POLYMER-BASED CATALYSTS**PROGRESS REPORT**

for Period July 1, 1980--June 30, 1981

MASTER

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PROGRESS REPORT

Title: Polymer-based Catalysts

Contract: EG-77-S-02-4446

Period Covered by Report: July 1, 1980--February 1, 1981

SUMMARY

Research carried out under this contract period has centered around the following: (1) developing methods for probing active site mobility, macroenvironment, microenvironment and efficiency of triphase catalysts, (2) preparing and evaluating a variety of polyether-based triphase catalysts, (3) synthesizing key monomers from which sequestered ligands are to be prepared, and (4) demonstrating the synthetic utility of simple poly(acrylamide) gels as solid phase cosolvents.

I. Detailed Report

A. Triphase Catalysis. Influence of Percent Ring Substitution on Active Site Mobility, Macroenvironment, Microenvironment and Efficiency.

The precise relationship between macrostructure, microenvironment, and activity of polymer-based triphase catalysts is poorly understood. Although kinetic studies have proven valuable in defining the synthetic utility of certain triphase reactions, they have provided little mechanistic insight. Recent attempts to rationally design new and more active catalysts have focused primarily on the nature of the catalytic site, where close analogy has been made to phase-transfer catalysis. Little consideration, however, has been given to the concentration of these sites within the polymer.

During the present contract period, we have closely examined the physical and chemical consequences of changing the active site concentration in typical triphase catalysts. For this purpose, we have selected polymers 1a, 1b, 2a, and 2b. Our reason for choosing these polymers was fourfold. First, phosphonium-based

functionalized microporous polystyrene --

1% divinylbenzene

3, X = Cl

4, X = OMs

1a, 17 percent ring substitution (prs) ; X = Cl

1b, prs = 52; X = Cl

2a, prs = 17; X = OMs

2b, prs = 52; X = OMs

resins are among the most active triphase catalysts. Second, these polymers span the range of loadings which have been employed in most synthetic applications. Third, low cross-link densities provide maximum catalyst efficiencies; they also afford reasonably narrow ^{13}C NMR line widths in solvent-swelled resins, making spectral analysis and evaluation of site mobility possible using conventional instrumentation. Fourth, the mesylate ion in 2a and 2b allows for examination of ionically as well as covalently attached sites.

Data which we have obtained from ^{13}C NMR, swelling, product distribution and kinetic analysis show that the percent ring substitution has a substantial influence on the mobility, macroenvironment, microenvironment and catalytic efficiency of tri-n-butylphosphonium groups attached to cross-linked polystyrene under triphase conditions. Full details of this work are reported in a manuscript which is now in press in Macromolecules.

B. Influence of Aqueous Salt Concentration on Triphase Catalytic Activity.

We have previously published the kinetic features of the triphase displacement by chloride ion on n-decyl methanesulfonate using polymers 1a and 1b (reaction 1).

During the current contract period we have examined this reaction further under comparable biphasic stoichiometric, triphase stoichiometric and triphase catalytic conditions. The purpose of this study was to establish the importance of the nucleophilic salt concentration present in the aqueous layer on triphase catalytic activity. Based on kinetic comparisons among these three systems, we have now obtained definitive evidence

that (1) the aqueous salt concentration plays a critical role in defining the hydration state of the polymer, and (2) imbibed water substantially influences catalyst activity. Details of this work are now being incorporated into a manuscript which will be submitted to J. Am. Chem. Soc., shortly.

C. Polyether-based Triphase Catalysts. A Synthetic Comparison.

Because of their susceptibility toward dequaternization, all practical applications of cross-linked phosphonium and ammonium-based triphase catalysts are limited to relatively mild reactions and conditions. Insoluble polyethers avoid this problem and, in principle, should become the catalysts of choice in many instances. Surprisingly, there is very little information available concerning the efficacy of such resins. Only two types of polyethers have been employed in triphase reactions (cross-linked polystyrene bearing pendant crown ethers or polyglymes) and no synthetic comparisons have been made between them.

During the present contract period we have developed improved syntheses of hydroxymethyl-18-crown-6 (Scheme I) and have made operational comparisons between triphase catalysts derived from this crown ether, poly(ethylene glycol monomethyl ether) and dibenzo-18-crown-6 for cyanide, iodide and phenoxide displacement on 1-bromooctane. Our principal results which have recently been submitted to J. Org. Chem as a Note, reveal that pendant 18-crown-6 offers no special advantage over polyglymes and that polymerized forms of dibenzo-18-crown-6 have remarkably high activity.

D. Sequestered Ligands.

Several attempts have been made in recent years to generate highly reactive transition metal catalysts on polymer supports. The basic hope has been that by preventing chelation or self aggregation, coordinatively unsaturated catalysts with high activity may be produced. Only modest success has come from these efforts which probably reflects the difficulty in producing isolated sites on solvent-swollen cross-linked polystyrene.

In an effort to raise the number of truly isolated sites per gram of resin-catalyst to a more practical level, we are attempting to change the configuration of the polymer by making it in the form of a micelle.

Our expectation is that such a polymer will be tightly compact and highly ordered and will exhibit substantially reduced site-site interaction compared to a disordered non-cross linked analog. Progress made in this area has been in the synthesis of desired monomers. Specifically, monomers 2a and 2b have been prepared as shown below.

2a, $n = 7$

2b, $n = 14$

Further studies aimed at developing polymerized micelles as ligands based on 2a and 2b are in progress and are described in our renewal proposal.

E. Solid Phase Cosolvents.

Hexamethylphosphoric triamide (HMPA), dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) are effective polar aprotic solvents for promoting nucleophilic displacement reactions. Recently, it has been reported that N,N-diethylacetamide (DEA) and N-ethylpyrrolidone (NEP) have similar properties. Based on this disclosure, it occurred to us that cross-linked polyamide analogs of DEA might exhibit useful "catalytic" features, acting as solid phase cosolvents. By virtue of their insolubility, such materials would be particularly attractive since they could be recovered by filtration and would avoid the toxicity problems associated with many of the above solvents. During the present contract period, we have evaluated a series of poly(acrylamide) gels as cosolvents for phenoxide displacement on 1-bromoheptane in dioxane, conducted as biphasic reactions. Substantial "catalytic"

activity by these polymers has been observed. In general, the apparent activity/g of polymer showed little sensitivity to the cross-link density but was highly dependent on the length of the N-alkyl chain. The latter appears to be due to the change in amide concentration in the polymer; i.e., when N,N-dimethyl- and N,N-di-n-octylacrylamide gels were compared on the basis of moles of amide used, similar activity

was observed. Comparison of poly(acrylamide) gels with other soluble solvents indicates that they are more active (per gram) than DMSO, DMF and DEA and similar to HMPA for promoting phenoxide displacement on 1-bromoheptane. Details of this work have been submitted to J. Org. Chem. for publication.

II. Publications.

1. "Poly(acrylamide)-based Solid Phase Cosolvents",
S. L. Regen, A. Mehrotra, A. Singh, J. Org. Chem.,
submitted.
2. "Polyether-based Triphase Catalysts. A Synthetic Comparison",
K. Fukunishi, B. Czech, S. L. Regen, J. Org. Chem., in press.
3. "Influence of Aqueous Salt Concentration on Triphase Catalytic
Activity", N. Ohtani, S. L. Regen, manuscript in preparation.
4. "Triphase Catalysis. Influence of Percent Ring Substitution
on Active Site Mobility, Macroenvironment, and Efficiency",
N. Ohtani, C. A. Wilkie, A. Nigam, S. L. Regen, Macromolecules,
in press.
5. "Triphase Catalysis. Backbone Structure-Activity Relationships",
S. L. Regen, D. Bolikal, C. Barcelon, J. Org. Chem., submitted.
6. "Chemistry at Hydrocarbon-Water Phase Boundaries. Biphasic
Hydrolysis of Organic Halides", N. Ohtani, J. J. Besse,
S. L. Regen, Bull. Chem. Soc. Jpn., in press.

III. Staffing

Professor S. L. Regen

Dr. A. Mehrotra

Dr. K. Fukunishi

Dr. N. Ohtani*

Mr. D. Bolikal*

Ms. C. Barcelon*

*Chemicals and supplies only.

IV. Projected Expenditures

Projected expenditures are detailed in the Budget section of the renewal proposal.

V. Percentage of Time Spent on Project by Principal Investigator

The PI (S. L. Regen) has spent approximately 20% of his total time with this project. A similar percentage of time will be spent for the remaining period of the contract.