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PHASE TRANSFER CATALYSIS OF MODIFIED DEXTRAN ANION EXCHANGERS

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Abstract: Dextran anion exchangers with lipophilic substituents have been synthesized, which were found to be useful as phase transfer catalysts for displacement and hydrogenation reactions under triphase conditions.

A number of organic reactions involving anionic species are effectively catalyzed by quaternary ammonium or phosphonium halides under phase transfer conditions.[1] One of the recent major developments in the technique of phase transfer reaction is the use of polymer-supported insoluble catalysts for organic-aqueous two phase reactions. Examples are ammonium or phosphonium salts, crown ethers, and cryptands immobilized on cross linked styrene resins[2] or silica gels.[3]

Now we wish to report on the new polymer catalysts derived from cross linked dextran anion exchangers having quaternary ammonium groups and those obtained by the introduction of ammonium groups by siloxane linkages into the lipophilic dextran gels. The importance of the lipophilicity for the catalytic efficiency will be demonstrated on halogen and cyanide displacement reactions as well as hydrogenation of acetophenone by sodium borohydride under organic-aqueous-solid triphase reaction conditions.

Three kinds of catalyst were prepared as follows:

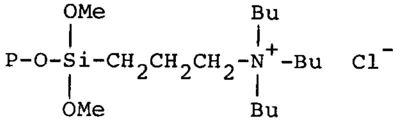
1) Hydroxypropylated dextran gel (Pharmacia Sephadex LH-20,[4] 20 g) was treated with 3-chloropropyltrimethoxysilane (20 ml) in toluene (20 ml) at 120 °C for 24 h. Then the gel was subjected to extraction by benzene with a Soxhlet extractor for 5 h, dried in vacuum, and then reacted with excess tributylamine at 120 °C for 48 h. The soluble substances in the product were again extracted by benzene for 5 h, and the gel was dried in vacuum (C-1). Active chloride content determined by $AgNO_3$ titration was 0.60 meq/g.

2) To the mixture of dextran ion exchanger (QAE Sephadex A25,[5] 10 g), hexamethyldisilazane (17.6 ml), and acetonitrile (40 ml), chlorotrimethylsilane (2 ml) was added with stirring. The mixture was stirred at room temperature for 30 min and then at 50 °C overnight. Then the gel was filtered, washed with water, ethanol, and acetone, and dried in vacuum (C-2).

3) The mixture of QAE Sephadex (5.0 g), tetramethylammonium bromide (0.10 g), and 50 % aqueous sodium hydroxide (10 ml) was stirred at 40 °C for 1 h. Then, benzyl chloride (26 g) was added dropwise, and the reaction mixture was heated

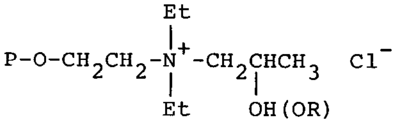
at 80 °C for 5 h with stirring.[6] After the reaction, the gel was washed with water, ethanol, and acetone, and dried in vacuum (C-3).

The catalytic sites of the catalysts are as follows:



$$\mathrm{P{-}O{-}\overset{OMe}{\underset{OMe}{Si}}{-}CH_2CH_2CH_2{-}\overset{Bu}{\underset{Bu}{N^+}}{-}Bu\quad Cl^-}$$

C-1



$$\mathrm{P{-}O{-}CH_2CH_2{-}\overset{Et}{\underset{Et}{N^+}}{-}CH_2\underset{OH(OR)}{CH}CH_3\quad Cl^-}$$

C-2(R:SiMe$_3$), C-3(R:CH$_2$Ph)

The supporting polymers of C-1, C-2, and C-3 are hydroxypropylated, trimethylsilylated, and benzylated dextrans, respectively. Although the hydroxyl groups of hydroxypropyl substituents in C-2 and C-3 are considered to be most reactive to trimethylsilylation and benzylation, the exact site and degree of the reactions have not been clarified. The structure of the catalysts is currently studied by IR and elementary analysis.

The catalytic efficiency of the catalysts was estimated on the displacement and hydrogenation reactions (Table 1). Dextran gels without ammonium groups are inefficient for these reactions, indicating that quaternary ammonium groups are essential for the catalytic activity. However, QAE Sephadex itself has no catalytic ability, and furthermore, when a simple dextran gel (Sephadex G25, not hydroxypropylated) was treated with 3-chloropropyltrimethoxysilane and then with tributylamine similarly to C-1, the product was a poor catalyst for the halogen displacement reaction (less than 10 % yield of 1-iodooctane from 1-bromooctane). These results clearly indicate that lipophilicity of the supporting polymer is an important factor controlling the catalytic efficiency of the polymer ammonium salts. The situation is quite similar to that of soluble quaternary ammonium salts, in which lipophilic nature of the salt enhances the catalytic ability.[2f,7]

As shown in Table 1, the prepared catalysts are effective for halogen displacement reactions and give products in fairly good yields, though differences are found in the catalytic ability, which may be due to the difference in the content of ammonium group and lipophilicity of the catalysts. It is interesting to note that size selectivity is observed for the triphase reactions. It is obvious that 1-bromobutane reacts with iodide ion faster and gives higher yields of the iodide than 1-bromooctane. Regen and Nigam[8] reported similar size selectivity in the triphase catalytic reactions of bromoalkanes with phenoxide ion in the presence of polystyrene-based catalysts. The degree of cross linking and the nature of substituents on the dextran resins would impose different magnitude of size selectivity to the catalysts.

Table 1. Triphase reactions.[a)]

Substrate	Product	Catalyst(g)	Temp.(°C)	Time(h)	Yield(%)
1-Bromobutane[b)]	1-Iodobutane	C-1, 1.43	80	6	83
		C-2, 1.00	80	4	90
		C-3, 1.00	80	6	86
		C-4, 2.00	80	6	70
1-Bromooctane[b)]	1-Iodooctane	Sephadex LH-20 2.00	80	6	2
		QAE-Sephadex 0.55	80	6	2
		TEAE Cellulose 2.00	80	6	2
		C-1, 2.00	80	12	65
		C-2, 1.00	80	6	78
		C-4, 2.00	80	11	40
1-Bromobutane[c)]	Pentanenitrile	C-2, 1.00	100	10	95
1-Bromooctane[c)]	Nonanenitrile	C-2, 0.75	100	30	95
$PhCOCH_3$[d)]	$PhCH(OH)CH_3$	C-1, 1.07	rt	4	93
		C-2, 1.00	rt	2	90

a) All the reactions were carried out with mechanical stirring of around 700 rpm. The yield was determined by GLC analysis of organic phase.

b) Bromoalkane 0.046 mol, potassium iodide 0.115 mol, water 16 ml, and benzene 5 ml.

c) Bromoalkane 0.046 mol, saturated aq. potassium cyanide solution 16 ml, and benzene 5 ml.

d) $PhCOCH_3$ 0.050 mol, $NaBH_4$ 0.030 mol, water 25 ml, and benzene 10 ml.

Table 2. Repeated catalytic reactions of 1-bromobutane with aqueous potassium iodide at 80 °C.[a)]

Catalyst(g)	Time(h)	Run	Yield(%)
C-1, 1.43	6	1	83
		2	78
		3	83
C-2, 1.00	4	1	90
		2	85
		3	81
C-3, 1.00	6	1	86
		2	85
		3	86

a) 1-Bromobutane 0.046 mol, potassium iodide 0.115 mol, water 16 ml, and benzene 5 ml.

One of the advantages of polymer-supported phase transfer catalysts is the facile recovery of the catalysts by filtration. The results of the study on the repeatability of the dextran-based catalysts for the displacement reaction are summarized in Table 2. It is obvious that the catalyst C-3 is highly and more stable than C-2. The latter has siloxane bonds and the hydrolysis of which may be responsible for the gradual loss of catalytic activity. Contrary to C-2, C-1 is resistant to hydrolysis, though it also has siloxane bonds which bind the ammonium groups to the resin. The repeatability and substrate selectivity as well as stereoselectivity of these catalysts in other reactions are currently being studied.

Finally, a cellulose anion exchanger (TEAE cellulose, 0.82 meq/g) was also treated with hexamethyldisilazane (C-4) similarly to C-2, and the catalytic activity of the product was examined on halogen displacement reactions (Table 1). It gave iodides from bromides in moderate yields, but the catalyst is partly soluble in organic phase making its recovery more difficult than cross linked dextran-based catalysts.

References and Notes

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