Cooperation between catalytic sites on a bicipital supported phosphonium phase-transfer catalyst

James H. Clark,*[a] Stewart J. Tavener[a] and Simon J. Barlow[b]

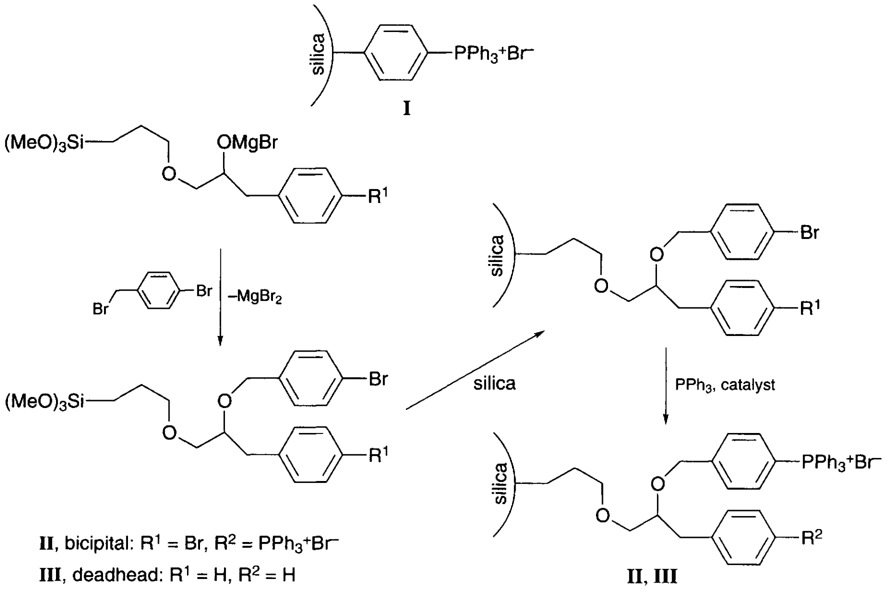
[a] *Department of Chemistry, University of York, Heslington, York, UK YO1 5DD*
[b] *Contract Catalysts Ltd, Knowsley Industrial Park, Prescot, Merseyside, UK L34 9HY*

A novel bicipital tetraarylphosphonium salt grafted to silica gel is prepared and characterised, and gives unusually high catalytic rate enhancements in some nucleophilic substitution reactions, which suggest cooperation between the neighbouring phosphonium centres.

The concept of triphase catalysis, whereby a phase-transfer catalyst (PTC) is immobilised onto a support material and the resulting solid catalyst is then used in a typical biphasic aqueous–organic solvent reaction mixture, has been appreciated for 20 years.[1,2] While most known triphase catalysts are based on organic polymers, inorganic materials including silica, alumina and clays have also been used as supports.[3–5] As part of our research into environmentally friendly catalytic methods, we are developing synthetic strategies for the chemical surface modification of mesoporous materials, which are known to enable good diffusion rates in many liquid-phase organic reactions.[6,7] We have recently reported the preparation and thermal properties of silica-supported tetraphenylphosphonium bromide (**I**) which was prepared from chlorinated silica.[8] We now report the preparation of a new material which possesses surface-bound bicipital ('two-headed') phosphonium centres (**II**) and exhibits cooperative behaviour in catalysing aliphatic nucleophilic substitution reactions under liquid–liquid–solid triphasic conditions.

The silane precursor to the bicipital material was prepared by initially reacting the commercially available 3-glycidoxypropylsilane with 4-bromophenylmagnesium bromide in ethoxyethane. The intermediate magnesium alkoxide was then further reacted with 4-bromobenzyl bromide in refluxing xylene to introduce the second bromophenyl group. Reaction with silica gel gave the bis(bromoaromatic) derivatised material which was characterised by diffuse reflectance FTIR spectroscopy (DRIFTS) and ^{13}C CP MAS NMR spectroscopy. This organosilica was then treated with triphenylphosphine in the presence of either $Pd(O_2CMe)_2$ or $NiBr_2$ to give the supported tetraarylphosphonium bromide (Scheme 1). DRIFTS of the final material shows activity due to aromatic C–H (3065, 753 and 725 cm^{-1}), alkyl C–H (2935 and 1412 cm^{-1}), aromatic ring (1596, 1483 and 691 cm^{-1}) and P–Ar (1440 cm^{-1}); the C–O stretch is masked by the strong and broad Si–O activity between 1200 and 1000 cm^{-1}. The ^{13}C CP MAS NMR spectrum shows broad but reasonably well resolved peaks in the regions of 0–10 (Si–*C*H_2–R), 10–25 (Si–CH_2*C*H_2CH_2O–), 55–80 (–CH_2O–, Ar–*C*H_2–), and 115–130 (aromatic carbons). The ^{31}P CP MAS NMR spectrum shows a single peak at δ +21.9 (referenced to crystalline $NH_4H_2PO_4$) typical of supported- and solution-phase (*i.e.* isolated sites) tetraarylphosphonium salts;[8] crystalline tetraphenylphosphonium bromide has a lower chemical shift of δ +18.2.[9] Elemental analyses were also consistent with the proposed surface structure (atomic C : P ratio: found 28 : 1; expected 27.5 : 1) and with loadings in the range 0.18–0.36 mmol g^{-1} for several batches; quantitative DRIFTS give similar values. Thermogravimetric analysis shows no mass loss (other than loosely held solvent and water) below *ca.* 280° C, above which point the organic groups begin to decompose.[8]

The activity of the supported bicipital catalyst is highly dependent on the pore size of the silica support with the 100 Å material being over ten times more active than the 60 Å material (at 90° C) and considerably more active than other supported phosphonium salts in the model nucleophilic substitution reaction of 1-bromooctane with potassium iodide (Table 1). When toluene is used as the organic solvent the 100 Å bicipital catalyst is reusable at least four times with no loss of activity,



Scheme 1 Preparation of silica supported tetraarylphosphonium salts

Table 1 Rates of the reaction of 1-bromooctane with potassium iodide catalysed by supported tetraarylphosphonium bromides[a]

Catalyst	Support pore size/Å	T/°C	$10^6\ k_{obs} \pm 2\sigma$/s^{-1}	Loading[b]/ mmol g^{-1}	$10^3\ k_2 \pm 2\sigma$[c]/ mol^{-1} dm^3 s^{-1}
None	—	95	0.00[d]	—	—
I	60[e]	95	27.5 ± 0.4	0.33	1.95 ± 0.02
II	—[f]	95	27.8 ± 0.6	0.10	6.51 ± 0.02
II	60	95	25.1 ± 0.5	0.30	1.96 ± 0.04
II	100	95	322 ± 2	0.36	20.9 ± 0.1
III	100	95	60.7 ± 0.6	0.18	7.98 ± 0.08
II	205	95	9.2 ± 0.9	0.09	2.39 ± 0.24
II	100	75	79 ± 2	0.36	5.35 ± 0.12
III	100	75	6.4 ± 0.6	0.18	0.83 ± 0.08

[a] Reactions carried out in 5 ml of toluene and 7.5 ml water using 0.250 g catalyst, 5 mmol 1-bromooctane and 50 mmol potassium iodide. Reactions were monitored by removing small samples from the stirring reaction mixture, and measuring concentrations by GC, correcting for response factors. [b] Determined by elemental analysis or DRIFTS. [c] $k_{obs} = k_2$[cat]. [d] No measurable conversion after 8 h. [e] Ref. 8. [f] Non-porous aerosil material.

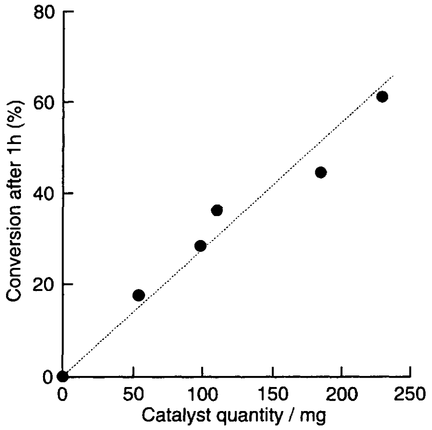


Fig. 1 The effect of catalyst quantity on the rate of reaction of 1-bromooctane with potassium iodide in a toluene–water system at 95 °C

Table 2 Thermodynamic parameters for the substitution reaction of 1-bromooctane with potassium iodide under phase-transfer conditions[a]

Catalyst	E_a/kJ mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
Supported bicipital catalyst	77 ± 9	74 ± 9	−77 ± 24
Supported deadhead catalyst	123 ± 14	120 ± 14	40 ± 38

[a] Data calculated from at least seven rate constants over the temperature range 75–95 °C.

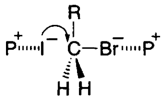


Fig. 2 Proposed transition state for the nucleophilic substitution of 1-bromooctane by iodide catalysed by the supported bicipital phosphonium material

and there are no observable changes in the DRIFT spectrum of the recovered catalyst. The rate of reaction is first order with respect to catalyst quantity (Fig. 1). The bicipital catalyst is effective in non-polar solvents such as toluene and cyclohexane in which unsupported tetraphenylphosphonium bromide is insoluble and therefore inactive. The activity of the supported reagent catalyst is very dependent on the organic solvent with the rate of the model reaction following the order: no solvent > perfluorocarbon (tetrafluoroethene pentamer, ex ICI) > toluene > cyclohexane ≈ chloroform. Reusability is limited to two or three runs when the organic solvent is chloroform, and the DRIFT spectrum of the catalyst clearly shows loss of organic functionality. Most significantly, the 'deadhead' analogue (**III**) of the 100 Å bicipital material is significantly less active per phosphonium centre than the bicipital material. Use of the bicipital material leads to a reduction in the activation enthalpy and in the activation entropy when compared to the deadhead material (Table 2). This suggests a more ordered transition state in reactions catalysed by the bicipital material which somehow provides a lower energy pathway for the reaction to follow. Computer modelling of the bicipital catalyst shows an enzyme-like niche into which the organic substrate can fit. The enhanced activity of the catalyst can be explained by cooperation between the neighbouring phosphonium cations: polarisation of the C–Br bond of the substrate by one phosphonium centre is accompanied by simultaneous attack by the I$^-$ supplied by the neighbouring cation (Fig. 2). The distance between the phosphorus atoms in the model (10.5 Å) is indeed a little greater than the sum of the covalent radii of the atoms involved in the proposed transition state (8.6 Å).

A smaller but still significant enhancement in site activity was also measured in the nucleophilic substitution reaction of 1-bromobutane with potassium iodide, and the much slower reaction of 1-chlorooctane with potassium bromide (the 100 Å bicipital catalyst being *ca.* twice as active as the deadhead catalyst per phosphonium centre). In the reactions of benzyl bromide with potassium iodide and benzyl chloride with potassium bromide, however, no cooperation between sites is evident with the activities of the bicipital and deadhead catalysts per phosphonium cation being identical within experimental error. This may be due to the relatively weak PhCH$_2$–X bonds following a more S$_N$1-like substitution pathway, effectively making the simultaneous polarisation of the C–X bonds by the bicipital catalyst redundant, although steric factors cannot be ruled out. These reactions will proceed without catalysis, but with pseudo-first-order rate constants (k_{obs}) 4 to 16 times slower than in the presence of a catalyst.

We gratefully acknowledge the financial support of EPSRC and Contract Chemicals Ltd. and we thank other members of the Envirocats and York Clean Synthesis research groups for their helpful suggestions.

References

1 S. L. Regen, *J. Am. Chem. Soc.*, 1976, **98**, 6270.
2 J. H. Clark and S. J. Tavener, in *Chemistry of Waste Minimisation*, ed. J. H. Clark, Chapman and Hall, London, 1995.
3 P. Tundo, *J. Chem. Soc., Chem. Commun.*, 1977, 641.
4 P. Tundo, P. Venturello and F. Angeletti, *J. Am. Chem. Soc.*, 1982, **104**, 6551.
5 Y. V. Subba-Rao and B. M. Choudary, *Synth. Commun.*, 1992, **22**, 2711.
6 J. H. Clark, S. R. Cullen, S. J. Barlow and T. W. Bastock, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1117.
7 J. H. Clark, *Catalysis of Organic Reactions using Supported Inorganic Reagents*, VCH, New York, 1994.
8 J. H. Clark, S. J. Tavener and S. J. Barlow, *J. Mater. Chem.*, 1995, **5**, 827.
9 S. J. Tavener, D.Phil. Thesis, University of York, UK, 1996.

Received, 16th August 1996; Com. 6/05718G