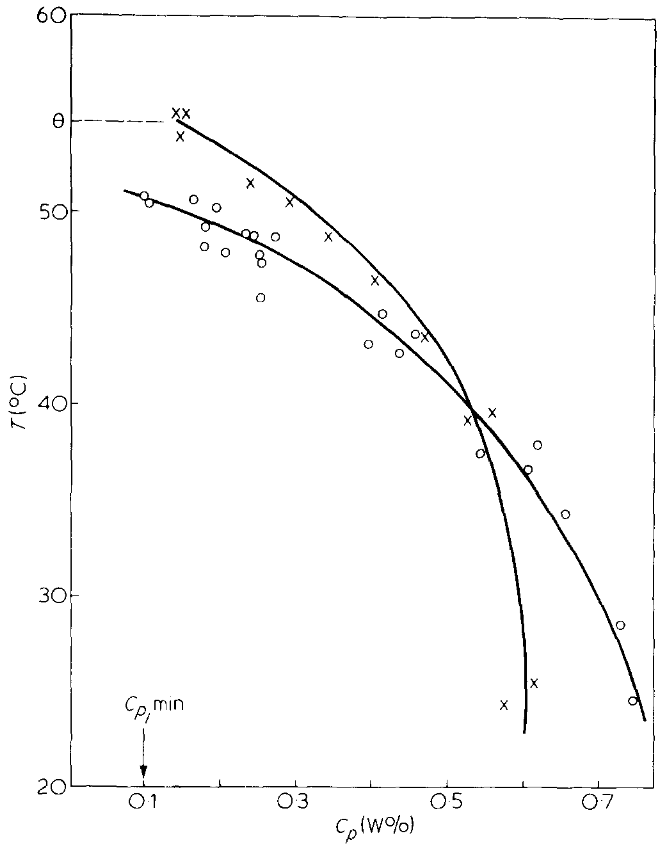

Figure 4 The cloud points curve (O) and the dependence of the equilibrium polymer concentration (x) on the temperature. C_p is the polymer concentration of the swollen gel and C_{p_l} min represents the minimal concentration at which the network structure still exists (l = 10, c_0 = 6 w%). The lines are guides for the eye

of some samples can be understood if we compare the cloud points curve with that of the equilibrium concentration curve. It can be seen that there is a certain region of a stable separated network at temperatures below the intercept.

The films show quite different structures which are more disperse than those of the cylinders, but the crust can also be seen here. Experiments to obtain more information about the molecular structure of the turbid sphere and to determine the spinodal temperatures are in progress.

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Substrate selectivity effects involving polymer-supported phase transfer catalysts

W. M. MacKenzie and D. C. Sherrington
Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building,
295 *Cathedral Street, Glasgow G*1 1*XL, UK*
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Introduction

The use of polymer resins as supports for catalysts and reagents has increased enormously over the last few years and from time to time there have been reports of so-called 'substrate selectivity' effects, i.e. circumstances when a resin-bound reagent displays a higher reactivity for one substrate relative to another, over and above that observed with the analogous non-supported reagent[2,3]. Depending upon the magnitude of this effect and the particular substrates and reactions involved, such phenomena could of course have considerable commercial significance. Substrate selectivity might arise from a specific interaction of one substrate with a binding site close to a reactive centre as with enzymes. However, with resin-supported reagents, it might in principle arise from (i) less specific thermodynamic factors, in that one substrate may be sorbed into the resin in preference to another, or (ii) kinetic factors when one substrate may diffuse more rapidly into a resin than another. These two cases might be distinguished as 'thermodynamic substrate selectivity' and 'kinetic substrate selectivity'. We have previously established the criteria for the latter effect to manifest itself in the case of alkyl halides reacting with resin-supported pyridine groups[4]. In general, the inherent rate of the chemical reaction at sites within the resin must be rapid in comparison with the rate at which substrates diffuse from the bulk reaction medium. Under these circumstances a concentration gradient will be maintained across the resin interior, and substrates will react according to their rates of diffusion and not their inherent chemical reactivities[5]. In general, of course, larger substrates will diffuse more slowly than smaller ones and hence their overall relative reactivity is more likely to be reduced. In addition, less porous resins, e.g. more highly crosslinked ones, are more likely to provide the conditions for diffusion to become rate controlling. In the case of ion exchange resins all of these factors have been considered before and have been very elegantly treated[6]. However, these principles are only now being adequately

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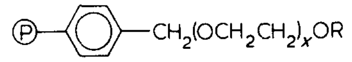
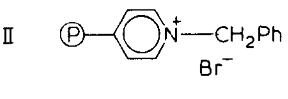
applied to the multitude of polymer-supported reactions which have been described in recent years.

This communication describes our attempts to reproduce the diffusional control demonstrated in the quaternisation of resin-bound pyridine groups in reactions involving closely related polymer-supported phase transfer catalysts. Two types of polystyrene resin-bound species were examined, I and II, and a comparison made with their unbound analogues, III and IV.

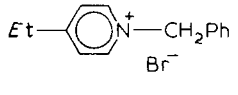
I 

Ia — 2% crosslinked, $x=3$, $R=CH_3$, 61% loaded;
Ib — 2% crosslinked, $x=30$, $R=Ph$, 8% loaded;

II 

IIa — 5% crosslinked, 15% loaded;
IIb — 37% crosslinked, 15% loaded;

III $HO(CH_2CH_2O)_xR$

IV 

IIIa — $x=3$, $R=CH_3$;
IIIb — $x=30$, $R=Ph$.

I and III were employed as catalysts in the reactions of solid potassium phenoxide with 1-bromobutane and 1-bromooctane in toluene at 105°C as previously described[7] while II and IV were used in the reactions of aqueous solutions of potassium phenoxide and 2-naphthoxide with benzyl bromide and 2-bromomethyl-naphthalene in toluene.

Experimental

Materials. Catalysts Ia and Ib were prepared from IIIa (Fluorochem Ltd.) and IIIb (Lankro Chemicals Ltd.) respectively as previously described[7]. IIa and IIb were obtained by exhaustive quarternization of corresponding styrene/divinylbenzene/4-vinyl pyridine terpolymer beads[4] using benzyl bromide in refluxing pentan-2-one. Resins were Soxhlet extracted using acetone and vacuum dried at 30°C. Microanalyses (Br and N) confirmed a molar ratio of Br/N of ~1. The pyridinium salt, IV, was prepared from 4-ethylpyridine and benzyl bromide by refluxing in pentan-2-one. The initially oily product was recrystallised from 50% methanol/acetone and being hygroscopic was stored in a dessicator (M.pt. 190°C. Found: C, 59.30; H, 6.04; Br, 28.67; N, 4.87. Calculated for $C_{14}H_{16}BrN$: C, 60.44; H, 5.80; Br, 28.72; N, 5.02).

Phase transfer catalysed reactions. These were carried out on a small scale essentially as previously described[7]. The magnetically stirred reactions were monitored by quantitative g.l.c. methods and initial rates of reaction were calculated from substrate decay curves. The experimental details are included in *Tables 1* and *2*.

Substrate distribution measurements. Standard toluene solutions (2 ml) of 1-bromoalkanes were assayed using quantitative g.l.c. methods with nonane as the internal standard. Each analysis was repeated 10 times and the results averaged. Resin-supported catalyst, Ia, (1.16 mmol 0) was added and each solution was re-analysed at room temperature and after equilibration at 100°C. Finally water (2 ml) was added to form a separate aqueous phase and the organic phase re-analysed at room temperature and 100°C.

Results and discussion

The results of the solid/liquid reactions using the oligoether catalysts Ia, Ib, IIIa and IIIb are summarized in *Table 1*, while *Table 2* shows the results of the liquid/liquid reactions catalysed by the various pyridinium bromides, IIa, IIb and IV.

With the oligoether catalysts there is little difference in reactivity between bound and unbound species. Furthermore, there is virtually no effect of substrate size in changing from 1-bromobutane to 1-bromo-octane, unlike that reported for the analogous liquid/liquid reactions[3]. The difference in rates of reaction of the two alkyl bromides is ~3 with catalysts Ia and Ib, and ~1.5 and ~3 with their unbound analogues IIIa and IIIb. This probably represents the intrinsic reactivity difference of these halides. Since the polymer support employed is only lightly crosslinked and reactions are relatively slow (~100% conversion in ~3 h) the likelihood of the support

Table 1 Reactions of toluene solutions of alkyl halides with solid potassium phenoxide at 105°C catalysed by polyethers

Catalyst[a] (% loading)	Alkyl halide[b]	Initial rate x 10^5 ($M s^{-1}$)	Loss of alkyl halide (%) (time, h)
IIIa(–)	$C_8H_{17}Br$	6.7	96(3)
Ia(61)	$C_8H_{17}Br$	3.4	82(3)
IIIa(–)	C_4H_9Br	9.1	98(3)
Ia(61)	C_4H_9Br	10	94(3)
IIIb(–)	$C_8H_{17}Br$	4.8	85(2)
Ib(8)	$C_8H_{17}Br$	5.3	77(2)
IIIb(–)	C_4H_9Br	16	98(2)
Ib(8)	C_4H_9Br	16	96(2)

[a] 1.16 mmol of oxygen; [b] [alkyl halide]$_{initial}$ = 0.24 M (2 ml solution)

Table 2 Reactions of toluene solutions of alkyl halides with aqueous solutions of potassium salts at 100°C catalysed by pyridinium bromides[c]

Catalyst (Xlink ratio, %; mmol N)	Nucleophile[a]	Alkyl[b] halide	Initial rate x 10^5 ($M s^{-1}$)	Loss of alkyl halide (3 h) (%)
IIa(5;0.112)	PhO^-	$C_6H_5CH_2Br$	2.5	42
IIb(37;0.15)	PhO^-	$C_6H_5CH_2Br$	1.1	32
IV(–;0.15)	PhO^-	$C_6H_5CH_2Br$	17	95 (1.5 h)
IIa(5;0.15)	PhO^-	$C_{11}H_9Br$	3.8	67
IIb(37;0.15)	PhO^-	$C_{11}H_9Br$	1.1	33
IV(–;0.15)	PhO^-	$C_{11}H_9Br$	28	99 (1 h)
IIa(5;0.15)	$C_{10}H_7O^-$	$C_6H_5CH_2Br$	6.4	83
IIb(37;0.15)	$C_{10}H_7O^-$	$C_6H_5CH_2Br$	4.2	91
IV(–;0.15)	$C_{10}H_7O^-$	$C_6H_5CH_2Br$	24	99 (0.75 h)

[a] 2 mmol (2 ml water)
[b] [alkyl halide]$_{initial}$ = 0.24 M (2 ml solution)
[c] no attempt was made to assess the proportions of O– and C–alkylated products

Table 3 Distribution of alkyl halides between toluene and resin phases[a]

Substrate	Temperature (°C)	Change in halide concentration (%) (No H_2O)	Change in halide concentration (%) (H_2O present)
1-Bromobutane	20	3.0	3.9
1-Bromobutane	100	4.6	7.4
1-Bromooctane	20	1.7	−0.5
1-Bromooctane	100	2.2	−1.7

[a] Resin (Ia)

imposing diffusion control can be discounted[4]. The much larger differences (up to factors of ~60) reported in analogous liquid/liquid reactions[3] have been attributed to sorption or thermodynamic factors. *Table 3* shows the results of the measurements of the distribution of alkyl halides between the bulk toluene phase and the swollen resin, Ia. Positive changes indicate a relative increase in the concentration of halide within the resin, while negative values refer to a relative exclusion of the substrate from the resin interior. The difference in distribution between both alkyl halides is quite small and the absolute individual percentage changes very small indeed. The difference in behaviour is enhanced, however, by addition of water and increasing the temperature. The 'solubility' of 1-bromobutane in the resin phase increases, whilst that of 1-bromo-octane somewhat surprisingly decreases. The differences agree reasonably well with those reported for the liquid/liquid systems. Even so it is difficult to believe that these small percentage changes can alone account for the large differences in reactivity reported[3], and other as yet unknown factors may well be important. In the case of the reactions of butyl, octyl and hexadecyl halides with solid sodium phenoxide catalysed by poly(ethylene oxide), the rate dependence on chain length of the halide has been attributed[8] to 'steric hindrance of complexed polymer chains in the vicinity of the solid phenoxide salt'. It is difficult to know, however, what molecular comparisons can be made between this sytem and the one presently reported.

We were more optimistic about observing kinetic selectivity in the case of the supported pyridinium salt catalysts because these involved intrinsically more reactive alkaryl halides and resins which were more highly crosslinked. Indeed reactions between aqueous solutions of potassium phenoxide and benzyl bromide and 2-bromomethylnaphthalene in toluene, catalysed by resins IIa and IIb, were about an order of magnitude slower than analogous reactions catalysed by IV. This is strongly indicative of diffusional control by the support matrices. Furthermore, reactions were slowed more effectively (a factor of ~2–3) by the more highly crosslinked resin IIb than IIa, again keeping with out knowledge of the effect of such structures[4]. However, these changes were virtually the same for both benzyl bromide and 2-bromomethylnaphthalene, i.e. in spite of the resin matrix presenting a diffusional barrier virtually no selection of substrate halide is apparent. Since this observation is contrary to our previous experience with these molecules[4] it seemed plausible that diffusion of these species was not rate controlling, but that diffusion of the nucleophile, PhO^-, was rate controlling. To check this possiblity we examined the behaviour of the bulkier 2-naphthoxide anion. Rather surprisingly, with benzyl bromide as the common substrate, the relative reactivity of 2-naphthoxide *versus* phenoxide was ~1.5, ~2 and ~4 for catalysts V, IIa and IIb respectively, i.e. 2-naphthoxide is relatively more reactive with the resin-supported catalysts than with the unbound analogue, and the reactivity difference increases with increasing crosslink ratio of the support. This is of course quite contrary to what would be expected if molecular size was the controlling factor[4], and it can only be concluded that favourable sorption of 2-naphthoxide ion, relative to phenoxide, into resin matrices more than compensates for its larger molecular bulk and its effect on diffusion.

Thus, in summary, we can say that in phase transfer reactions resin-bound pyridinium salts do display some of the diffusional characteristics apparent in quarternisation reactions of resin-bound pyridine groups[4]. However, the substrate selectivity features shown in the latter are not reproduced when the fully quaternised resins are themselves used as catalysts. Why this is so is not entirely clear but the generation of a charged resin matrix from a neutral starting point may be of relevance in the quarternisation reactions. In addition, the change in the reaction conditions, from the purely organic one used in the latter reactions to be combined aqueous/organic environment characteristic of the catalysis work, may be an important factor.

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