Reactions

Phase Transfer Catalysis

2. The Reaction Between Phenol and n-Butyl Bromide Catalyzed with Polyethyleneglycols Fixed on Macroporous Glycidylmethacrylate Copolymers

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Summary

By using a model reaction between sodium phenoxide and n-butyl bromide, the PTC activity of a number of polyethyleneglycols (PEG) fixed on the macroporous glycidyl methacrylate copolymer (0.09 - 0.7 mmol PEG/g) was tested and compared with that of dissolved polyethyleneglycols. Both systems are catalytically active; 1 mmole of fixed PEG raises the reactivity 168 times, and in solution 139 times compared with the uncatalyzed reaction. In the case of immobilization, PEG 2000 and higher are catalytically somewhat more active than in solution; the lower activity of immobilized PEG's with mol. wt up to 1550 is interpreted by the lower mobility of parts of the chain due to immobilization. The rise in catalytic activity with the molecular mass of fixed PEG is in accord with their higher sorption ability towards cations of alkali metals.

Introduction

Polyethyleneglycols are potential phase transfer catalysts (PTC). Their relatively low price and low toxicity make them more advantageous compared with crowns. In the case of reactions catalyzed with PEG, it was the effect of the chain length of polyethyleneglycols on catalytic activity that was investigated in the first place; as a rule, the activity increases with the chain length and does not change to any considerable extent starting from PEG 2000. With respect to their catalytic activity, polyethyleneglycols can be compared with crowns (BANTHIA et al., 1981), where the salt transfer mechanism is similar. It seems that at low temperatures polyethyleneglycols are more active (HRADIL and ŠVEC, 1983), although here the main role is of course played by the character of the reaction. By joining crowns to PEG with M.W. 300-14 000, no rise in the PTC activity was achieved (HARRIS et al., 1982), while after the binding of cryptands the activity somewhat increased. Three-block copolymers polystyrene-polyethylene glycol are very active as PTC (KELLY et al., 1979, 1982).

After the immobilization of PEG on silicagel, the activity was the same as with free coronands (SAVICKY, 1982). The activity of polyethylene glycol ether bound to the styrene-divinylbenzene copolymer (REGEN and DULAK, 1977) is also high.

In our paper, we have compared the activity of polyethyleneglycols immobilized on the macroporous copolymer glycidylmethacrylate - ethylenedimethacrylate with that of non-
immobilized polyethyleneglycols.

Experimental

Investigation of the reaction kinetics

2 mmoles of sodium phenoxide, 0.26 g of dry sorbent (polyethyleneglycol immobilized on the macroporous glycidylmethacrylate copolymer), x) 2 ml water (in the case of soluble polyethyleneglycols, 2 ml of a solution of 0.5 g PEG in 10 ml H2O) and 2 ml of the solution of 0.3491 g (2.548 mmole) of n-butyl bromide in toluene (1:6) were introduced into a stirred reactor, 5 ml in volume. The reactor was heated to 50°C ± 0.03°C and stirred with a propeller stirrer (1300 r.p.m.). From the reaction mixture, two samples of the organic phase were taken in 30 min. intervals and analyzed immediately by gas chromatography on a column 1 m long and packed with Chromosorb N-AW-DMCS with 10% of the deposited PEG 1550 (grain size 0.16 – 0.20) at 90°C. The concentrations of n-butyl bromide were calculated from two measurements of samples and calibration standards with toluene as the internal standard, relative error being ± 1.0%.

Assuming a first-order reaction rate (HARRIS et al., 1982), the rate constants k1 (s⁻¹), rate constants related to 1 mole of PTC, k1' (s⁻¹ mmole⁻¹), relative rate constants for PEG immobilized against free PEG, k_r₁, and relative rate constants for 1 mmole PEG related to the uncatalyzed reaction, k_r₁ (mmol⁻¹), were calculated.

Chemicals

Polyethyleneglycols 200, 400, 600, 1550, 2000 and 4000 pract. (SERVA, Feinbiochemica, Heidelberg). G-60-PEG 200, 400, 600, 1550, 2000 and 4000 prepared by a reaction between sodium polyethyleneglycol (NaH + PEG) and the macroporous copolymer glycidylmethacrylate - ethylenedimethacrylate (40 wt.% crosslinking agent, S₆ 55.5 m²/g, V₆ 1.47 ml/g, porosity 65%) in dioxan (100°C, 12 h). These sorbents were characterized by the content of PEG groups estimated from the elemental analysis of carbon, sorption of KCl, content of carbonyl groups and porosity in water.

Results and Discussion

Characteristics of immobilized polyethyleneglycols

By reacting the macroporous glycidylmethacrylate copolymer crosslinked with 40 wt.% of ethylenedimethacrylate with sodium salts of several polyethyleneglycols having molecular weights between 200 and 4000, a number of derivatives containing 0.1 – 0.7 mmole PEG/g carrier were prepared (Table I). The content of PEG introduced into the carrier decreases systematically with the molecular weight of PEG. This finding may be explained by carrying out the reaction under equilibrium conditions of the stirred reactor, and thus by employing the lower mobility of PEG with higher molecular weights during the diffusion in beads of the macroporous copolymer. Another factor is

x) The authors are indebted to Dr J. Kahovec for kind supply of the sample; its preparation and properties will be reported by the same author in a separate paper.