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TRIPHASE CATALYSIS OF POLYMER-BOUND AMINE OXIDE IN CYANIDE DISPLACEMENT ON 1-BROMOOCTANE

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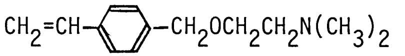
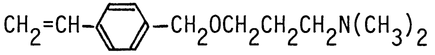
Cross-linked polystyrene supported tertiary amines and amine oxides are found to be a very efficient catalyst for a nucleophilic substitution reaction. The amine oxide resin (MPE-5-AO) was one of the most effective and economical catalysts and can be used several times without the loss of the catalytic activity.

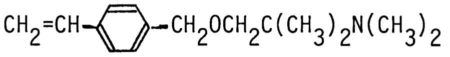
Phase transfer catalysis is becoming an increasingly important technique in organic synthesis.1) One practical limitation to this method, however, is that many phase transfer catalysts promote stable emulsions which render work-up difficult. In recent papers, Regen introduced the new concept of triphase catalysis, in which the catalysts and each of a pair of reagents are located in separated phases.2-4) The major advantage of triphase catalysis over phase transfer catalysis is that the catalyst can be removed from the reaction mixture by simple filtration.

We wish to introduce a very efficient and new type triphase catalyst containing amine oxides. Recently we observed that fatty alkylamine oxides accelerated aqueous-organic phase reactions.5) It is well-known that amine oxides are highly polar but exhibit nonionic properties under neutral and alkaline conditions. Thus they could not be the "true" phase transfer catalyst. It appeared of interest to investigate further the scope and mechanism of the amine oxide catalysis.

Since there is a high probability that polymers prepared from the reaction of the appropriate amine with a chloromethylated polystyrene resin contain a small fraction of quaternary ammonium groups,3) we synthesized some new monomers of styrene derivatives containing tertiary amino groups shown below.


(EE) (bp.102°C/0.4 ; y. 33%)


(PE) (bp.110°C/0.4 ; y. 40%)


(MPE) (bp.115°C/0.5 ; y. 31%)

Copolymers of these monomers (5, 10, 20 and 50mol%) with styrene and divinylbenzene (4mol%) were prepared by suspension polymerization using 2,2'-azobisisobutyronitrile as an initiator. The polymer-supported tertiary amines (TA) were converted to the resin-supported amine oxides (AO) by hydrogen peroxide and to the resin-supported quaternary ammonium salts (QA) by methyl iodide.

A series of the copolymer catalysts6) were prepared and tested for their ability to catalyze the reaction of sodium cyanide (0.163mol) with 1-bromooctane (0.027mol) in water (25ml) at 70°C in the presence of the catalyst (1g). The catalytic effects of the most active resins on the reaction are shown in Fig. 1 along with the results of hexadecyltrimethylammonium bromide (CTAB) and dimethyldodecylamine oxide (DDAO). The most active catalysts, MPE-5-AO in AO resins and EE-50-TA in TA resins, have a catalytic capacity comparable with a typical phase transfer catalyst, CTAB, and the most active amine oxide, DDAO. Moreover, the catalysts, MPE-5-AO and EE-50-TA, can be used several times without the loss of the catalytic activity in the reaction. The catalyst, EE-5-QA, is the most active one in the QA resins but less effective than the other resins.

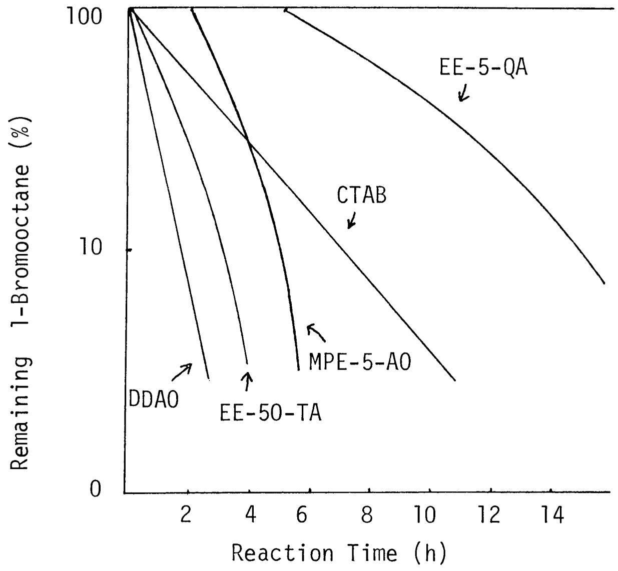


Fig.1 The Catalytic Effects

Table 1 Pseudo First-order Rate Constants

Catalyst	$k_{obsd} \times 10^5 s^{-1}$	Catalyst	$k_{obsd} \times 10^5 s^{-1}$
EE-5-AO	9.8	EE-5-QA	6.2
EE-10-AO	7.2	EE-10-QA	5.6
EE-20-AO	3.9	EE-20-QA	3.6
EE-50-AO	3.5	EE-50-QA	3.5
PE-5-AO	17.0	EE-5-TA	6.0
PE-10-AO	10.5	EE-10-TA	8.5
PE-20-AO	9.0	EE-20-TA	8.8
PE-50-AO	4.1	EE-50-TA	19.1
MPE-5-AO	22.4	DDAO	30.5
MPE-10-AO	14.5		
MPE-20-AO	10.9	CTAB	9.5
MPE-50-AO	5.3		

The pseudo first-order rate constants in the reaction are shown in Table 1.[7)]

The feasibility of triphase catalysis was first demonstrated by the reaction of cyanide ion with 1-bromooctane using a crosslinked polystyrene resin bearing quaternary ammonium groups as the catalyst,[3)] and the mechanism of the reaction was explained in terms of ion transfer like phase transfer catalysis.[8)] In our new AO resins there are no cationic sites to bind with cyanide ion and activity of the resins for absorption of cyanide ion in the preliminary conditioning time[7)] was very poor. Although the detailed nature of the catalytic processes reported here needs further clarification, the results of the activity of these catalysts may be explained on the basis of the microenvironment of the phase bondary like micellar catalysis. Further work is in progress on the mechanism of the catalytic activity of the resins.

References and Notes

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6). In the abbreviation of the name of the resins (for example, EE-5-AO), the first one expresses the comonomer amino styrene in the resins, the second number refers to the molar content of the amino styrene in the resins, and the last part means the type of the amines.
7). In the two phase catalysis (CTAB, DDAO), the rate clearly showed a first-order dependency on the 1-bromooctane concentration, while the reaction catalyzed by the resin catalysts seems to start slowly and proceeded more rapidly as 1-bromooctane was converted to 1-cyanooctane. When the resin catalysts were stirred with a sodium cyanide solution and 1-cyanooctane (2.6g) for 24h at room temperature before the reaction started, the induction period disappeared and the rate of the reaction showed a first-order dependency on the 1-bromooctane concentration. The rate constants in Table 1 were calculated by this procedure. The resin was swelled by the solvent to allow better accessibility of substrate and reagents to the catalytic site.[8)]
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