Influence of Spacer Chains and Percentage Ring Substitution on Phase-transfer Catalytic Activity of Phosphonium Salts Bonded to Polystyrene Matrix

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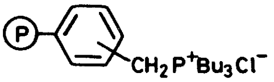
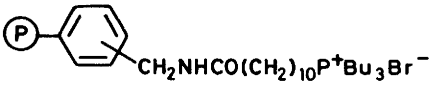
In nucleophilic aliphatic substitutions carried out under liquid–liquid phase-transfer conditions, the catalytic activity of tributylphosphonium groups directly bonded to a polystyrene matrix through a methylene bridge decreases by about one order of magnitude on passing from 10 to 60% ring substitution; log $k_{obs.}$ is linearly related to the loading of the catalytic sites. When tributylphosphonium groups are bonded to the polymer matrix by a linear spacer chain of 13 atoms for 10—30% ring substitution, $k_{obs.}$ increases 1.7—3.1 times with respect to directly bonded catalysts. However, for spaced catalysts with 60% ring substitution, the observed rate increase is 4.1—10-fold. This behaviour is explained by the combination of two opposing effects: (i) a polarity increase at the catalytic site by increasing percentage ring substitution leading to a decrease of nucleophilic activity of the anions; (ii) a polarity decrease at the catalytic site by insertion of spacer chains, due to the intrinsic lipophilicity of the alkyl chains as well as the more even distribution of catalytic sites within the polymer matrix. The reactivities of the catalysts, all prepared from chloromethylated polystyrene (200—400 mesh), are independent of the size of particles separated by sieves.

The efficiency of polymer-bonded phase-transfer catalysts depends on the complex interaction of several factors, related to the intrinsic properties of the catalytic sites, as well as to problems of diffusion peculiar to the polymeric matrix.[1] Many of these factors have been extensively studied by us [2] and other authors.[3,4] However, in several cases, their interaction is still difficult to analyse and the individual roles are not defined. In this paper we examine (i) the variation of catalytic activity of alkyltributylphosphonium salts as a function of the frequency of catalytic sites bonded directly or through a spacer chain to the polystyrene matrix and (ii) the role played, under particular conditions, by catalyst particle size.

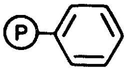


(1a) (10·6)
(1b) (28·8)
(1c) (60·0)



(2a) (8·7)
(2b) (25·4)
(2c) (57·3)

(3a) (6·7)
(3b) (36·1)



microporous polystyrene, 1% [(1) and (2)] and 2% [(3)] cross-linked with divinylbenzene (% ring subtitution in parentheses)

Results and Discussion

Catalysts.—Catalysts have structures (1)—(3). Catalysts (1a—c) and (2a—c), in which the tributylphosphonium group is bonded to the polystyrene matrix through a methylene bridge or a 13 atom linear spacer chain, respectively, were obtained from commercial chloromethylated polystyrene, 1% cross-linked with divinylbenzene, with 1.04, 2.63, and 5.0 mequiv. Cl g^{-1}, respectively, as previously described.[2] In both series (1a—c) and (2a—c) ring substitutions ranged from 10 to 60%. Catalysts (3a and b) were derived from 2% cross-linked polystyrene, with 0.7 and 3.5 mequiv. Cl g^{-1}, respectively.

Standard reactions were Br–I exchange in 1-bromo-octane and OSO_2Me–I and OSO_2Me–Br exchanges in n-octyl methanesulphonate in toluene–water at 60 and 90 °C, in the presence of 0.01—0.05 mol. equiv. of catalysts (1) and (2). These reactions and, more generally, anion-promoted nucleophilic reactions catalysed by polymer-supported quaternary 'onium salts, follow a pseudo-first-order kinetic equation (1),

$$\text{rate} = k_{obs.}[\text{substrate}] \qquad (1)$$

and the observed rate constants ($k_{obs.}$/s^{-1}) are linearly dependent on the molar equivalent of immobilized catalysts.[2a]

Number of Catalytic Sites on the Polymer Support (*Percentage Ring Substitution*).—The activity of catalysts (1) in which the tributylphosphonium group is directly bonded to polystyrene matrix through a methylene bridge decreases about one order of magnitude on passing from 10% [(1a)] to 60% [(1c)] ring substitution, and log $k_{obs.}$ is linearly related to the loading of catalytic sites (Figure 1). The same behaviour is observed at both 60 and 90 °C for all the reactions examined, even when using different kinetic conditions.

Insertion of a spacer chain between the polymer backbone and quaternary cation leads to increased catalytic activity (on average 2—3-fold).[2a,4] This is the case for catalysts (2).

However, in catalysts (2), as for (1), $k_{obs.}$ also depends on the frequency of catalytic sites. For 10—30% ring substitution, the relation between the two parameters is completely similar in both series of catalysts: on passing from (1a, b) to (2a, b), $k_{obs.}$ increase 1.7—3.1-fold for all the reactions examined. However, catalyst (2c), with 60% ring substitution, behaves differently, in that its reactivity is always 4.1—10-fold higher than that of the directly bonded catalyst (1c).

This general behaviour can be explained in terms of different polarity around the catalytic site.[2] In catalysts (1), whose quaternary groups are rigidly bonded to the polymer matrix, the microenvironment polarity should increase when the percentage ring substitution increases.[2b]

As in classical phase-transfer catalysis, this markedly decreases nucleophilic substitution rates. Indeed, as shown in previous papers,[1f,2] phase-transfer reactions promoted by polymer-supported quaternary salts follow a mechanism identical to that observed in classical phase-transfer catalysis

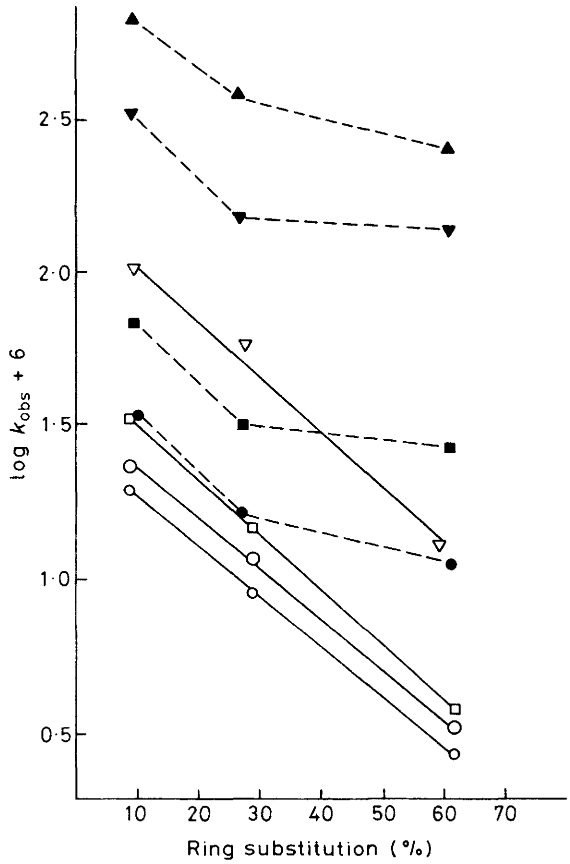


Figure 1. Dependence of the observed pseudo-first-order rate constants ($k_{obs.}$) on percentage ring substitution. Catalysts (1a—c), empty symbols; catalysts (2a—c) full symbols. Br-I exchange: □, ■ (60 °C); ▲ (90 °C); ▽, ▼ (90 °C, different kinetic conditions, see Experimental section). OSO_2Me-I exchange: ○, ● (60 °C). OSO_2Me-Br exchange: ○ (60 °C)

promoted by soluble quaternary salts. The reaction occurs in the organic solvation shell firmly surrounding the catalytic site; anions are exchanged at the water-organic solvent interface; charge parity is provided by the inorganic cation and the polymer-supported cation in the aqueous and organic liquid phase, respectively.[1f,2]

Insertion of aliphatic spacer chains may lead to two effects, (i) increased lipophilicity of the polymer support[4f] and (ii) more even distribution of polar catalytic sites within the polymer matrix. Both factors contribute to decreased polarity at the catalytic site, and therefore to increased anionic reactivity. However, only the former factor seems to be involved in the case of (2a and b), since the influence of the loading increase is identical in series (1) and (2), whereas both effects should be significant in highly loaded catalyst (2c).

The importance of mobility on the activity of polymer-supported catalysts has been recently discussed.[1c] Results similar to ours were obtained by Regen[3b,f] for catalysts directly bonded to the polymer. They were explained[3f] in terms of increasing steric congestion through the lattice, leading to lower diffusion rates: this interpretation is not consistent with our data on catalysts bonded to spacer chains.*

Catalyst Particle Size.—Tomoi and Ford[3d,e] have shown that particle size may strongly affect the catalytic activity of polymer-supported quaternary 'onium salts due to mass-transfer limitations within the particle deriving from diffusion phenomena.

Table. Dimensions of polymer particles after separation with sieves at catalyst stage

Particle size		Weight (%)	
Mesh	*d*/μ	Catalyst (2a)	Catalyst (3b)
≤35	≥500	8.8	[a]
35—45	500—355	15.7	[a]
45—60	355—250	12.6	[a]
60—80	250—180	11.3	1.70
80—100	180—150	9.4	2.83
100—120	150—125	5.0	11.85
120—140	125—106	2.5	6.28
140—170	106—90	5.0	23.47
170—200	90—75	14.5	37.20
200—230	75—63	8.8	7.08
230—270	63—53	10.7	8.59
270—325	53—45	0.6	0.99

[a] Insignificant.

With only one exception, none of the catalysts (1)—(3) showed this behaviour. Internal diffusion has no influence on the reactivity of polymer-bonded catalysts when the intrinsic reactivity at the catalytic site is very low, and hence is the rate-limiting factor.[3d,e] However, this explanation is unlikely for alkyltributylphosphonium salts (1)—(3) which, in agreement with their structure, are among the most reactive polymer-immobilized phase-transfer catalysts.[2a]

The independence of catalytic activity of polymer particle size seems to have a different origin. We functionalized beads of commercial chloromethylated polystyrene, already reduced to a narrow range of particle size (200—400 mesh). Functionalization may eventually diminish, but not increase, the size of particles because of the mechanical fragility of the polymer.[1d,5] Therefore, low mesh fractions obtained by sieving catalyst beads after functionalization (an example is reported in the Table) seem to derive from a weak aggregation of particles. This aggregation rapidly disappears during catalyst conditioning, even in the absence of stirring. Accordingly, microscopic inspection of solvent suspensions of two catalyst samples, sieved in quite different mesh ranges, showed substantial identity of particle size.

The only exception is catalyst (3b), with 2% cross-linking and a relatively high loading (36% frequency) of quaternary phosphonium groups bonded through a spacer chain. In this case the observed rate constants are linearly related to the reciprocal of particle radius 2/*d*, in the range between 125 and 53 μ diameter (120 and 270 mesh, respectively). The straight line passes through the origin (Figure 2), which means that catalytic activity is nil for a hypothetical particle of infinite

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* A referee has correctly pointed out that there is also the possibility that variation of microenvironment polarity and/or of support hydrophobicity may influence the local concentration of the organic substrate, thus contributing to the apparent variation in $k_{obs.}$. This effect would most likely arise with highly loaded resins, that is to say resins in which the most significant differences in reactivity between spaced and non-spaced catalysts are indeed observed. The following should be noted: mass balances of single drawings for g.l.c. analyses were constantly >95%; control experiments showed that the concentration of the internal standard (tetradecane) in the bulk solution was constant within the limits of the experimental errors, both in the presence and in the absence of polymeric catalysts. We think therefore that variations of local concentration of organic substrate within the resin matrix, if any, should be negligible as far as the observed rate constants are concerned.

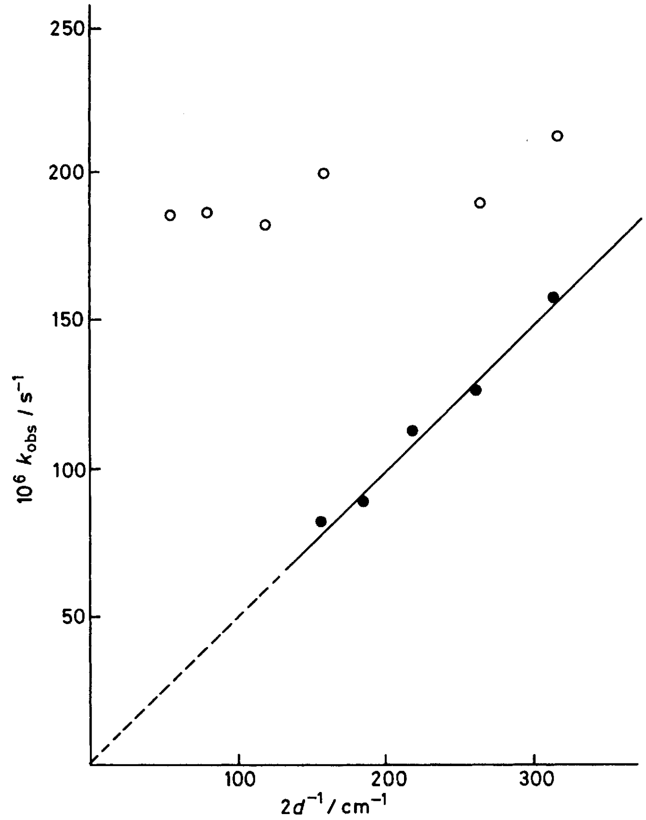

Figure 2. Dependence of the observed pseudo-first-order rate constants ($k_{obs.}$) on particle size and percent cross-linking for Br–I exchange reaction for 1-bromo-octane, toluene–water, 90 °C, 0.01 mol equiv. catalysts (2a) (○) and (3b) (●), 15 h conditioning without stirring

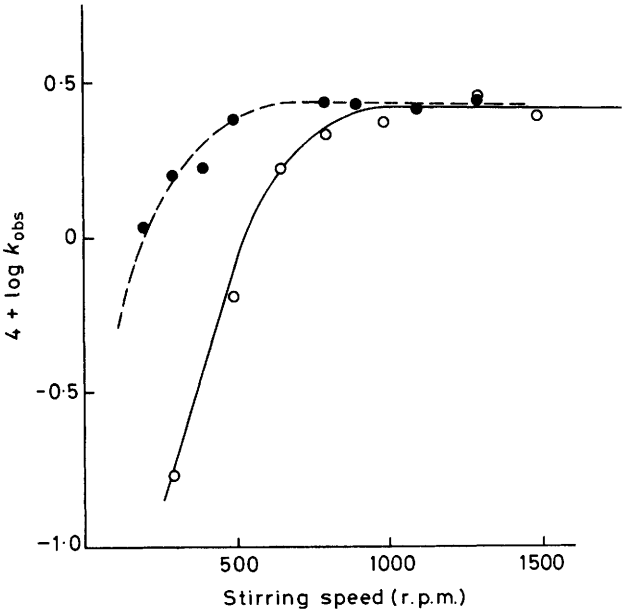

Figure 3. Dependence of the observed pseudo-first-order rate constants ($k_{obs.}$) on stirring speed, for Br–I exchange reaction in 1-bromo-octane, toluene–water, 90 °C, 0.015 mol equiv. catalyst (3b); (○) standard stirring; (●) turbulent stirring

dimensions, as expected for a catalyst whose reaction rate is limited by intraparticle diffusion.

For catalyst (3a), which differs from (3b) only in the much lower percentage ring substitution, $k_{obs.}$ is completely independent of the particle dimensions. Thus the particular behaviour of (3b) seems to be related to the presence of a high number of pendant chains, which may interact to give more stable ‘ aggregates ’.

A final comment concerns the stirring speed and mode. The thickness of the liquid film surrounding the catalyst particle (Nernst layer) diminishes on increasing the stirring speed.[1,3d] However, under uniform motion conditions, it constitutes a substantially static phase on the polymer surface, and turbulent motion is required to facilitate mass transport. We have found that introduction of a breakwater sheet perpendicular to the fluid motion direction gives rise to turbulence conditions even more efficiently than those achieved [2a] with a reactor having vertical creases.

Indeed, constant reaction rates are obtained at *ca.* 600 r.p.m. with a magnetic stirrer, whereas in the absence of the breakwater sheet a plateau is not reached until 800—900 r.p.m.[2a] (Figure 3).

All this confirms that the attainment of a plateau in $k_{obs.}$ as a function of stirring speed depends on the operating conditions.[2a,3d] The latter include not only the type of reactor, but also the structure of polymer-supported catalysts which should thus be prepared under strictly comparable conditions to allow comparison of the results obtained from different authors.*

Experimental

Catalysts (1a—c) and (2a—c) were prepared from commercially available chloromethylated polystyrene (Fluka AG) cross-linked with 1% divinylbenzene with 1.04, 2.63, and 5.0 mequiv. Cl g^{-1}; catalysts (3a and b) derived from Fluka AG Merrifield polymer (2% cross-linking, 0.7 and 3.5 mequiv. Cl g^{-1}) respectively, as previously described.[2a] Particles of catalysts were separated with sieves in fractions ranging from 35 to 325 mesh using Endecotts test sieves with Endecotts sieves shaker. G.l.c. analyses were performed on a Hewlett–Packard model 5840 flame ionization instrument (2 ft × 0.125 in UCW 982 on Chromosorb W column at 120 °C). Organic and inorganic reagents were ACS reagent grade.

Kinetic Measurements.—Reactions were run in a 50 ml flask, equipped with a Teflon-lined screw cap, thermostatted at 60 or 90 °C with circulating butyl phthalate and a magnetic stirrer. The temperature was controlled to within ±0.01 °C by an Exacal 200 bath circulator. The stirring speed (1 300 ± 50 r.p.m.) was controlled using a strobe light. For reactions carried out at 60 °C (Figure 1) the flask was charged with potassium iodide (8.3 g, 50 mmol) in water (6.5 ml) or with potassium bromide (6.0 g, 50 mmol) in water (11 ml), toluene (3 ml), tetradecane as internal standard (2 ml of a 0.1M solution in toluene), and 0.25 mequiv. catalyst. The mixture was left at 60 °C for 15 h at 200 r.p.m. stirring speed in order to condition the catalyst. n-Octyl bromide or methanesulphonate (5 ml of a 1M solution in toluene) was added at zero time, and the mixture stirred at 1 300 r.p.m.

The same conditions were followed for the reaction between

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* For example, Tomoi and Ford found reaction rate increases up to 600 r.p.m. under mechanical stirring conditions, but they could not obtain any further increase by turbulent vibro-mixing, nor by ultrasonic mixing.[3d] It should be observed that, in the latter case, a suitable apparatus must be set up for this methodology to be efficient (V. Ragaini, personal communication).

n-octyl bromide and potassium iodide at 90 °C. For other kinetic measurements at 90 °C the flask was charged with potassium iodide (12.0 g, 72 mmol), water (10 ml toluene (3 ml), tetradecane as internal standard (2 ml of a 0.1M solution in toluene), and 0.14 mequiv. catalyst. The mixture was conditioned for 15 h at 90 °C at 1 300 r.p.m. stirring speed. n-Octyl bromide (5 ml of a 2.8M toluene solution) was added at zero time, and the mixture stirred at 1 300 r.p.m. The reactions were followed by g.l.c. analysis up to *ca.* 70% conversion. The pseudo-first-order rate constants ($k_{obs.}$) were obtained by following ln[substrate] *versus* time and determining the slope of the straight lines.

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