

The Co-operative Effect in the Activation of the Phenoxide Anion with Oligo(oxyethylenes) containing Quaternary Ammonium Groups

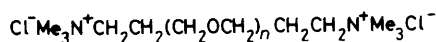
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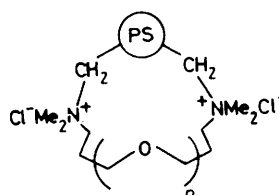
An unusual increase in activity accompanying the catalysis of a model substitution reaction between sodium phenoxide and 1-bromo-octane with oligo(oxyethylenes), linear or bound to the polymer, was observed after the introduction of quaternary ammonium groups as terminal groups into the oligo(oxyethylene) chain.

Linear and cyclic oligo(oxyethylenes) are well known to form associates and well-defined complexes with metal and ammonium cations.^{1,2} The formation of these associates strongly affects the interaction between cation and counterion; hence, the presence of a catalytic amount of oligo(oxyethylene) as co-solvent may considerably affect the rate of nucleophilic substitution.³ Linear oligo(oxyethylenes) bound to a cross-linked polymeric matrix and having so-called pseudo-crown ether structures⁴ are suitable candidates for catalytic purposes, and may replace the expensive crown ethers.⁵ Polymers containing bound quaternary ammonium and phosphonium groups are highly active catalysts of reactions proceeding by the transfer of reactants through the water-organic solvent phase boundary,⁶ their effect being due to the interaction between anions and the onium group. The disadvantage of polymeric catalysts is that, with a few exceptions, their activity is lower than that of low-molecular weight analogues.⁷ Hence, efforts are continuing to prepare more active polymer catalysts, which have concentrated on the synthesis of polymers with new functional groups, of soluble polymers, and of micron polymer particles. As far as we know, there have been no reports so far about the use of such polymer

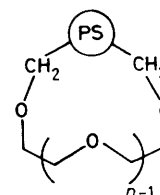
catalysts which contain two different types of functional group bound in a single catalytic site, one of which is capable of direct interaction with the cation and the other with the anion. Such structures may create suitable conditions for co-operation between both types of functional groups, and hence for a



(1) $n = 6.5$



(2) $n = 6.5$



(3) $n = 6.4$

Table 1. Catalysis of the reaction between sodium phenoxide (0.25 mol l⁻¹) and 1-bromo-octane (1.00 mol l⁻¹), 1,4-dioxane, 75 °C, stirring (600 rev. min⁻¹).

Entry	Catalyst	c_{OE}^a /mmol l ⁻¹	$k_o \cdot 10^5$ /l mol ⁻¹ s ⁻¹	$k_s \cdot 10^5$ /l ² mol ⁻² s ⁻¹	ξ^b (%)
1	None	0	Not determined		<1
2	HO(CH ₂ CH ₂ O) ₄ H	0.10	3.5	35	38
3	HO(CH ₂ CH ₂ O) ₇ H	0.10	5.32	53	50
4	18-Crown-6	0.30	9.00	30	66
5	(1)	0.083	9.30	113	69
6	(2)	0.0664	11.1	167	75
7	(2)	0.133	22.8	172	94
8	(3)	0.038	1.00	26	14
9	Ⓟ-N+Me ₂ C ₄ H ₉ Cl ^{-c}	— ^d	0.66	14 ^e	8
10	(3) + Ⓟ-N+Me ₂ C ₄ H ₉ Cl ^{-f}	0.0664	2.37	36	25

^a c_{OE} = molar concentration of oxyethylene units. ^b ξ = Extent of reaction after 4 h with respect to sodium phenoxide; determined by g.l.c. ^c The polymer was prepared by quaternization of dimethylbutylamine chloromethylated with poly(styrene-98-co-divinylbenzene-2) (36% r.s., 2.29 mmol N/g). ^d Concentration of quaternary ammonium groups 0.046 mol/l. ^e k_s was calculated by using the concentration of quaternary ammonium groups. ^f The molar amount of quaternary ammonium groups was identical with entry 6, i.e. 0.020 mmol.

more pronounced influence on the bond between cation and anion, thus favourably affecting the catalysed reaction.

We now report an unusual increase in the specific rate constants of the model reaction between sodium phenoxide and 1-bromo-octane in anhydrous 1,4-dioxane, catalysed with linear oligo(oxyethylenes) possessing quaternary terminal ammonium groups (1) and with the same structural units bound to a poly(styrene-co-divinylbenzene) carrier (2), compared to the catalysis with oligo(oxyethylenes), either free or bound to the same polymer carrier (3).

The oligo(oxyethylene) (1) containing terminal quaternary ammonium groups was synthesized from the oligo(oxyethylene) with terminal amino groups (M_n 430) by using Leuckart-Wallach methylation followed by quaternization with dimethyl sulphate.⁸ Polymers (2) containing oligo(oxyethylene) branches bound to the crosslinked matrix through quaternary ammonium groups were prepared by the reaction of the oligo(oxyethylene) possessing terminal dimethylamino groups with chloromethylated poly(styrene-co-divinylbenzene) (microporous, 2.98 mmol Cl/g, beads, 200–400 μm) and containing 1.66 mmol N/g (calc. 1.62 mmol N/g). The activity of these catalysts was compared with that of linear free oligo(oxyethylenes) and that of oligo(oxyethylenes) bound to the polymeric matrix (3). The latter were prepared by the reaction of chloromethylated poly(styrene-co-divinylbenzene) with poly(oxyethylene), M_n 300 (3.75 mmol of oxyethylene units/g). The activity of catalysts in the model reaction was expressed in terms of the observed rate constants, k_o , and specific rate constants, $k_s = k_o/c_{\text{OE}}$, where c_{OE} is the molar concentration of oxyethylene units, $-\text{CH}_2\text{CH}_2\text{O}-$, in the reaction mixture (Table 1).

In the absence of the catalyst the reaction virtually does not proceed. In the presence of tetra- and hepta-(oxyethylene) and 18-crown-6, k_s varies between 30 and 54×10^{-5} l² mol⁻² s⁻¹. In the catalysis with quaternary ammonium groups modified with oligo-oxyethylene (1) k_s is more than double the original value, however (compare entries 2–4 and 5). An analogous, but more pronounced, difference can be seen with similar structures bound to the crosslinked polymeric matrix (entries 6–8). The quaternary ammonium groups alone bound to the same polymer carrier, PS-

CH₂N+Me₂BuCl⁻ (2.29 mmol N/g, 33% of ring substitution in the polystyrene matrix, microporous type, beads) have a very weak specific activity (entry 9). At the same time, a mixture of two crosslinked and thus mutually non-communicating polymers, one of which contains quaternary ammonium groups and the other oligo(oxyethylene) groups in molar quantities identical with those present in the reaction catalysed with polymer (2), possesses an activity approaching a simple sum of k_s (entries 8, 9 vs. 10). This strongly supports the view that in the case of the catalysis with polymer (2) both types of groups, i.e. quaternary ammonium and oxyethylene groups, synergistically co-operate in the activation of the phenoxide anion. The principle of activation of the reactants with polyfunctional polymers may provide a route to a pronounced increase in the activity of polymer catalysts in organic reactions. Polymers with new combinations of communicating functional groups are being further investigated.

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