Heterogeneous Phase-transfer Catalysts: High Efficacy of Catalysts Bonded by a Long Chain to a Polymer Matrix

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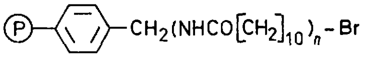
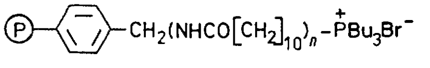
Summary Heterogeneous phase-transfer catalysts, such as phosphonium salts and crown-ethers, immobilized on a polystyrene matrix, show an increase in activity approaching that of the corresponding non-immobilized catalysts, when they are bonded with a long spacer chain to the polymeric support.

HETEROGENEOUS phase-transfer catalysts immobilized on a polymer matrix have been recently described by us[1] and by others.[2,3] When alkyl chains capable of imparting sufficient organophilicity to the systems were bonded to immobilized ammonium and phosphonium salts, crown ethers, and cryptands, the structural dependence of catalytic activity was very similar to that found for non-immobilized phase-transfer catalysts.[1] However the reaction rates were noticeably slower because of the difficulty in bringing the reacting species in contact with the catalytic site.

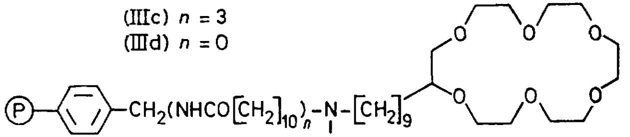
In order to overcome this drawback, we used a long chain to bind the catalysts to the polymer matrix, under the assumption that, by allowing the catalytic site to 'protrude' into the solution, it would be more solvated and, in a sense, would be 'soluble' in the reaction medium.[4] Improvement in phase-transfer catalytic activity of immobilized quaternary ammonium salts, upon lengthening of the spacer alkyl chain, was recently reported by Brown,[3] and by Sparrow[5] to improve yields in the Merrifield synthesis of polypeptides.



(IIa) $n = 1$
(IIb) $n = 2$
(IIc) $n = 3$



(IIIa) $n = 1$
(IIIb) $n = 2$
(IIIc) $n = 3$
(IIId) $n = 0$



(Va) $n = 0$
(Vb) $n = 1$
(Vc) $n = 2$

We studied systems (IIIa—c) and (Va—c), in which the tributyl phosphonium cation and 18-crown-6 ring are bonded to the polystyrene matrix by 1, 2, or 3 sequences of 11—13 linearly disposed atoms. They were synthesized from a chloromethylated polystyrene resin (I) ($3{\cdot}5 \times 10^{-3}$ equiv. of Cl per g of polymer; 2% divinylbenzene). Conversion of (I) into aminomethyl polystyrene [K-phthalimide, dimethylformamide (DMF), 12 h, 100 °C; $N_2H_4.H_2O$, EtOH, 6 h reflux] and condensation of the latter with ω-bromoundecanoyl chloride (C_6H_6, C_5N_5N, 3 h, room temp.), gave the bromo-derivative (IIa), which was allowed to react with tributylphosphine (5 days, 50 °C) to give the phosphonium salt (IIIa). By similar sequences of reactions the homologous phosphonium salts (IIIb) and (IIIc) were prepared; (IIId) ($n = 0$) had been previously described.[1] Condensation of chloromethylated polystyrene (I) with ω-ethylaminononyl 18-crown-6 (IV) gave the polymeric catalyst (Va).[1] Likewise, homologous catalysts (Vb) and (Vc) were prepared (DMF, 7 days, 60—65 °C) from the bromides (IIa) and (IIb), respectively.†

The activity of the immobilized heterogeneous catalysts (IIIa—d) and (Va—c) has been studied for anion-promoted substitution reactions, such as Br → I and Br → PhS for n-octyl bromide. Both reactions were carried out under magnetic stirring in the presence of 0·01 mol. equiv. of catalyst, with a substrate: solvent ratio of 1:3 (v/v). The other reagents were: KI (2·5 mol. equiv.) in a saturated aqueous solution, and PhSK (1·5 mol. equiv.) in a 3M aqueous solution, respectively. These conditions were similar to those classically employed in phase-transfer processes between two immiscibile aqueous and organic phases.

An induction period was observed until swelling of the resin allowed the catalyst to reach a constant activity. For this reason, the systems were first equilibrated for 2 h at 90 °C in the presence of all the components, except one reagent which was added at the beginning of the reaction (KI at 90 °C and $C_8H_{17}Br$ at 25 °C, in the synthesis of octyl iodide and phenyl octyl sulphide, respectively). The reactions followed pseudo-first order kinetics, and were monitored by g.l.c. analysis.

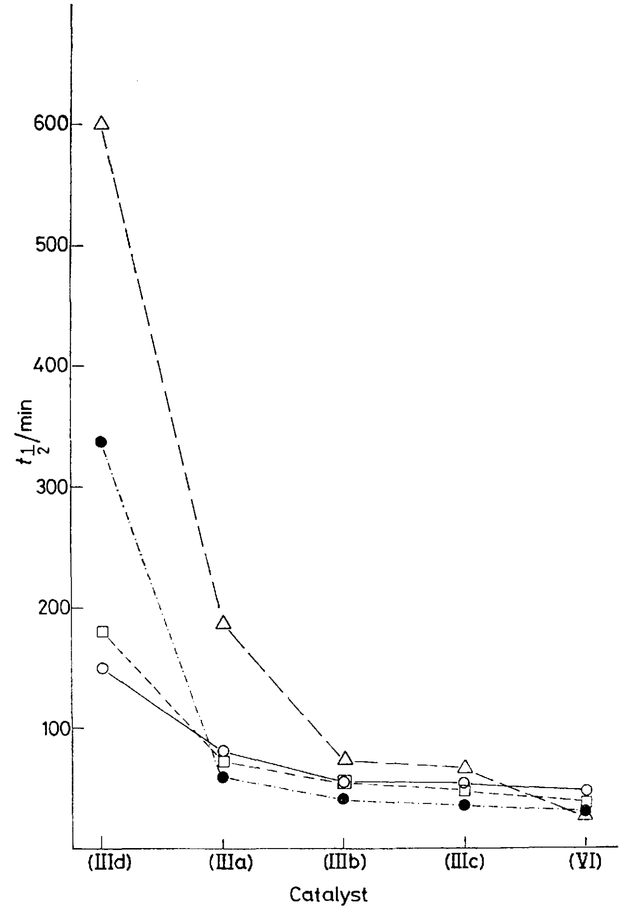


FIGURE. Influence of solvent and spacer chain length in the conversion of 1-bromo-octane into 1-iodo-octane: substrate: solvent = 1:3 (v/v); ○ = PhCl, □ = PhMe, △ = n-C_7H_{16}, ● = no solvent.

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† Conversions were almost quantitative, except in the bindings of the crown ether (IV) to the terminal halogenated carbon of (I), (IIa), and (IIb), which occur with *ca.* 50% yield. For this reason, the frequency of functionalized monomeric units in the polymer is on average 1:3 for phosphonium salts (IIIa—d) and 1:6 for crown ethers (Va—c): these values are approximately equal to, and half of, respectively, the frequencies of chloromethyl groups in polystyrene (I). Frequencies were determined by titration of ionic and/or covalent halogen in compounds (IIa—c), (IIIa—d), and (Va—c), and results were confirmed by the observed variations in weight at each step and by elemental analyses (C, H, and N).

In the conversion of 1-bromo-octane into 1-iodo-octane the half-life times, as a function of the catalyst, were as follows (in min, toluene): (IIId) 180, (IIIa) 72, (IIIb) 54, (IIIc) 48, (Va) 53, (Vb) 45, and (Vc) 42. Thus, a continuous increase in rate was observed with lengthening of the spacer chains, the increase being relatively smaller in going from (IIIb) to (IIIc) and from (Vb) to (Vc), respectively. With catalysts (IIIc) and (Vc) the rates approached those measured under identical reaction conditions in the presence of comparable soluble phase-transfer catalysts, n-$C_{16}H_{33}P^+ Bu_3Br^-$ (VI) and n-decyl 18-crown-6 (VII) [half-life times: 36 and 35 min, for (VI) and (VII), respectively]. In the conversion of 1-bromo-octane into phenyl octyl sulphide, the half-life times in toluene were: (IIId) 240, (IIIa) 102, (IIIb) 70, (IIIc) 60, (VI) 20, (Va) 70, (Vb) 45, (Vc) 39, and (VII) 33.

For these heterogeneous catalysts the influence of the chain length on the reaction rates depends on the polarity of solvent and is a maximum for n-heptane, and a minimum for chlorobenzene. An important consequence is that reaction rates notably increase upon increasing the polarity of solvent for catalysts directly bonded by short chains to the polymer, whereas such a dependence is very limited for catalysts bonded through long chains. The latter behaviour is similar to that shown by catalysts (VI) and (VII) under the same conditions (Figure).

The advantage of using heterogeneous phase-transfer catalysts is that reactions are extremely clean, so that products can be isolated by simple filtration from the catalyst and separation of the aqueous phase. This is particularly interesting for catalysts such as crowns (V) which are quite stable even under extreme conditions and can thus be recycled a number of times with no loss of catalytic activity.

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