Effect of trace quantities of water*

Preliminary experiments demonstrated that the presence of an aqueous phase in a corresponding liquid–liquid system gives rise to a considerable reduction in the activity of these bound catalysts[8] and so a series of experiments were carried out with the solid–liquid system to which increasing quantities of water were added. *Table 3* summarizes the results for both catalysts. Normal experiments employed Analar grade toluene and other reagents which had not been subjected to any vigorous drying procedures. When carefully-dried materials were used in an 'anhydrous' reaction the initial reaction rate actually fell slightly for both catalysts. Addition of 20 μl of water to a normal reaction mixture gave a slight rate enhancement whereas 100 μl of water reduced the rate again. With 2000 μl the conventional liquid–liquid system is established and the reaction rate is low. Thus trace quantities of water appear to facilitate the catalysis in each case whereas the appearance of a discrete aqueous phase causes dramatic inhibition.

## DISCUSSION

### *Mechanism*

The unbound catalyst, II, seems to function in a similar way to crown ethers[16]. It solubilizes the potassium phenoxide in toluene[17] by specific interaction with the cation, allowing the bimolecular displacement reaction to occur as the rate-controlling process. Simultaneously, the nucleophilicity of the anion is probably enhanced since it is not encumbered by water molecules. In addition, the tightness of the alkali metal phenoxide ion pair is likely to be reduced on simple electrostatic grounds. No experimental evidence on these points is presented here though additional data to appear in a separate paper strongly suggests this[17].

Superficially the bound catalyst, I, appears to behave in a similar fashion to II and all the kinetic evidence points to the rate-controlling process being the same in each case. This in the first instance seems surprising, since the presence of the polymer support might have been expected to reduce the effectiveness of the catalyst. Not only is this not so, but a wide range of resin types behave similarly. All of the polymer-bound polyether moieties are active in catalysis as indicated by the kinetic studies and confirmed by the lack of a particle size dependence. Even a crushed resin catalyst has the same activity as the species from which it is derived. Clearly, therefore, the molecular processes involved allow the rapid transport of phenoxide salt to the entirety of the resin bound catalyst and the same displacement reaction as that occurring with the unbound species II is rate-controlling. This is quite different to the matrix diffusion-controlled reaction of bound pyridine groups reported before[12] and the diffusion-limited chemical reaction described recently for

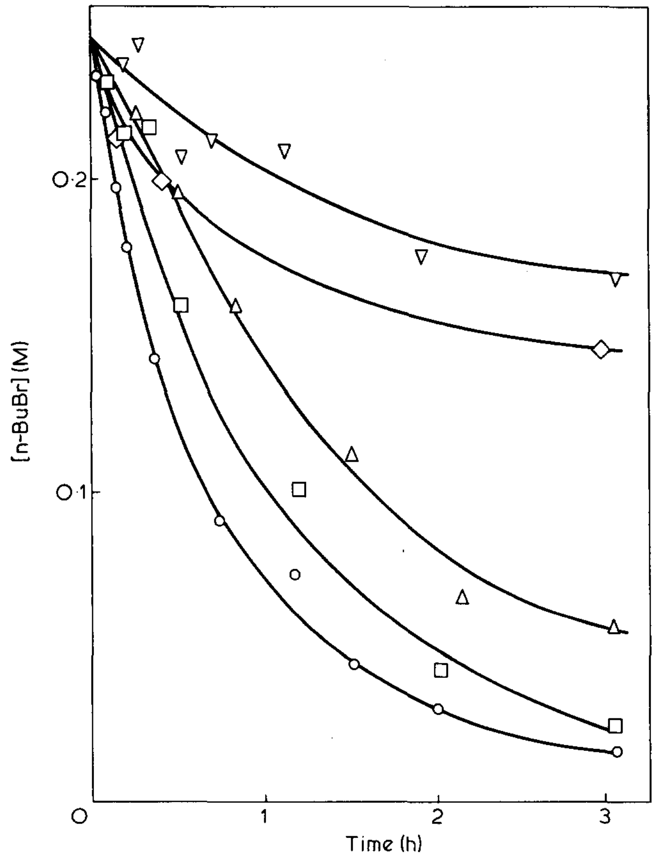


*Figure 5* Effect of stirring, $K^+OPh^-$ crystal size and $K^+OPh^-$/catalyst separation on the rate of reaction. [n-BuBr] = 0.24 M; $K^+OPh^-$ = 2.0 mmol; catalyst = 1.16 mmol of oxygen (61% loaded). Temperature = 105°C

⊙, Powdered $K^+OPh^-$, stirrer speed ~700 rpm
⊡, Powdered $K^+OPh^-$, no stirring
△, Large crystals $K^+OPh^-$, no stirring
◇, Partitioned cell used, both compartments stirred
△, Partitioned cell used, no stirring

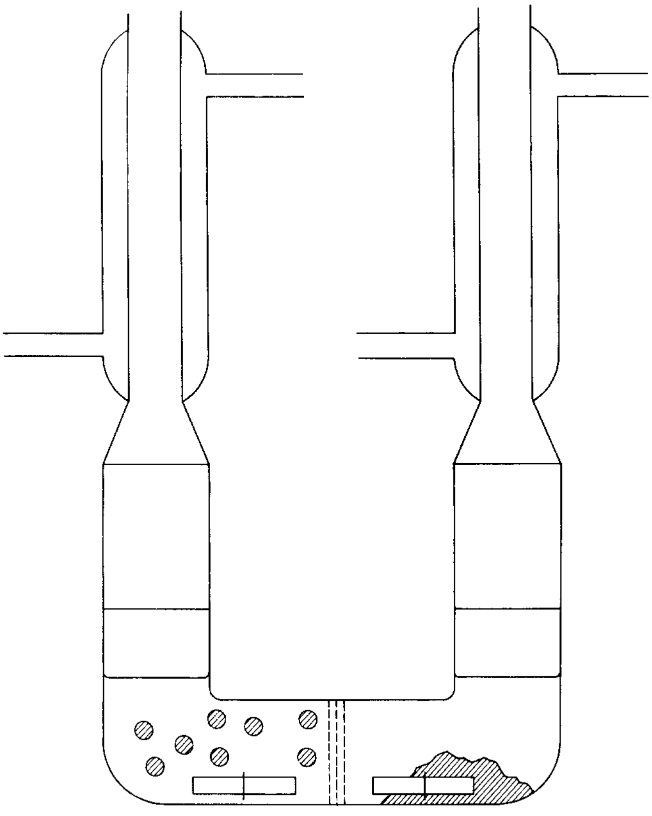


*Figure 6* Partitioned cell reactor. LHS, polymer-supported catalyst; RHS, solid $K^+OPh^-$

*Table 3* Effect of water on rate of reaction[a]

| Catalyst[b] | Initial rate x $10^5$ ($M^{-1}\,s^{-1}$) | Loss of n-BuBr[c] (%) | Quantity of water (μl) |
|---|---|---|---|
| ®X2E3Me | 3.7 | 79 | Anhydrous[d] |
| | 5.0 | 69 | Normal[d] |
| | 5.5 | 83 | 20 |
| | 3.3 | 69 | 100 |
| | ~0.1 | 7 | 2000 |
| HOE3Me | 3.9 | 56 | Anhydrous[d] |
| | 4.1 | 74 | Normal[d] |
| | 5.4 | 81 | 20 |
| | 2.0 | 65 | 100 |
| | 0.1 | 14 | 2000 |

[a] $[n\text{-BuBr}]_{initial}$ = 0.24 M; $K^+OPh^-$ = 2.0 mmol; catalyst = 1.16 mmol of oxygen; temperature 90°C
[b] See Experimental for designation
[c] After 3 h
[d] See Experimental for details

a liquid–liquid reaction catalysed by a resin bound phosphonium salt[18].

There are three possible molecular processes by which the resin bound catalyst may become associated with $K^+OPh^-$ ion pairs and hence effect the observed phase transfer process. In mechanism (a) shown in *Figure 7*, a discrete molecular solubility of $K^+OPh^-$ in toluene is required for the rapid absorption of the salt by the supported catalyst. A fast equilibrium might be established in which $K^+OPh^-$ in solution and within the resin volume is replenished by the reservoir of solid $K^+OPh^-$. This direct process certainly seems to play a significant role in the case of solid sodium iodide where the solubility in benzene[10] at 80°C is ~3 x $10^{-4}$ M. However, in the case of $K^+OPh^-$ in toluene the measured solubility is $\leqslant 0.5$ ppm corresponding to $\leqslant 4 \times 10^{-6}$ M, and such low reactant concentrations are not consistent with an efficient transport of salt into the resin catalyst nor with the observed reaction rates. Furthermore, in experiments employing the partitional reactor, if the salt did have a significant solubility in toluene, it would be difficult to rationalize the large decrease in rate even allowing for some restricted diffusion through the glass frit.

In the second mechanism (b) it might be argued that some unbound polyether, an impurity associated with the resin bound species, could act as a 'ferry', solubilizing $K^+OPh^-$ in the toluene and transporting it to the surface or directly to the interior of resins. Once again this seems unlikely, first because the washing procedures used in the preparation of the resin bound species are thorough, and second because reclaimed resin catalyst has the same activity as a new sample. If an unbound component was involved, some or all of this would be lost during the first use of a catalyst so that its activity would be expected to fall on subsequent re-use. In addition, the experiments with the partitional reactor are also very telling, since the presence of a 'ferry' catalyst would allow relatively easy transfer across the reactor. It is important to point out, however, that Yanagida and coworkers[10] have observed the growth of an infra-red band at 1720 $cm^{-1}$ in polymer-supported polyethers. They have tentatively assigned it to a carbonyl function, possibly arising from oxidative cleavage of the benzyl ether linkage attaching the catalyst to the polystyrene support. We have also observed this band in our supported

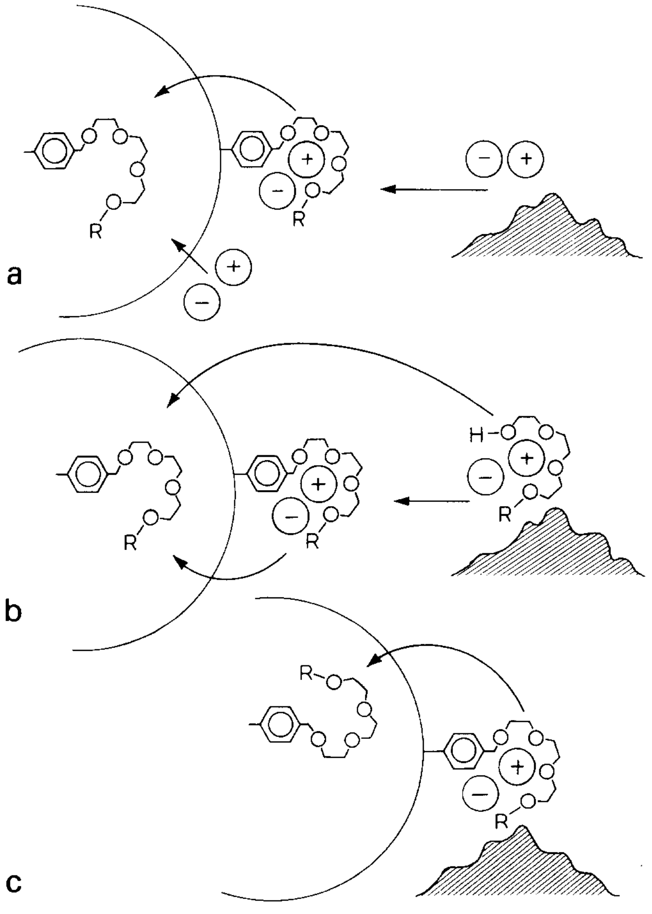


*Figure 7* Possible mechanisms for transfer of $K^+OPh^-$ to the interior of resin-bound catalysts

catalysts when left unused for 16 months. Exhaustive Soxhlet extraction of such a resin revealed ~4% decrease in weight, which we can only assume arises from slow cleavage of the catalyst from the support. Nevertheless, in the case of fresh materials, the presence of unbound polyether does not appear to be significant.

Mechanism (c) which we feel best fits all the experimental evidence requires discrete resin–salt contact. During this surface interaction, polyether groups attached to the resin exterior solubilize or complex $K^+OPh^-$ which is then transferred rapidly to the interior of the resin via the network of polyether chains. Generally, loadings are so high that the bound polyether molecules could almost be regarded as a second interpenetrating network through the polystyrene matrix. $K^+OPh^-$ ion pairs associated with polyether molecules then react in a bimolecular process with the alkyl halide, present as a molecular solution in toluene, in a rate-controlling step essentially the same as that which occurs with the unbound catalyst. Probably the tightness of the ion pairs is simultaneously reduced, though again this work presents no independent evidence on this issue. Mechanism (c) explains all the observed kinetic features and is consistent with the experiments in which resin–salt contact is eliminated. In addition, when large crystals of $K^+OPh^-$ were refluxed in toluene in the presence of a known weight of resin bound catalyst (2% gel type, 70% loaded) in spite of the inherently low solubility of the salt in toluene, the crystals were observed to have 'dissolved' completely in the polymer matrix over a period of 15 min, when the polymer assumed a brown–red colouration similar to that displayed during reactions. In this semiquantitative experiment the molar ratio of salt–polyether chains achieved within the resin was ~0.44:1.

### *Catalyst loading*

The variation in reaction rate with the catalyst loading on the resin can be explained in two ways. For a 'pseudo-homogeneous' bimolecular reaction of a bound reagent X with a mobile species Y the loading of X on its support would not be expected to alter the rate of disappearance of Y measured by monitoring the bulk solution[19]. In the present case, however, it is possible that the number of catalyst groups associated with each potassium ion may change as the local concentration of bound polyether is varied, hence further influencing the effective concentration of phenoxide ions and thence the reaction rate. While no directly significant measurements have been made in the case of bound polyethers, the ratio of potassium phenoxide to unbound polyethers, in toluene solutions of the latter, does vary markedly with the overall concentration of polyether dissolved in the solvent[17]. An alternative or complementary explanation is that the transport of phenoxide salt throughout the resin support, via the secondary network of bound catalyst chains, may be impaired as the loading is reduced. Thus some polyether groups may fail to contribute to the solubilization–activation process.

### *Effect of water*

The effect of trace quantities of water appears to be the same with both bound and unbound catalysts. Where a discrete aqueous phase exists then unbound polyether remains largely in the aqueous phase and is only poorly effective in achieving transfer of the inorganic salt into the organic phase, and this confirms earlier observations[20]. In the case of bound polyethers, the nature of aqueous and organic phases present simultaneously within resin interiors has been discussed in detail[3], and the role of such catalysts may simply be to increase the effective surface area between the two liquid phases, thereby increasing the rate of what is essentially an interfacial reaction, i.e. true phase transfer of ion pairs may play a small role. Where the amount of water is considerably reduced so that no discrete aqueous phase is detectable, rates of reaction are optimized realtive to both the strictly anhydrous system and the liquid–liquid case. Why small quantities of water achieve this is not known, but the situation seems similar to that observed with crown ethers[1], where it has been suggested that micro-solubilization of the salt by water occurs prior to transfer by the crown ether into the organic phase. In the present work it appears that water initially becomes associated with the solid salt phase and specific solvation of ions within the crystal lattice by water may contribute to a reduction in the lattice energy of these, aiding breakdown and subsequent transfer by bound or unbound polyether molecules.

### *Qualification*

It must be emphasized that the molecular processes suggested as being operative with the bound catalyst, I, are specific to this sytem and it is not valid to generalize this situation to other bound catalysts or indeed other reactions. We have, for example, strong evidence to suggest that in the case of much longer polyether chains (~30 ethylene oxide residues) supported in a similar manner, loading of the resin occurs largely in the outer shells of individual beads, and so catalysis occurs largely in this outer surface. Such bound species, therefore, can behave quite differently to the relatively uniformly distributed system, I, in reactions which are, say, matrix diffusion-controlled rather than chemically-controlled.

## ACKNOWLEDGEMENTS

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## REFERENCES

1 Weber, W. P. and Gokel, G. W. in 'Phase Transfer Catalysis in Organic Synthesis', Springer–Verlag, Heidelberg, 1977
2 'Compendium of Phase-Transfer Reactions and Related Synthetic Methods', (Ed. W. E. Keller), Fluka, Buchs, Switzerland, 1979
3 Regen, S. L. *Angew. Chem. (Int. Edn)* 1979, **18**, 421
4 Sherrington, D. C. 'Polymer-Supported Reactions in Organic Synthesis', (Ed. P. Hodge, and D. C. Sherrington), Wiley, London, Ch 3, in press
5 Regen, S. L. and Dulak, L. *J. Am. Chem. Soc.* 1977, **99**, 623
6 Regen, S. L., Besse, J. J. and McLick, J. *J. Am. Chem. Soc.* 1979, **101**, 116
7 Regen, S. L. and Nigam, A. *J. Am. Chem. Soc.* 1978, **100**, 7773
8 MacKenzie, W. M. and Sherrington, D. C. *Chem. Commun.* 1978, p 541
9 Yanagida, S., Takahashi, K. and Okahara, M. *Yukagaku* 1979, **28**, 14
10 Yanagida, S., Takahashi, K. and Okahara, M. *J. Org. Chem.* 1979, **44**, 1099
11 MacKenzie, W. M. and Sherrington, D. C. Preprints of the IUPAC 26th International Symposium on Macromolecules, Mainz, 1979, Vol 1, p 566
12 Greig, J. A. and Sherrington, D. C. *Polymer* 1978, **19**, 163
13 Kornblum, N. and Lurie, A. P. *J. Am. Chem. Soc.* 1959, **81**, 2705

14 Greig, J. A. and Sherrington, D. C. *Eur. Polym. J.* 1979, **15**, 867
15 For definitions see ref 4, Ch 1
16 Dehmlow, E. V. *Angew. Chem. (Int. Edn)* 1977, **16**, 493
17 MacKenzie, W. M. *PhD Thesis* University of Strathclyde, Glasgow, 1979
18 Regen, S. L. and Besse, J. J. *J. Am. Chem. Soc.* 1979, **101**, 4059
19 See ref 4, Ch 1
20 Lee, D. G. and Chang, V. S. *J. Org. Chem.* 1978, **43**, 1532
21 Molinari, H., Montanari, F., Quici, S. and Tundo, P. *J. Am. Chem. Soc.* 1979, **101**, 3920