Silica Gel as a Polymeric Support for Phase-transfer Catalysts

By Pietro Tundo

(*Istituto di Chimica Organica dell'Università, Via Bidone* 36, *Torino* 10125, *Italy*)

Summary Heterogeneous phase-transfer catalysts such as phosphonium salts immobilized on silica gel show catalytic activity for anion-promoted reactions both in liquid–liquid and solid–liquid systems; kinetic measurements show the influence of the polar silica support.

The use of polymeric matrices as a support for various types of catalysts combines the recovery of the catalyst with the advantages of a 'clean' reaction; the choice of the support may bring about an interesting selectivity. It has been shown[1] that phase-transfer catalysts may be advantageously linked to polystyrene resins and that the activity of the latter depends on the type of catalyst and on their distance from polymeric matrix. Since silicon polymers, in contrast to polystyrene resins, are polar substrates and silica gel is a low-cost starting material, systems (I) and (II) have been synthesized.

They were prepared from the corresponding bromoderivatives (III) and (IV) by reaction with PBu^n_3 for 5 days at 70 °C; (III) was obtained from condensation of silica gel (70—230 mesh; activated by refluxing in conc. HCl for 4 h[2]) and 3-bromopropyltriethoxysilane in toluene at 110 °C for 3 h [3-bromopropyltriethoxysilane (b.p. 110 °C at 14 mmHg) was obtained from 3-bromopropyltrichlorosilane[3] by treatment with abs. EtOH and Et_3N in benzene (yield 84%)]. System (IV) was prepared by reaction of 11-bromoundecanoyl chloride with (V)[2] in benzene and Et_3N.†

The activity of phase-transfer catalysts (I) and (II) has been tested in various types of anion-promoted reactions, both in liquid–liquid and solid–liquid systems, giving satisfactory results; some of these are reported in Table 1. The activity of hexadecyl tributylphosphonium bromide (VI) and (−)-*N*-dodecyl-*N*-methylephedrinium bromide (VII) is reported for comparison.

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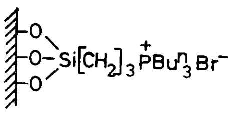
† Elemental analyses and ^1H n.m.r. spectra correspond to the proposed formulae. Analyses of polymers (I)—(IV) have been carried out by titrating ionic and/or covalent bromide; the results show that the titre of the halogen on the silica gel is $1{\cdot}0 \times 10^{-3}$ equiv. Br g^{-1} for (III) and $0{\cdot}9 \times 10^{-3}$ equiv. Br g^{-1} for (IV); the conversions of (III) and (IV) into (I) and (II), respectively, are almost quantitative, resulting in a ratio of 1 mol catalyst : 15 mol SiO_2 for compound (I) and 1 mol catalyst : 13 mol SiO_2 for compound (II).

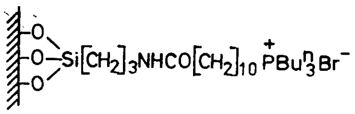
Table 1

Substrate[a]	Reagent	Solvent	Catalyst[b]	T/°C	Time/h	Yield (%)[c]	Product[d]
n-$C_8H_{17}Br$	KI[e]	None	(I)	80	1·1	95	n-$C_8H_{17}I$
"	"	"	(II)	80	2·8	95	"
"	"	"	(VI)	80	0·4	95	"
n-$C_6H_{13}COMe$	$NaBH_4$[f]	Benzene	(I)	25	1·5	96	n-$C_6H_{13}CH(OH)Me$
"	"	"	(II)	25	5·4	85	"
"	"	"	(VI)	25	6·5	85	"
"	"	Toluene	(VII)	25	0·5	98	"
$PhCH_2Cl$	K-Phthalimide[g]	"	(I)	60	2·7	95	*N*-Benzylphthalimide
"	"	"	(II)	60	4·6	95	"
"	"	"	(VI)[h]	60	0·33	98	"

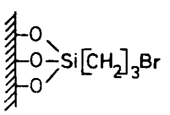
[a] 2 mmol. [b] 0·05 mol. equiv. [c] By g.l.c. and liquid chromatography analysis. [d] The products were characterized by g.l.c. or liquid chromatography (l.c.) retention times and by comparison with authentic samples (i.r. and ^{1}H n.m.r. spectra). [e] 5 mmol; H_2O (0·65 cm^3). [f] 2 mmol; benzene (1·2 cm^3), H_2O (2·0 cm^3). [g] 2·5 mmol; toluene (1·0 cm^3). [h] From D. Landini and F. Rolla, *Synthesis*, 1976, 389 (catalyst, 0·1 mol. equiv.).



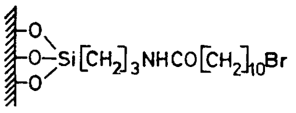
(I)



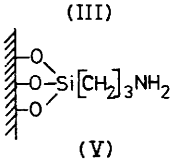
(II)



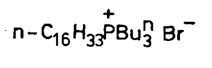
(III)



(IV)

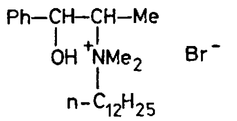


(V)



$n\text{-}C_{16}H_{33}\overset{+}{P}Bu^n_3\ Br^-$

(VI)



(VII)

In contrast to the catalysts polystyrene bonded to resins no induction period is observed and silica gel shows no physical alteration in the course of the reaction other than a small deformation due to stirring. All the observed reactions follow pseudo-first order kinetics and the reaction rate is directly proportional to the concentration of the functionalized silica gel; this is analogous to non-bonded catalysts.

The effect of the polymeric substrate on the reaction rate is evident from the reduction of ketones with $NaBH_4$; this reaction does not proceed in non-polar solvents such as benzene, and even with classic phase-transfer catalysts it appears to take place slowly. However, if the catalyst contains a polar group, such as ephedrinium salts,[4] the reaction is dramatically accelerated. In this reaction (II), and especially (I), are more active than (VI) and approach the activity of (−)-*N*-dodecyl-*N*-methylephedrinium bromide (VII).

Though (II) is easier to prepare than (I), it is, however, less reactive. This reactivity difference has been tested in solvents with various degrees of polarity such as PhCl, toluene and n-heptane for the reaction n-$C_8H_{17}Br \rightarrow$ n-$C_8H_{17}I$ (Table 2).

Table 2. K_0/h^{-1} values[a] for the pseudo-first-order reaction n-$C_8H_{17}Br \rightarrow$ n-$C_8H_{17}I$ catalysed by (I) and (II) at 80 °C.

Catalyst	No solvent	PhCl	Toluene	n-Heptane
(I)	2·60	0·69	0·62	1·03
(II)	1·04	0·40	0·40	0·43

[a] n-$C_8H_{17}Br$ (2 mmol), KI (5 mmol), H_2O (0·65 cm^3) solvent (1·05 cm^3) (solvent: substrate ratio 3 : 1 v/v), catalyst (0·05 mol. equiv.).

Such different behaviour seems to be due to a balancing of the positive effect of the polymeric polar support on the side of the lipophilic organic chain. Catalysts (I) and (II) may be used several times after filtration, with almost unchanged catalytic activity.

While being able to catalyse phase-transfer reactions in strongly alkaline water, (I) and (II) are not recoverable since the silica gel is completely dissolved in this medium.

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