Polymer-supported Phase Transfer Catalysts in Solid–Liquid Reactions

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Summary Polystyrene-supported oligoethylene oxides function as very efficient catalysts in the displacement reactions of solid alkali metal phenoxides on 1-bromobutane in toluene.

The use of phase transfer catalysts[1] in liquid–liquid reactions is now a useful practical tool.[2] Their application in solid–liquid reactions has also been well characterised[3] as have their polymer-supported analogues in liquid–liquid

TABLE. Phenoxide displacements on 1-bromobutane in refluxing toluene[a]

Catalyst	Polymer loading (%)	Loss of Bu^nBr (%)	Yield of[b] PhOBu (%)	Initial[c] rate × 10^5 ($M\,s^{-1}$)	'O' in polyether (mmol)	polyether (mmol)	Wt. of catalyst (g)	Nature of nucleophile
None	—	12 (5 h)	9 (5 h)	—	—	—	—	Solid NaOPh from H_2O
„	—	—	7 (5 h)	—	—	—	—	Solid KOPh from H_2O
„	—	19 (5 h)	18 (5 h)	0·26	—	—	—	Aqueous NaOPh
$Me[OCH_2CH_2]_3OH$	—	*ca.* 100 (6 h)	*ca.* 100 (6 h)	4·8	3·30	0·83	0·137	Solid NaOPh from H_2O
$Ph[OCH_2CH_2]_{30}OH$	—	11 (5 h)	10 (5 h)	0·66	1·16	0·039	0·053	Aqueous NaOPh
$Ph[OCH_2CH_2]_{30}OH$	—	98 (2 h)	98 (2 h)	16	1·16	0·039	0·053	Anhydrous KOPh
(I)	73	21 (5 h)	17 (5 h)	0·56	1·16	0·29	0·090	Aqueous NaOPh
„	„	94	95	12	2·57	0·64	0·200	Solid NaOPh from H_2O[d]
„	„	89	89	8·3	2·57	0·64	0·200	Anhydrous NaOPh
„	„	50	48	3·2	1·16	0·29	0·090	Anhydrous NaOPh
„	„	22	20	1·4	0·257	0·064	0·020	Solid NaOPh from H_2O
„	„	32	—	2·5	0·257	0·064	0·020	Anhydrous NaOPh
„	„	92	93	11	1·16	0·29	0·090	Anhydrous KOPh
„	„	52	51	5·3	0·257	0·064	0·020	Anhydrous KOPh
(II)	61	50	40	3·2	1·16	0·29	0·097	Anhydrous NaOPh
„	„	93	94	12	1·16	0·29	0·097	Anhydrous KOPh
(III)	40	92	90	7·8	1·16	0·13	0·094	Anhydrous NaOPh
„	„	17	14	0·71	1·16	0·13	0·094	Aqueous NaOPh
(IV)	3	41 (5 h)	35 (5 h)	1·2	1·16	0·039	0·284	Aqueous NaOPh
„	8	98	94	23	1·16	0·039	0·116	Anhydrous NaOPh
„	8	97	99	28	1·16	0·039	0·116	Anhydrous KOPh
„	3	*ca.* 100	96 (1·5 h)	40	1·16	0·039	0·284	Anhydrous KOPh

[a] See text for other experimental details. [b] After 3 h unless otherwise specified. [c] From 1-bromobutane decay curves. [d] Evaporated directly on polymer-supported catalyst.

reactions,[4] where additional advantages accrue during product isolation. However, the idea that a solid-supported species can catalyse the reaction between a solid and a liquid at first sight seems unlikely, though one report by Tundo already exists in the literature.[5] We can now confirm that this novel and apparently implausible catalysis does occur, and with some considerable efficiency.

In our preliminary investigations we have prepared a number of polymer-supported phase transfer catalysts (I)—(IV), similar to one described by Regen,[6] by reaction of the sodium salts of poly(ethylene glycol monoethers) with chloromethylated cross-linked polystyrene resins.

$$(\text{Polymer})C_6H_4\text{-}p\text{-}CH_2[OCH_2CH_2]_xOR$$

(I); R = Me, $x = 3$ (10% cross-linked,[a] 73% loaded)
(II) R = Me, $x = 3$ (2% cross-linked, 60% loaded)
(III); R = C_9H_{19}—$C_{11}H_{23}$,[b] $x =$ *ca.* 9 (2% cross-linked, 40% loaded)
(IV); R = Ph,[c] $x =$ *ca.* 30 (2% cross-linked, 8 and 3% loaded)

[a] Porous polymer made in the presence of toluene. [b] A commercial surfactant (Lankro, Ethylan CD919). [c] A commercial surfactant (Lankro, Ethylan HB30).

In a typical preparation a chloromethylated[7] polystyrene resin (5 g, Biobead Sx2, 4·2 mmol of Cl per g of polymer) was refluxed for 70 h in a tetrahydrofuran solution (10 ml) of the sodium salt of 2-{2-(2-methoxyethoxy)ethoxy}-ethanol, prepared *in situ* by reaction of sodium hydride (50% w/w in paraffin oil, 50 mmol) with 2-{2-(2-methoxyethoxy)ethoxy}ethanol (100 mmol). In this instance virtually quantitative reaction was achieved† based on Cl microanalyses, producing a polymer with *ca.* 60% of its pendant groups loaded with catalyst species.

The catalysts (I)—(IV) were used in phenoxide displacements on 1-bromobutane in toluene solvent. Typically, a 1-bromobutane (0·48 mmol) solution in toluene (2 ml) and catalyst containing 1·16 mmol of ethereal oxygen were refluxed with sodium phenoxide (2 mmol) while being magnetically stirred. Visual observation indicated the proportion of solubilized phenoxide to be very small, and for some mechanical damage‡ to the catalyst to occur. The loss of alkyl bromide was monitored by g.l.c., and initial rates and final conversions obtained in the usual way. Phenyl butyl ether yields were determined similarly on completion of reactions. Experiments involving both aqueous and organic phases were carried out analogously employing 2 ml of water. Since control experiments showed stirring to have little effect on rates while encouraging frothing, no stirring was employed.

The results are shown in the Table from which the following most relevant features emerge. In the absence of water and catalyst no significant reaction occurs. The presence of an aqueous phase produces small yields with low reaction rates, while the additional presence of (I) enhances the rate modestly by a factor of *ca.* 2, to a value comparable to that already reported.[6] However, use of solid phenoxide in the presence of (I) produces a further and more significant rate enhancement of *ca.* 6, and with appropriate amounts of (I), (II), (III), or (IV) virtually quantitative conversions can be achieved in conveniently short times.§ Little difference occurs with solid phenoxides prepared from aqueous solutions and from anhydrous preparations, while the potassium salt is consistently more reactive than the sodium salt.

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† This was not always so, though unreacted chloromethyl groups appeared not to interfere in subsequent reactions as indicated in the Table.

‡ It may be possible to alleviate this by the use of rotating reactors (J. A. Grieg, W. M. MacKenzie, and D. C. Sherrington, *Polymer*, 1977, **18**, 1291).

§ Polystyrene-supported phosphonium salts are also highly effective.

The catalytic effect also rises significantly as the length of the attached polyether chain is increased, (IV) being a particularly potent catalyst, a further *ca.* 8 times better than (I). This difference is paralleled somewhat with the unsupported polyethers, and has been described before in another solid–liquid reaction.[8] With (I) and (II) loaded with the same short polyether the differing structures of the polymer supports do not affect the catalytic action. The two samples of (IV) examined showed the polymer with the lower catalyst loading to be more effective. For equimolar amounts the required weight of this is *ca.* 3 times that of the more highly loaded sample, and hence its higher activity may be associated with the larger total surface area employed.[9]

Finally, in the comparison of the supported and non-supported polyethers the former appear to be a factor of *ca.* 2 more effective on an equimolar basis. While considerable differences in local concentrations are involved, the detailed explanation for this observed activation is not yet clear.

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