

Phase - Transfer Catalysis

New Chemistry,
Catalysts, and
Applications

EDITED BY
Charles M. Starks



Phase-Transfer Catalysis

New Chemistry, Catalysts, and Applications

Charles M. Starks, EDITOR
Vista Chemical Company

Developed from a symposium sponsored by
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Foreword

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Preface

SCIENTIFIC KNOWLEDGE AND INDUSTRIAL APPLICATION of the phase-transfer catalysis (PTC) technique have expanded greatly during the last 15 years. As its practical simplicity and economic advantages have become more recognized, this field appears to be growing even more. Growth of PTC is easily measured (1) by the number of entries indexed by *Chemical Abstracts*, (2) by the fact that *Chemical Abstracts* has decided to form a separate "C. A. Selects" on PTC, (3) by the increasing number of phase-transfer agents offered for sale by chemical supply companies, (4) by the worldwide increase in specialized publications on PTC in a variety of languages, and (5) by the less easily measured but clearly exponential growth in the use of PTC for industrial chemical processing. I estimate the volume of phase-transfer catalysts totaled about 40,000 lb of catalysts per year in 1980 but grew to more than 1 million lb of catalyst per year in 1985.

I am grateful to the authors who took the time and effort to prepare manuscripts, often on tight deadlines. I also wish to thank the many reviewers who helped to bring out points of particular interest, to clarify ambiguous areas, and to generally improve the quality of already excellent writing. I am especially grateful to Lisa Butler who single-handedly and cheerfully handled and prepared numerous letters, notices, copies, revisions, reviews, and manuscripts.

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August 20, 1986

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Chapter 1

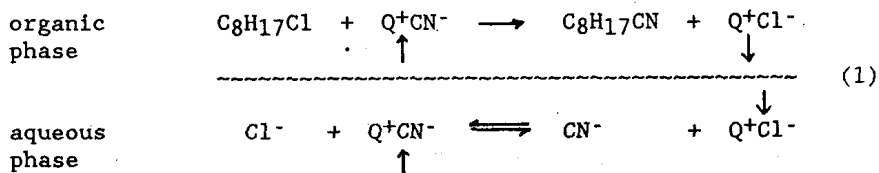
Phase-Transfer Catalysis: An Overview

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Uniquely interesting, complex and useful activities and phenomena occur at interfaces: one need only to look at the interfaces between the land, the atmosphere, and the sea to find this truth. The same truth occurs in chemical interfaces, although sometimes it is the lack of activity that draws our attention. In many chemical situations where two species cannot collide and therefore cannot react because they are separated by an interface, the lack of activity has been overcome by use of the technique of PHASE TRANSFER CATALYSIS (PTC), which not only allows reaction to occur, but often to occur in very selective ways.

An early and clear example of PTC(1) demonstrated that the lack of reactivity between a mixture of 1-chlorooctane and aqueous sodium cyanide (without organic solvent) could be overcome by the use of a phase transfer agent, whose function was to transfer cyanide ion in reactive form from its normal aqueous phase into the chlorooctane phase. Use of a small amount of phase transfer agent makes the system catalytic, since the phase transfer agent can repeatedly transfer active cyanide ions into the organic phase for reaction with 1-chlorooctane. This sequence of steps is represented by equation 1, where Q^+ represents a quaternary salt containing sufficiently long alkyl groups or other organic structure as to make QCN predominantly soluble in the organic phase.



Other classic examples illustrating the use of quaternary salts as phase transfer catalysts were published by Makosza(2), and by Brandstrom(3). Subsequent development of crown ethers(4-7) and cryptands(7-8) as phase transfer catalysts gave PTC an entirely new dimension since now the inorganic reagent, as sodium cyanide in the above equation, need no longer be dissolved in water but can be used

as a dry solid. This development gave rise to liquid-solid PTC as a partner to liquid-liquid PTC.

Since 1971 phase transfer catalysis has emerged as a broadly useful tool(9-16), not only in organic chemistry, but also in inorganic chemistry(17), for new analytical applications(18), in electrochemistry(27a), photochemistry(27b), and especially in polymer chemistry.(21,27-31) The substantial number of publications, patents, reviews, and books (200 to 400 per year since 1980) concerned with PTC in both scientific and commercial applications attests to the high level of interest that this technique has generated.

Commercial usage of PTC techniques has increased markedly during the last five years not only in the number of applications (currently estimated to be fifty to seventy-five different uses(22)), but also in the volume of catalysts consumed (estimated to be about one million pounds per year(22)) and in the volume of products manufactured (estimated to be fifty to one hundred million pounds per year(22)) in the United States alone. Many indicators point to additional extensive commercial applications of the PTC technique all around the world, and these indicators suggest that future chemical manufacturing processes will more and more incorporate PTC because of its advantages of simplicity, reduced consumption of organic solvents and raw materials, mild reaction conditions, specificity of reactions catalyzed, and enhanced control over both reaction conditions, reaction rates, and yields. For some currently produced polymers PTC provides the only reasonable and practical commercial method of manufacture(22).

Enormous progress has been made in recent years in all aspects of phase transfer catalysis, and the symposium on which this volume is based(23) was organized to provide a sample of some of the advances in three areas: (1) theory and application of the method; (2) design of specific catalysts for increased efficiency and selectivity; and (3) use of PTC in polymer chemistry. The excellent chemists and their co-workers who have most generously contributed to this publication present a broad range of work and viewpoints which stimulate and delight those of us who have a strong interest in PTC.

Applications

The general concept of phase transfer catalysis applies to the transfer of any species from one phase to another (not just anions as illustrated above), provided a suitable catalyst can be chosen, and provided suitable phase compositions and reaction conditions are used. Most published work using PTC deals only with the transfer of anionic reactants using either quaternary ammonium or phosphonium salts, or with crown ethers in liquid-liquid or liquid-solid systems. Examples of the transfer and reaction of other chemical species have been reported(24) but clearly some of the most innovative work in this area has been done by Alper and his co-workers, as described in Chapter 2. He illustrates that gas-liquid-liquid transfers with complex catalyst systems provide methods for catalytic hydrogenations with gaseous hydrogen,

catalytic oxidations with gaseous oxygen, and carbonylation of alkyl halides, olefins and acetylenes with carbon monoxide.

A portion of substantial theoretical and historical importance in PTC has centered around the question of 'what is the nature of the species transferred, and where in the reaction sequence do the slow steps take place.' These questions prompted much debate during the early years of PTC when development and understanding of the reaction sequence and mechanism of PTC was emerging. It generally came to be recognized that small changes in the complex sequence of steps of even the simplest phase transfer catalyzed system can result in differing kinetics, differences in optimal catalyst structure, and different optimal reaction conditions, even for similar reactions. Of particular interest in this volume is Chapter 3 by Liotta and co-workers, who have found that even the amount of water present in liquid-solid PTC may substantially affect the site where final reaction occurs. These observations have led Liotta to postulate a new phase in which reaction may occur. Montanari and co-workers, who have been prolific contributors in PTC, have also provided (Chapter 6) significant insight into the effect of water on PTC reactions.

In a series of highly useful applications phase transfer catalysis has given the chemist the ability to conduct reactions between organic compounds and strong inorganic oxidants such as permanganate, dichromate, hypochlorite, and hydrogen peroxide(25). Use of these oxidants previously has been limited and experimentally inconvenient because of the narrow range of stable organic solvents which one could use to bring the oxidants and substrate into contact. The power of PTC for permanganate oxidations and the use of PTC to study the mechanism of these oxidations is demonstrated by Lee in Chapter 8.

Catalyst Improvements

Although quaternary ammonium salts, phosphonium salts, crown ethers, and cryptands are generally excellent catalysts for most PTC applications, there are many potential PTC applications where these agents have deficiencies. For example, ordinary tetraalkyl quaternary salts decompose at high temperatures (greater than 120-149°C), or at low temperatures under highly alkaline conditions or in the presence of highly nucleophilic anions such as phenoxide. Crown ethers and cryptands are stable under these conditions but are much more expensive (100 to 1000 fold cost) than quaternary salts, and for practical commercial use they must be completely recovered for re-use. Open-chain polyethers, mainly polyethylene glycols, catalyze some kinds of two-phase reactions, are stable and are quite low in cost, but their limited utility substantially restricts their application to a narrow range of reactions.

The possibility of solving the catalyst recovery problem by attaching active catalyst centers to insoluble polymeric substrates was recognized early(26), as was the possible use of chiral PTC catalysts to introduce chirality in products(1). Much work in both these areas has been partially successful(27). However, the results have not been completely satisfactory in that resin bound catalysts have shown much lower catalytic activity than soluble catalysts and they frequently lose their activity with repeated use. Chiral

catalysts generally give products low chiral selectivity, with enantiomeric excesses usually less than fifty percent. A further problem in PTC has been that no really superior catalysts have been introduced for use with divalent or trivalent anions, or with the difficult transferable hydroxide anion.

In face of the above discouraging results, recent innovative catalyst work has led to highly effective solutions for some otherwise very difficult and expensive problems. For example, Dolling and co-workers (Chapter 7) have shown that by careful choice of PTC catalyst and use of optimal reaction conditions one can obtain high chiral selectivity (greater than 90% enantiomeric excess) and have applied this chemistry to a commercial process for production of the diuretic drug candidate Indacrinone.

Brunelle, in Chapter 5, has provided a solution to the problem of quaternary ammonium catalysts being unstable at elevated temperatures in the presence of highly nucleophilic anions. He found that catalysts based on p-dialkylaminopyridinium salts are approximately one hundred times more stable than simple tetraalkylammonium salts and are useful even up to temperatures of 180°C. Especially valuable is the fact that under these conditions a variety of nucleophilic displacement reactions on aryl halides occurs, making possible the economical commercial synthesis of otherwise difficultly available poly aryl ethers and sulfides.

Brunelle, Chapter 5, also demonstrated that bis-quaternary salts with appropriate spacing between the quaternary nitrogens are dramatically better than mono-quaternary salts as catalysts for transfer of divalent anions, such as the di-anion of bisphenol A. Thus the ion pair formed from the di-anion and a bis-quat appears to be more easily formed and transferred than the species formed from the di-anion and two mono-quaternary cations.

Idoux and co-workers, Chapter 14, have also prepared high-activity multi-site phase transfer catalysts bound to insoluble resins. Although not yet experimentally demonstrated, this type of catalyst may also be useful for transferring multivalent anions such as carbonate, sulfite, sulfide, sulfate or phosphate, since the compounds used have two phosphonium cationic centers in close proximity to each other. However, these workers present work which shows that a multi-site catalyst can exhibit greater selectivity in displacement on organic reagents containing two displaceable groups.

Montanari and co-workers, Chapter 6, have developed special cyclic ethers which, when properly bound to cross-linked resins, exhibit a high degree of catalytic effectiveness, generally comparable to that of soluble quaternary ammonium and phosphonium salts. This great increase in activity for resin-bound catalysts represents a breakthrough development, and although these catalysts would be highly expensive, their ability to maintain high activity after repeated use and for extended times in continuous reactors would mitigate their initial cost and avoid the problem of catalyst removal from products.

Taking an entirely different tack on supported phase transfer catalysts, Sawicki, Chapter 12, initially used polyethers chemically bound to silica. But, he also demonstrated that solid silica or alumina alone may function as liquid-solid phase transfer catalysts, probably through mechanisms entirely different than the classical PTC sequence.

Exploration by Gokel and co-workers, Chapter 4, of a diverse set of polyether structures and their ability to bind with cations has provided compounds which have many potential applications for use in PTC.

Phase Transfer Catalysis in Polymer Chemistry

Aside from the use of polymers as supports for phase transfer catalyst centers, much excellent work has been reported on the use of PTC in polymer chemistry for polymerization methods(28), for the chemical modification of already formed polymers(29), for the modification of polymer surfaces without change of the bulk polymer(30), and for the preparation and purification of monomers(31).

Rasmussen and co-workers, Chapter 10, have shown that many free-radical polymerizations can be conducted in two-phase systems using potassium persulfate and either crown ethers or quaternary ammonium salts as initiators. When transferred to the organic phase persulfate performs far more efficiently as an initiator than conventional materials such as azobisisobutyronitrile or benzoyl peroxide. In vinyl polymerizations using PTC-persulfate initiation one can exercise precise control over reaction rates, even at low temperatures. Mechanistic aspects of these complicated systems have been worked out for this highly useful and economical method of initiation of free-radical polymerizations.

Production of polymers through poly-substitution or poly-condensation reactions would be expected to be a natural extension of simple PTC chemistry. To a large extent this is true, but as Percec has shown, Chapter 9, the ability to use two-phase systems for these reactions has enormously extended the chemist's ability to control the structure of the polymers produced. Kellman and co-workers (Chapter 11) have also extensively studied poly-substitution displacements on perfluorobenzene substrate to produce unique polymers.

The simple reaction of polymers with inorganic reagents has historically been a difficult chemical problem and generally such transformations have been far too expensive to practice on a commercial scale. The use of PTC makes this kind of problem vastly simpler, as innovatively demonstrated in an adaptation by Nicholas (Chapter 13), to find low-cost chemistry for converting scrap rubber into a material more nearly resembling the structure of new rubber.

PTC Development

About ten years ago a knowledgeable organic chemist offered the opinion that "almost all the things that can be done via phase transfer catalysis has already been done." He was wrong, of course, as one can now look back and see that the great bulk of PTC chemistry now known came after his comment was made. While it may be true that many of the obvious and direct applications of PTC, especially for anion transfer, have been identified, it seems most likely to this author that a vast amount of new applications and more complex catalyst systems based on PTC await discovery and exploitation.

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Chapter 2

Phase-Transfer Reactions Catalyzed by Metal Complexes

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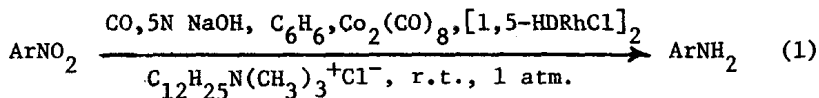
Recent studies indicate that phase transfer catalysis is useful for effecting a variety of interesting metal catalyzed reactions. Developments in the author's laboratory, in three areas, will be considered: reduction, oxidation, and carbonylation reactions.

Reduction

Nitro Compounds

Aliphatic and aromatic amines can be obtained in excellent yields by the ruthenium carbonyl catalyzed reduction of nitro compounds using carbon monoxide, aqueous base, benzene or toluene as the organic phase, and benzyltriethylammonium chloride as the phase transfer agent. This reaction occurs at room temperature and 1 atmosphere pressure(1). The ruthenium(II) complex, $\text{RuCl}_2(\text{PPh}_3)_3$, can also be used as the catalyst for this transformation, although product yields are highest when synthesis gas is used instead of carbon monoxide(2).

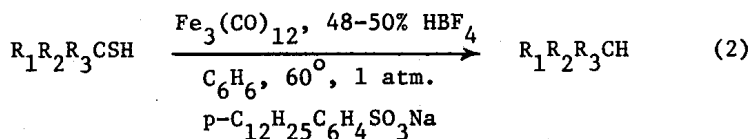
Although neither cobalt carbonyl nor chloro(1,5-hexadiene)rhodium(I) dimer (or other rhodium(I) complexes) were effective for the reduction of nitro compounds, the use of both catalysts and phase transfer conditions resulted in the formation of amines in good yields(3). Subsequent studies demonstrated



that this apparent bimetallic phase transfer process is a consequence of a novel coincidence effect. That is, the nitro reduction is catalyzed by the rhodium(I) complex alone under biphasic conditions but the presence of a phase transfer agent results in inhibition of the reaction. Reactivation of the system is achieved by addition of the second metal catalyst, cobalt carbonyl(4).

Mercaptans

Activated mercaptans undergo desulfurization to hydrocarbons using cobalt carbonyl or triiron dodecacarbonyl as the metal complex, and basic phase transfer conditions(5). Acidic phase transfer catalysis has been little investigated, the first example in organometallic chemistry being reported in 1983 (reduction of diarylethylenes)(6). When acidic phase transfer conditions (sodium 4-dodecylbenzenesulfonate as the phase transfer catalyst) were used for the desulfurization of mercaptans [$\text{Fe}_3(\text{CO})_{12}$ as the metal complex],



hydrocarbons were obtained in modest yields together with sulfides and disulfides. Good to excellent yields of hydrocarbons were realized when the reaction was effected in the absence of the phase transfer agent (i.e., as a biphasic process). Some results are listed in Table I(7).

Table I. Biphasic and Acidic Phase Transfer Catalyzed Reactions of
of Mercaptans with $\text{Fe}_3(\text{CO})_{12}$ and 48-50% HBF_4

Mercaptan	Products	Yield(%)	
		Phase Transfer	Biphasic
$\text{p-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{SH}$	$\text{p-CH}_3\text{OC}_6\text{H}_4\text{CH}_3$	10	72
$\text{p-ClC}_6\text{H}_4\text{CH}_2\text{SH}$	$\text{p-ClC}_6\text{H}_4\text{CH}_3$	6	44
	$(\text{p-ClC}_6\text{H}_4\text{CH}_2)_2\text{S}$	11	19
	$(\text{p-ClC}_6\text{H}_4\text{CH}_2\text{S})_2$	40	6
$2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{CH}_2\text{SH}$	$2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{CH}_3$	73	74
	$(2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{CH}_2)_2$	5	10
	$(2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{CH}_2)_2\text{S}$	2	2
	$2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{CHO}$	3	3
$(\text{p-CH}_3\text{C}_6\text{H}_4)_2\text{CHSH}$	$(\text{p-CH}_3\text{C}_6\text{H}_4)_2\text{CH}_2$	- ^a	94
Ph_2CHSH	Ph_2CH_2	- ^a	84
	$(\text{Ph}_2\text{CH})_2\text{S}$		8

^a Not done