



ROLE OF PHASE TRANSFER CATALYST IN SYNTHETIC ORGANIC CHEMISTRY

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Abstract

Phase-transfer catalysis (PTC), a common technique for generating organic compounds, has been around for more than three decades. Reactions involving reagents in two immiscible phases are made possible by phase transfer catalysis (PTC), which uses catalytic doses of phase transfer agents to facilitate species inter-phase transfer. PTC is commonly used in the liquid-liquid and solid-liquid creation of a variety of chemical substances. Understanding numerous researches have focused on the breadth and operation of PTC. Incorporating a Phase transfer catalyst is more efficient when combined with other rate-increasing methods including ovens, electro-organic synthesis, and the process of photochemistry a topic of increasing investigation. Organic intermediates and fine chemicals can be created by using these applications; molecules appear to have almost no boundaries. PTC can be employed in several organic processes, such as Michael addition, aldol condensation, and nucleophilic substitution. Since it can aid in the solubilization of ionic species in non-polar solvents, it is especially helpful in processes involving ionic species. PTC is an effective instrument for transferring reactants between phases quickly and effectively, which promotes the reaction at the interface between them. In many cases, it is used as an intermediate in the synthesis of many different chemical molecules and has developed into a significant technology in both academia and industry.

Keywords: Phase-transfer catalysis, Ammonium salt, Polar and non-polar phase, Phosphonium salts, Surfactant, Ionic-liquid, Zeolites.

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Introduction

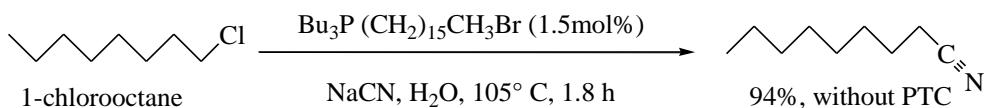
In organic synthesis, Phase-transfer catalysis facilitates the transfer of reactants between two phases by involving a type of catalysis called phase-transfer catalysis, often a polar and a nonpolar phase.¹ In this catalytic process, a catalyst facilitates the acceleration of the reaction at the boundary between the two phases by shuttling intermittently between them.² The catalyst for the most popular kind of PTC is a quaternary ammonium salt. This catalyst has the ability to shift from the aqueous phase to the organic phase, promoting the acceleration of the reaction as the transition occurs.³ It is normally soluble in both. By interacting with the reactants at the boundary between the two phases, the catalyst lowers the reaction's activation energy and speeds up the process. Some organic reactions can make use of PTC, including Michael addition, aldol condensation, and nucleophilic substitution. Since it can aid in the solubilization of ionic species in non-polar solvents, it is especially helpful in processes involving ionic species.^{4,5} PTC is an effective instrument for transferring reactants between phases quickly and effectively, which promotes the reaction at the interface between them.⁶ In addition to its use as a synthetic chemical, it is widely used in the manufacture of many different chemical molecules and has developed into a significant technology in both academia and industry.⁷ Phase transfer catalysis (PTC), which was first used around 1965, is now a well-recognized method in synthetic organic chemistry. The majority of research has focused on PTC-based synthetic techniques, although one of the main issues with employing PTC in soluble form is that it can separate from the reaction mixture.^{8,9} In PTC-based synthetic approaches, an additional step for isolating the catalyst and purifying the product is necessary. This ensures both effective catalyst utilization and adherence to product purity standards. To describe the crucial function of tetra-alkyl ammonium and the interaction between two chemicals ingested in separate immiscible phases that may be caused by the introduction of phosphonium salts ($Q^+ X^-$) is an aqueous phase in PTC.¹⁰ The initial application of phase-transfer catalysis, abbreviated as PTC, was introduced by Starks in 1971. The main concept of PTC, distinct from conventional organic synthesis methods, involves reactions occurring within heterogeneous two-phase systems characterized by minimal mutual solubility.¹¹ A catalyst that provides lipophilic cations is present in these systems. The organic phase is continuously exposed to the lipophilic

ion pairs produced by the reacting anionic species.¹² The PTC technique may be applied to the following two major groups of responses. Easily accessible anions in the form of sodium or potassium salts, like NaCN, KN₃, KMnO₄, CH₃COONa, etc., enable the catalyst's hydrophobic cations to efficiently transport these anions into the organic phase as hydrophobic ion pairs. These ion pairs are created through continuous ion exchange.^{8,13} When a base is present within the inorganic phase, the anions involved in the reaction need to be generated in the organic phase from suitable precursors, such as acids containing -CH, -OH, -NH, and -SH groups. In this context, the catalyst plays a crucial role in generating and transporting reactive anions into the organic phase. The mechanism of PTC operates distinctively: the organic phase consists of either pure organic reactants or those dissolved in organic solvents, while the inorganic phase exists as solid or aqueous forms of inorganic salts or bases.¹⁴ The catalyst, dissolved within the organic phase, continuously introduces the reactive species into this phase. As a result, reactions catalyzed by phase transfer (PT) not only occur in heterogeneous systems but also exhibit significant advancement within homogeneous solutions.^{15,16} Systems with two mutually immiscible phases are used to carry out PT-catalyzed reactions. There are two different kinds of such systems: liquid-liquid and liquid-solid.¹⁷ In liquid-liquid arrangements, the organic reactants create an organic phase that interfaces with an incompressible salt solution, whether the reactants are employed undiluted or within an organic solvent. This solution contains the necessary anions or utilizes a potent aqueous sodium hydroxide or potassium hydroxide solution as a base.¹⁸ The catalyst introduces the necessary precursors' deprotonated organic anions, or inorganic anions from the aqueous solution, into the organic phase.^{19,20} Within liquid-solid setups, the organic phase is immobilized within solid, granular inorganic salts or bases (like K₂CO₃, NaOH, etc.). The catalyst facilitates the transfer of inorganic anions from the surfaces of these salts or the organic anions generated by the bases' surfaces into the organic phase.²¹ The fundamental feature of reactions catalyzed by phase transfer is that the presence of reactive anions in the organic phase must not exceed the concentration of the catalyst, usually around 1% molar of the starting materials. This stipulation allows many phase transfer catalyzed reactions to be conducted without necessitating the use of an organic solvent, as long as the initial organic components are in liquid form.²⁰ The participating entities in the

reaction, as an alternative to the commonly used Li^+ , Na^+ , or K^+ ions, are the reactive anions within the organic phase, manifested as TAA salts. In these salts, there exists minimal partial covalent bonding and coordination between the anions and cations.¹⁹

Numerous desired reactions cannot occur because the reactants are not close to one another. Adding a solvent that has properties similar to both water and organic matter has traditionally been used to overcome the crucial challenge of combining electrophilic organic reagents that are hydrophobic in nature and nucleophilic reagents that are hydrophilic in nature.²² High transfer rates

are possible when the contact area is increased.²³ A well-known technique for accelerating reactions between chemicals with opposing solubility preferences is PTC. In these systems, the suitable solvent is dissolved within each individual reactant. The introduction of a PTC facilitates the transfer of one reactant into the other phase, particularly when the two solvents are inherently immiscible with each other.²⁴ The presence of hexadecyl-tributylphosphonium bromide as a PTC can substantially amplify the displacement of 1-chlorooctane from an aqueous NaCN solution (**Scheme 1**).²⁵



Scheme 1: Reaction of 1-chlorooctane with aqueous NaCN

Making the organic cyanide anion soluble and suitably nucleophilic by the formation of quaternary phosphonium cyanide, is the essential component of this enormous reactivity boost. While Starks, Makosza, and Brandstrom lay the groundwork for PTC in the middle to late 1960s, the catalytic efficacy of quaternary onium salts has been previously demonstrated. Subsequently, Phase-transfer catalysis has gained increasing favor within the chemical field due to its uncomplicated experimental protocols, mild reaction conditions, cost-effectiveness, environmentally benign nature for conducting extensive synthesis, and facilitation of access to chemicals and solvents.²⁶ Currently, the phase-transfer catalyst has emerged as a prominent and valued synthetic tool, finding widespread utility not only across various domains of organic chemistry but also within numerous industrial applications. The mechanistic features of PTC remain mysterious despite its progress in organic synthesis, primarily due to the complexities associated with investigating biphasic systems and the multifaceted elements requiring analysis, the phase transfer reaction involving 1-chlorooctane and aqueous NaCN in the presence of hexadecyl-tributylphosphonium bromide presents significant challenges.²⁷

1. Various categories of phase-transfer catalysts

A phase-transfer catalyst aids in the movement of reactants between immiscible phases, usually transitioning between aqueous and organic phases. Two-phase systems are crucial for many

organic reactions because they allow reactions to take place in two phases. Regarding phase-transfer catalysts, various categories exist, each possessing distinct characteristics and practical uses.¹³ Below are outlined some prevalent classifications of phase transfer catalysts:

- 1.1. Surfactant
- 1.2. Ionic liquid
- 1.3. Crown ethers
- 1.4. Zeolites

2.1. Surfactant

A phase transfer catalyst (PTC) is a substance that makes it easier to move reactants or ions between two immiscible phases. This is usually the case when an organic phase and one that is watery are involved. As a result of the reactants' immiscibility, makes it possible to perform reactions that are otherwise unfeasible or challenging.²⁸ On the other hand, surfactants are chemicals that lessen the surface tension between two immiscible phases, usually a liquid and a gas or a liquid and a solid. They interact with both polar and nonpolar substances because their molecular structure includes both hydrophilic and hydrophobic areas.²⁹ Some substances can operate as both phase transfer catalysts and surfactants, despite their distinct functions. Phase transfer catalyst surfactants or surfactant catalysts are the names given to these multifunctional molecules. In addition to facilitating the passage of ions or molecules between these phases, they can operate as a surfactant to solubilize reactants in various phases.³⁰ Surfactants that act given that phase transfer catalysts are frequently used in a wide

range of chemical processes, including nucleophilic replacements, oxidations, reductions, and polymerizations.³¹ By enhancing the contact between reactants in various stages, they improve

the efficiency and yield of these processes. Some of the Classification of surfactant in listed below in **Table 1**.

Table 1: Classification of surfactant

| Examples | Structures | Class | Reference |
|-------------------------------------|--|----------|---------------|
| Sodium stearate | CH ₃ (CH ₂) ₁₆ COO-Na ⁺ | Anionic | ³² |
| Sodium dodecyl sulfate | CH ₃ (CH ₂) ₁₁ SO ₄ -Na ⁺ | Anionic | ³² |
| Trimethyl dodecyl ammonium chloride | C ₁₂ H ₂₅ N ⁺ (CH ₃) ₃ Cl- | Cationic | ³³ |
| Cetyltrimethyl ammonium bromide | CH ₃ (CH ₂) ₁₁ NH ₃ ⁺ Cl- | Cationic | ³³ |

Surfactants act as solubilizers and facilitate mass transfer between incommensurable phases, making them crucial to phase transfer catalysis (PTC). Based on their method of action, interactions with the reactants, and interactions

with the phases, surfactants in PTC may be divided into different categories.³⁴ the following are the two main groups of surfactants used in PTC, elaborated in **Table 2** given below.

Table 2: Comparison of anionic and cationic surfactants

| Property | Anionic Surfactants | Cationic Surfactants | Reference |
|------------------------|---|---|---------------|
| Charge | Negative charge on hydrophilic head | Positive charge on hydrophilic head. | ³⁵ |
| Mechanism | Facilitates transfer of anions across faces | Facilitate transfer of cation across face. | ³⁶ |
| Selectivity | Suitable for reactions involving anionic species. | Suitable for reactions involving cationic species. | ³⁷ |
| Reactivity | Can be less reactive with certain organic substrates. | May exhibit higher reactivity with certain substrates. | ³⁸ |
| Solubility | Generally soluble in polar solvents. | Typically, soluble in organic solvents. | ³⁹ |
| Solvent compatibility | Often used in aqueous-organic biphasic systems. | Often used in organic-organic biphasic system. | ⁴⁰ |
| Ion pair formation | Forms ion pairs with oppositely charged ions. | Forms iron pairs with oppositely charged ions. | ⁴¹ |
| Reaction conditions | Typically used under milder condition. | Can be used under a range of conditions | ³⁸ |
| Steric effects | Bulkier and ionic headgroups may affect selectivity. | Bulkiness of Cationic headgroups can influence selectivity. | ³⁶ |
| Side reactions | May lead to unwanted side reactions. | Can sometimes trigger side reactions. | ³⁹ |
| Catalyst recovery | Can be challenging due to potential precipitation. | Often easier to recover due to any interactions. | ³² |
| Environmental concerns | Some anionic surfactants have potential environmental impact. | Cationic surfactants can also raise environmental concerns. | ³⁵ |

2.1.1. Mode of action of surfactants in PTC

The mode of action of surfactants as phase transfer catalysts is of utmost importance. Surfactants possess a distinctive amphiphilic nature, meaning they have both hydrophilic (water-attracting) and hydrophobic (water-repelling) parts within their molecular structure. This unique arrangement allows surfactants to form micelles or bilayer structures at the interface between two immiscible phases, such as water and organic solvents.⁴² these assemblies create an environment where reactants from both phases can be brought into proximity, facilitating their interaction, and promoting reaction efficiency.⁴³ The mode of action of surfactants in phase transfer catalysis involves several key aspects. Firstly, surfactants reduce the interfacial tension between the immiscible phases, enabling better

between two immiscible phases, such as water and organic solvents.⁴² these assemblies create an environment where reactants from both phases can be brought into proximity, facilitating their interaction, and promoting reaction efficiency.⁴³ The mode of action of surfactants in phase transfer catalysis involves several key aspects. Firstly, surfactants reduce the interfacial tension between the immiscible phases, enabling better

mixing and promoting the transport of reactants across the phase boundary.⁴⁴ Secondly, surfactant molecules can solubilize hydrophobic reactants or products into their hydrophobic micellar cores, effectively "shuttling" them from one phase to another.⁴⁵ This process enhances the accessibility of reactants to the catalyst and promotes efficient reaction kinetics. Furthermore, surfactants can also stabilize reactive species or intermediates formed during the reaction, preventing their undesired decomposition or side reactions. This stabilization effect is particularly crucial in reactions involving highly reactive or unstable species. The presence of a surfactant layer around these species can shield them from the surrounding environment, providing a controlled microenvironment conducive to the desired reaction pathway.⁴⁶

2.1.1.1. Solubilization

Surfactants can solubilize reactants or ions in one phase, particularly in their micellar aggregates, improving their accessibility for reaction and transfer to the other phase.⁴⁷ The mode of action of surfactants in phase transfer catalysis revolves around their exceptional ability to solubilize hydrophobic compounds within aqueous media, or vice versa. Surfactants are characterized by their amphiphilic nature, embodying both hydrophilic and hydrophobic components in their molecular structure.⁴⁶ This unique feature empowers them to form organized assemblies, such as micelles or bilayers, at the interface between disparate phases. These structures create a dynamic microenvironment where solubilization becomes a key mechanism for enhancing reaction rates and catalytic efficiency.⁴⁸ Solubilization entails the entrapment or encapsulation of hydrophobic molecules within the hydrophobic regions of surfactant assemblies. In the context of phase transfer catalysis, this process involves the migration of hydrophobic reactants from their native phase to the solvent phase where the catalytic reaction takes place.⁴⁹ Surfactant micelles, for instance, form spherical aggregates in aqueous solutions, with their hydrophilic outer shell interacting with the aqueous phase and their hydrophobic core solubilizing hydrophobic molecules. This molecular arrangement effectively creates a "shuttle" for the hydrophobic species, allowing them to traverse the interphase boundary and access the catalytic environment.⁴⁸

2.1.1.2. Ion Pair Formation

Surfactants, particularly cationic surfactants, can pair up with charged reactants or ions to produce ions which result in species that are more soluble or more easily transported between phases.⁵⁰ Ion pair formation is a process rooted in the unique molecular structure of surfactants, which possess both hydrophilic and hydrophobic segments. This amphiphilic character allows them to spontaneously assemble at the interface between immiscible phases, forming organized structures such as micelles or bilayers.⁵⁰ These structures create an environment where polar and nonpolar species can interact in a controlled manner, giving rise to ion pair formation and its consequential impact on phase transfer catalysis. In the context of PTC, ion pair formation entails the association of charged or polar species with oppositely charged ions present on the surfactant molecules. This interaction can occur within the aqueous phase, at the interface between the aqueous and organic phases, or even within the organic phase. The surfactant's hydrophilic head group interacts with the polar or charged species, while its hydrophobic tail aligns with the nonpolar medium, effectively creating a bridge between the two phases. This bridge facilitates the transport of ions or polar compounds, which would otherwise have limited solubility in the respective phases, across the phase boundary.⁵¹

2.1.1.3. Micro-emulsion Formation

Surfactants can help create micro-emulsions, which are mixes of two immiscible liquids that are thermodynamically stable.⁵² With the proximity of reactants from various phases created by microemulsions, contact and reaction rates are increased. Micro-emulsions, intricate and stabilized colloidal systems, stand as a captivating frontier in the realm of phase transfer catalysis (PTC). These structures, formed through the synergistic action of surfactants and co-surfactants, hold the potential to revolutionize catalytic processes by providing a tailored environment for reactions between immiscible phases, typically water and oil.⁵³ The mode of action of surfactants in micro-emulsion formation is a manifestation of their amphiphilic nature, wherein hydrophilic and hydrophobic segments coexist within a single molecular structure. This molecular design permits surfactants to self-assemble at the interface between water and oil, creating organized domains known as micro-emulsions. These domains encapsulate water droplets within an oil matrix or vice versa, forming nanoscale structures with unique properties that are distinct from their bulk counterparts.⁵⁴

2.1.1.4. Interface stabilization

Surfactants reduce interfacial tension and encourage the movement of reactants or ions across the phase boundary, stabilizing the interface between immiscible phases. Surfactants help move reactants through immiscible phases in PTC reactions by combining their solubilization and interfacial characteristics. They enhance mass transfer, boost reaction speeds, and allow reactions that phase separation would otherwise prevent.⁵⁵ Interface stabilization as a mode of action leverages the amphiphilic nature of surfactants, which embodies both hydrophilic and hydrophobic components within a single molecule. This unique molecular design equips surfactants with the capability to lower interfacial tension between immiscible phases, creating stable interfaces that serve as platforms for catalytic reactions. By reducing the energetic barrier between phases, surfactants facilitate the transfer of species across the phase boundary, initiating and accelerating chemical processes.⁵⁶ The significance of interface stabilization as a mode of action in phase transfer catalysis lies in its capacity to bridge the gap

between seemingly incompatible phases, creating a harmonious environment for reaction. This phenomenon exemplifies the elegant manipulation of interfacial science to facilitate chemical transformations that would be challenging to achieve using traditional methods. The symbiotic interaction between hydrophilic and hydrophobic elements within surfactant molecules showcases the potential for precise control over reaction environments and pathways.⁵⁷

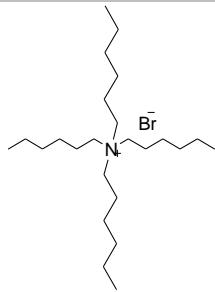
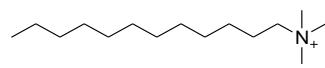
2.1.2. Examples of surfactant in Phase transfer catalyst

In this exploration of surfactants in phase transfer catalysis, we will delve into specific examples of how surfactants have been utilized to accelerate and optimize various chemical transformations. By examining these examples, we can gain insights into the mechanisms underlying these reactions and appreciate the ingenuity behind using surfactants as efficient phase transfer catalysts (**Table 3**).⁴¹

Table 3: List of various surfactant-PTC with their mode of action

| Surfactant | Structure | Mode of action | Reference |
|--|-----------|---------------------------------------|-----------|
| Tetra-n-butylammonium Bromide (TBAB) | | Solubilization and ion pair formation | 35 |
| Cetyltrimethylammonium Bromide (CTAB) | | Micelle formation and solubilization | 41 |
| Aliquat 336 (Tricaprylmethylammonium Chloride) | | Ion pair formation and solubilization | 38 |
| Crown Ethers | | Complexation and ion pair formation | 51 |
| Sodium Dodecyl Sulfate (SDS) | | Micelle formation and solubilization | 53 |

| | | | |
|---|--|--|----|
| Tetraoctylamm onium Bromide (TOAB) | | Micelle formation and solubilization | 57 |
| Benzylidimethyl hexadecylamm onium Chloride (BDHAC) | | Micelle formation and ion pair formation | 41 |
| Phosphonium Salts | | Ion pair formation and solubilization | 48 |
| Sodium Oleate | | Micelle formation and solubilization | 43 |
| Tetrabutylamm onium Hydroxide (TBAH) | | Phase transfer and deprotonation | 36 |
| Tetrabutylphos phonium Bromide (TBPB) | | Ion pair formation and solubilization | 57 |
| Dodecylamine | | Micelle formation and solubilization | 51 |
| Octadecylamin e | | Micelle formation and solubilization | 53 |
| Trioctylphosphhi ne Oxide | | Solubilization and complexation | 41 |
| Benzyltriethyl ammonium Chloride | | Solubilization and ion pair formation | 35 |

| | | | |
|------------------------------------|---|--------------------------------------|----|
| Tetrahexylamm onium Bromide |  | Micelle formation and solubilization | 43 |
| Dodecyltrimeth yl ammonium Bromide |  | Micelle formation and solubilization | 41 |

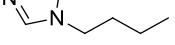
2.2. Ionic liquid-PTC

Ionic liquids can be used with phase transfer catalysts (PTCs) to speed up chemical processes. Salts are referred to as ionic liquids if they are liquid at room temperature or lower. They are desirable solvents for a variety of applications because of their distinctive qualities, which include low volatility, excellent thermal stability, and variable solvation characteristics.⁵⁸ PTCs can improve the transfer of reactants or ions between various phases, for as between two immiscible organic phases or an aqueous phase and an organic phase, when used in conjunction with ionic liquids. The PTCs play the role of intermediaries, enabling the reactants or ions to cross the phase barrier and interact with one another, resulting in the desired chemical change. The exact reaction and the necessary qualities will determine which PTC and ionic liquid to use. PTCs including quaternary ammonium salts, phosphonium salts, and crown ethers are

frequently utilized in ionic liquid systems. These substances can aid in the transfer of charged species by forming complexes or coordinating with the reactants or ions and have a high affinity for ionic liquids.⁵⁹ In chemical synthesis, combining PTCs with ionic liquids has several benefits. Ionic liquids can offer a homogenous reaction environment, while PTCs make it easier for reactants to move across phases, increasing the pace and selectivity of reactions. The use of ionic liquids also makes it possible to better regulate the factors that might affect the result of reactions, such as temperature and solvent polarity. Ionic liquids are categorized and have different modes of action depending on their unique characteristics and behavior.⁶⁰ There is a list of popular ionic liquids, their chemical formulae, and their scientific names. Ionic liquid category and mechanism of action are mentioned below in **Table 4**.

Table 4: A list of the common ionic liquids, along with their chemical formulas and systematic names

| Name | Chemical formula | Reference |
|--|------------------|-----------|
| 1-Amyl-3-methylimidazolium tetra fluoroborate | | 61 |
| 1-butyl-3-ethylimidazolium tetra fluoroborate | | 62 |
| 1-butyl-3-ethylimidazolium hexafluorophosphate | | 63 |
| 1-butyl-3-ethylimidazolium chloride | | 64 |

| | | |
|---|---|-------|
| 1-butyl-3-methylimidazolium chloride |  <chem>CN(C)C1=CN=C1CCCC</chem> | 64,65 |
|---|---|-------|

Ionic liquids can interact with certain functional groups or via electrostatic interactions to create complexes or coordinate with reactants or ions.⁶⁶ Through the stabilization, activation, or selective identification of certain species, this mechanism of action can affect the course of a process. Ionic liquids can serve as intermediaries for the transport of reactants or ions between incommensurable phases. Due to their special characteristics, such as low volatility and high viscosity, they can offer a medium where both polar and nonpolar species can be solubilized, enabling mass transfer and reaction across phases.⁶⁷ Due to their charged composition and potent electrostatic interactions, ionic liquids can function as polar solvents. Through interactions between ions and dipoles or between dipoles, they can solvate and dissolve polar reactants or ions.⁶⁸ The transfer of charged species is made easier by this method of action, which also allows for increased responsiveness. Certain cation and anion combinations in ionic liquids include nonpolar regions or hydrophobic characteristics.⁶⁸ Through dispersion forces or hydrophobic interactions, they can solvate or dissolve nonpolar reactants or species in this situation. The intrinsic characteristics of some ionic liquids or the presence of ions or functional groups can cause some ionic liquids to display catalytic activity on their own. The reaction kinetics or selectivity may be affected by their involvement in the reaction process.⁶⁹

2.2.1. Modes of action in ionic liquid

Understanding the modes of action in ionic liquids is pivotal to unraveling their unique behavior and applications. This section offers a succinct exploration of the underlying mechanisms that drive the distinct properties and versatile utility of these compounds. Through an examination of these fundamental processes, we gain insights into how ionic liquids function and contribute to various fields, ranging from chemistry to industry and beyond. Ionic liquids have a variety of modes of action based on the chemical system they are used in as well as their

unique features.⁷⁰ The following are some typical ionic liquid actions described briefly:

2.2.1.1. Stabilization of reactive intermediates: Ionic liquids can stabilize reactive intermediates including radicals, carbenes, and transition metal complexes. While the nonpolar areas can offer a favorable environment for stabilizing nonpolar intermediates, the polar parts of the ionic liquid can stabilize charged or polar intermediates.⁷¹

2.2.1.2. Solvation: Ionic liquids' distinct polar and nonpolar regions allow them to solvate both polar and nonpolar molecules. Ion-dipole or dipole-dipole interactions allow them to engage with charged species or polar functional groups, whereas dispersion forces or hydrophobic interactions allow nonpolar areas to connect with polar species.⁷² Ionic liquid solvation can increase the stability and reactivity of solvated species.

2.2.1.3. Catalytic effects: Some ionic liquids have catalytic activity and can be directly involved in the reaction process. As Lewis or Bronsted acids or bases, they can coordinate with reactants or catalyze particular chemical reactions.⁵⁸ The reaction kinetics or selectivity can be influenced by the ionic liquid itself.

2.2.2. Selective extraction and separation: Ionic liquids' solvation capabilities allow them to selectively extract and separate components from a mixture. They can selectively extract desired molecules or separate mixtures based on their varied solubility by generating ionic liquids with specific interactions.⁷³

2.2.3. Some Examples of Ionic liquid-PTC

In this exploration of ionic liquid-based phase transfer catalysis, we will delve into specific examples where these dual-functioning entities have been employed to drive various chemical transformations (**Table 5**).

Table 5: List of various ionic liquid-PTC with their advantages

| Name | Chemical formula | Advantages | Reference |
|---|------------------|---|-----------|
| [BMIM][PF ₆] (1-butyl-3-methylimidazolium hexafluorophosphate) | | High thermal stability; versatile PTC in various reactions | 70 |
| [HMIM][Br] (1-hexyl-3-methylimidazolium bromide) | | Efficient PTC in high temperature reactions; good solubility for organic substrates | 72 |
| [OMIM][Cl] (1-octyl-3-methylimidazolium chloride) | | Suitable for biphasic systems | 73 |
| [EMIM][NTf ₂] (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) | | Good solubility for a wide range of substrates | 71 |
| [C4MIM][PF ₆] (1-butyl-1-methylpyrrolidinium hexafluorophosphate) | | Enhanced reactivity and selectivity; good stability in various reactions | 70 |
| [BMMIM][Br] (1-butyl-2,3-dimethylimidazolium bromide) | | Mild and eco-friendly conditions | 58 |
| [Pyridinium][TFSI] (1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide) | | High thermostability; catalytical activity in various reactions | 73 |
| [Choline][OAc] (Choline acetate) | | Biocompatible and enzyme stabilizing; suitable for biotransformation | 71 |
| [BEH PY][NTf ₂] (1-butyl-1-ethyl-4,5-dihydroimidazolium bis(trifluoromethylsulfonyl)imide) | | Catalytic activity in chiral reaction | 72 |

2.3. Crown ethers

Crown ethers stands out as a distinct subset among PTCs due to its unique characteristic of the complete transfer of the inorganic salt into the organic phase upon dissolution in an onium salt. Within reactions catalyzed by crown ethers, the described reaction patterns outlined earlier can often be substituted with metal cation complexes of crown ether, enabling a flexible approach.^{74,75} Metal ions and other polar molecules may be specifically bound to crown ethers, which are cyclic polyether. Due to their unique properties, crown ethers are frequently used as complexing agents and PTCs. Crown ethers are used as PTCs to facilitate the transfer of anionic or cationic species across immiscible phases, frequently between an aqueous phase and an organic phase.⁷⁶ The crown ether can transport the target ion over the phase boundary from one phase to the other,

where it can interact with other reagents.⁷⁷ Crown ethers as PTCs provide a variety of advantages. First, crown ethers can hasten reactions and enhance selectivity by increasing the effective concentration of the reactive species by preferring binding polar molecules like metal ions.⁷⁸ Second, crown ethers can increase the solubility of polar compounds in nonpolar solvents, facilitating their interaction with nonpolar catalysts. Crown ethers can also prevent unexpected side effects by isolating the reactive species from interfering species.⁷⁹ During the process of organic synthesis, crown ethers find extensive application as phase transfer catalysts (PTCs) to facilitate various reactions like nucleophilic substitution, epoxidation, and alkylation. **Table 6** presents a compilation of frequently employed characteristics of phase transfer catalysts.

Table 6: List of various crown ether-PTC with their advantages

| Phase Transfer Catalyst | Application and recovery of catalyst | Activity and Stability | Cost | Reference |
|-------------------------|--|--|-----------|-----------|
| Ammonium salts | Commonly used, relatively difficult to recover | Moderately active and stable up to 100°C decomposed by Hoffmann elimination reaction under basic condition | Low | 12,80 |
| Phosphonium Salts | Large application and difficult to recover | Thermally stable than ammonium salts | Expensive | 81 |

| | | | | |
|--------------|------------------------------------|--|-----------|----|
| Crown ethers | Hardly used, difficult to recover | Highly active and stable at temperature | Expensive | 82 |
| Cryptands | Often used, recovery is quite easy | Low activity, more stable than quaternary ammonium salts | Expensive | 83 |

2.3.1. Mode of action in crown ethers

Crown ethers are cyclic polyether's that may be divided into several groups according to the size of their rings and the number of oxygen atoms in their structure. Crown ethers with 4, 5, and 6 oxygen atoms in the ring are the most often utilized types.⁸⁴ Crown ethers main method of action is dependent on their capacity to specifically bind and combine with metal cations or other polar entities. The following are some categories and ways that crown ethers work:

2.3.1.1. Solvent extraction: Crown ethers are frequently used in methods for solvent extraction. They may efficiently separate the metal cations from the aqueous solution by selectively binding to them in an aqueous phase and transferring them to an organic phase.⁸⁵ Numerous applications, including the recovery and purification of metals, use this method of action.

2.3.1.2. Metal cation binding: Crown ethers bind to metal cations by forming coordination complexes with them through their oxygen atoms. The metal cation and the oxygen atoms in the crown ether coordinate to form a stable complex. This complexation increases the metal cation's solubility and reactivity in the solution, facilitating its transfer or extraction.⁸⁶

2.3.1.3. Chelation and stabilization: Crown ethers can stabilize metal cations by chelating them by coordinating with them through several oxygen atoms in the ring. The metal cation complex is stabilized by this chelation, which also

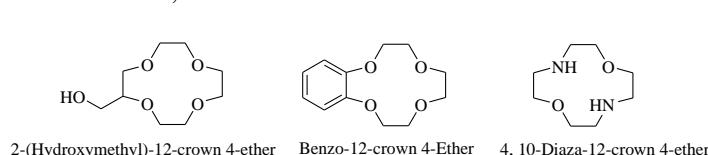
has an impact on its chemical behavior overall as well as its reactivity and selectivity.⁸⁷

2.3.1.4. Ion pair extraction: Crown ethers ability to form ion pairs with charged species makes it possible to extract and move ions across phases. The crown ether can help an ion move to another phase by complexing with it in one phase.⁸⁸ The transfer of charged species across immiscible phases is facilitated by the crown ether in phase transfer catalysis, which makes this mechanism of action particularly helpful.

2.3.1.5. Size-selective complexation: Crown ethers can preferentially combine with metal cations depending on the size of their ring. The capacity of the crown ether to accommodate a metal cation is contingent upon the size of its ring. For instance, a crown ether with a 6-oxygen atom ring (crown-6) may tolerate bigger metal cations like cesium or barium, but a crown ether with a 5-oxygen atom ring (crown-5) is frequently selective for alkali metal cations like sodium or potassium.⁸⁹ Specific metal cations can be separated from one another and extracted thanks to this size selectivity.

2.3.2. Examples of crown ethers

It is simple to locate many commercially available crown ethers, which are used as PTCs in a variety of processes.⁹⁰ Numerous studies have also been done on the use of crown ether as a PTC in polymer science. In **Scheme 5**, only a few of the crown ether are listed.



Scheme 5: Structure of Crown ethers.

2.4. Phase transfer catalyst in zeolites

Zeolites can also be used with phase transfer catalysts (PTCs) to form solid-supported PTC systems. Zeolites are well-defined microporous crystalline aluminosilicate minerals that have a large surface area as well as a network of channels and cages. Zeolites as solid supports for PTC have enhanced catalytic stability, ease of separation, and recyclability among other

benefits.⁹¹ the phase transfer catalyst is generally immobilized inside the zeolite structure or adsorbed onto the zeolite surface in solid-supported PTC systems utilizing zeolites. As a host matrix, the zeolite offers a regulated setting for the PTC reactions. Organic cations, such as quaternary ammonium salts, or metal complexes that function as phase transfer agents can serve as the PTC.⁹²

1.4.1. Modes of action of zeolites in PTC

3.4.1.1. Adsorption: Ionic interactions or coordination with active sites on the surface of the zeolite might cause the PTC to become adsorbed onto the zeolite. To help the transfer of reactants, the adsorbed PTC can coordinate with or solubilize charged or polar species.⁹³

3.4.1.2. Reaction Site Localization: By spatially separating reactants and products, the zeolite structure can increase selectivity and lessen undesirable side reactions.⁹⁴ The zeolite's PTC can localize the reaction at certain locations, promoting effective phase transfer and reaction.

3.4.1.3. Encapsulation: The PTC may occasionally be contained within zeolite tubes or cages. In the zeolite structure, the enclosed PTC functions as a mobile species, facilitating the effective transport of reactants across immiscible phases.⁹⁵

3.4.1.4. Size and shape selectivity: Zeolites have well-defined pore architectures, which contribute

to their size and shape selectivity.[43] This selectivity can affect the accessibility and reaction rates of reactants and products inside the pores of the zeolite, giving the PTC processes more control.

Zeolites may efficiently immobilize and contain the catalyst inside the zeolite structure, resulting in enhanced stability and recyclability when used as solid supports for PTC. Zeolites may also be used to provide controlled reaction conditions, size and shape selectivity, and better product separation.⁹⁷ These benefits make solid-supported PTC systems in zeolites intriguing for a range of catalytic applications, such as the generation of fine chemicals, medicines, and organic synthesis.

2.4.2. Examples of Zeolite in PTC

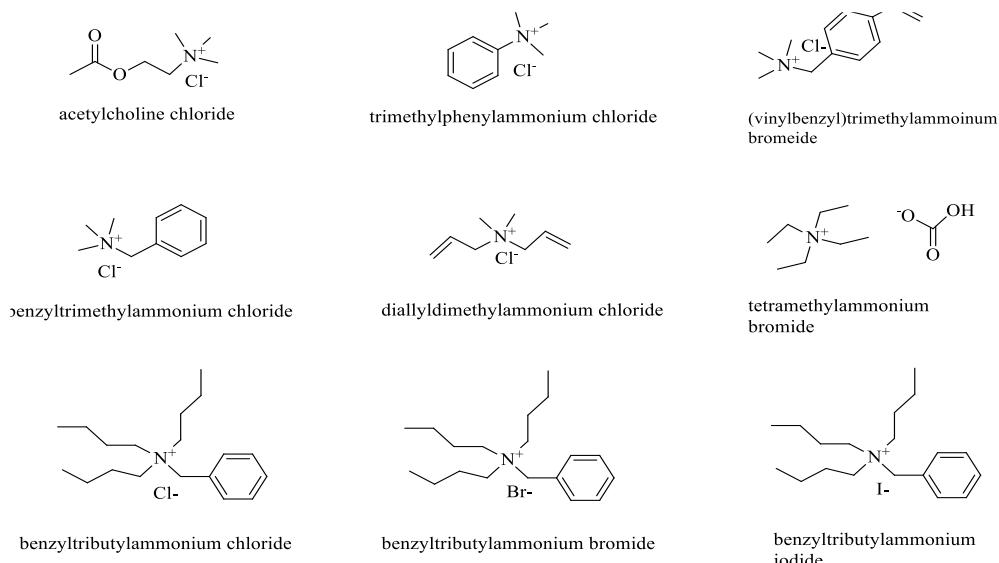
In this exploration of zeolite-based phase transfer catalysis (**Table 7**), we will delve into specific examples that showcase the application of zeolites as catalysts in a variety of chemical transformations.

Table 7: List of various zeolites in PTC with their applications

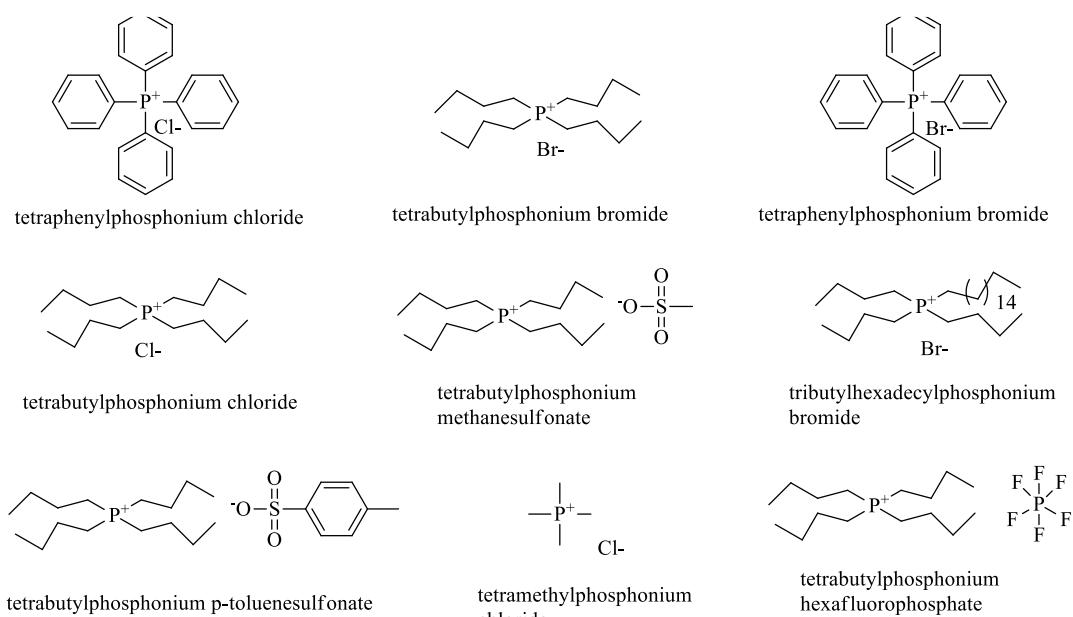
| Zeolite type | Application | Properties | Advantages | Reference |
|----------------|--|---|--|-----------|
| Beta Zeolite | Organic synthesis, Catalysis | Three-dimensional porous structure | Suitable for bulky substrates | 91 |
| Y Zeolite | Organic synthesis, Catalysis, Extraction | High thermal and hydrothermal stability | Modified structure enhances catalytic activity | 97 |
| MFI Zeolite | Organic synthesis, isomerization | Well-defined microporous | Catalyses various reaction | 94 |
| MCM-41 Zeolite | Catalysis, separations | Ordered Mesoporous structure | Can be functionalized for specific applications | 92 |
| FAU Zeolite | Catalysis, Extractions | Large pore size | Suitable for face transfer of bulky substrates | 91 |
| BEA Zeolite | Catalysis, isomerization | Cubic structure with interconnected pose. | Used in various catalytic processes | 94 |
| LTA Zeolite | Adsorption, Catalysis | Small pore size | Used in selective adsorption and catalytic processes | 93 |
| CHA Zeolite | Catalysis, Separations | Three-dimensional pore structure | Used in catalysis and separations | 91 |
| ZSM-11 Zeolite | Catalysis, isomerization | Different pore dimensions from ZMS-5 | Catalytic application including PTC | 95 |
| SSZ-13 Zeolite | Catalysis, adsorption | Small pore size with shape-selective property | Used in various catalytic processes | [43] |

In addition to ammonium and phosphonium salts, crown ethers, and cryptands, there are several other types of phase transfer catalysts, etc. The

most widely utilized are the quaternary ammonium salts in the business since they are the cheapest of them.

**Scheme 7:** Structure of Ammonium salts

These chemicals, which contain nitrogen in their skeleton, combined to create a salt with a unique structural makeup.²⁶ the ammonium salt category PTC, which is frequently used, is depicted in

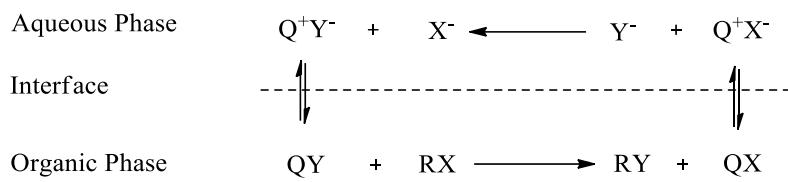
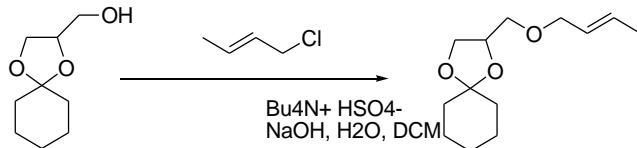
**Scheme 8:** Structure of Phosphonium salts.

These are comparable to ammonium salts as well, however, they contain phosphorous instead of nitrogen.⁹⁸ The frequently utilized PTC group of phosphonium is depicted in **Scheme 8**.

2. Mechanism of phase transfer catalyst

According to Starks's initial study, the PTC reaction mechanism involves the dissolving in the aqueous phase ($Q+X^-$) of a quaternary ammonium halide and an ion exchange with a different dissolved in water reactant's anion⁹⁹. Due to its lipophilic character, the generated ion pair ($Q+X^-$)

may now travel through liquid-liquid interfaces and undergoes diffusion to the lipophilic phase from the interface; Phase transfer is the term for this important stage.^{100,101} The nucleophilic anion from the ion pair conducts a reaction (nucleophilic substitution) with the organic reagents in the lipophilic phase, resulting in the formation of the eventual desired product (RY). The cycle is continually repeated once the catalyst returns to the aqueous phase after doing its job.¹⁰² The following **Scheme 9** explores the broad concept of PTC response.

**Scheme 9:** An overview of phase transfer catalyst reaction.**Scheme 10:** Synthesis of acetal group is present in primary alcohol under alkaline conditions.

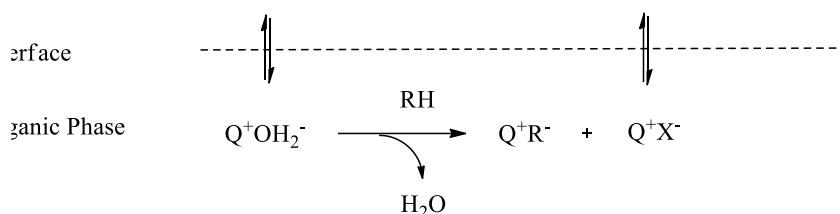
In **Scheme 10** there is an acetal group present in the starting material, as well as a primary alcohol group. Acids easily destroy acetals, so alkaline conditions are crucial. As a result, NaOH produces these outcomes, but it is insoluble in organic solvents. When the main chloride is utilized, only the SN_2 reaction typically takes place, which results in a nucleophilic assault of a more stable product with a more strongly replaced alkene at the main centre.¹⁰³ The starting material in this case has both a main alcohol group and an acetal, which makes it fascinating. The environment must be kept strictly alkaline since acetals are extremely readily damaged by acid.¹⁰⁴ While NaOH accomplishes this, organic solvents cannot dissolve it. Dichloromethane (DCM or CH₂Cl₂) and water are used in a two-phase system for the procedure that is demonstrated here.¹⁰⁵ While NaOH is located in the water layer, organic compounds are found in the DCM layer.

3. Activation of acidic organic compounds by inorganic bases in phase transfer catalyst

In asymmetric phase-transfer catalysis, the biphasic reaction system involves an organic phase containing an acidic methylene or methine molecule and an electrophile, alongside an aqueous or solid phase containing an inorganic base like alkali metal hydroxide (Na, K, Cs) or carbonate.¹⁰⁶ In this type of reaction, the primary reactive intermediate is the onium carbanion species, often in the form of onium enolate or nitronate, which engages with the organic-phase electrophile to yield the subsequent outcome.

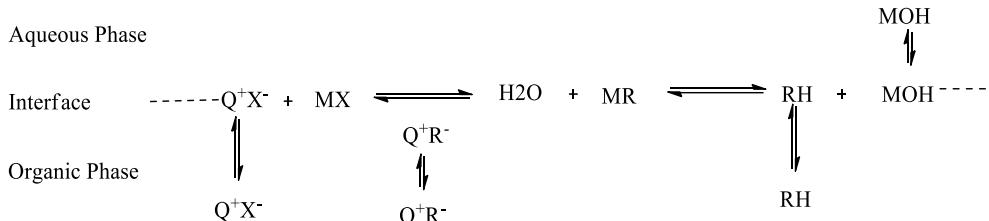
5.1. Creation of Reactive Onium Carbanion Species

Regarding the specific procedure for creating the reactive onium carbanion species, the Starks extraction process and the Makosza interfacial mechanism frequently disagree.¹⁰⁷ With the Starks extraction technique, the PTC switches back and forth between the organic and aqueous phases as shown in **Scheme 11**.¹⁰⁸

**Scheme 11:** Mechanisms of Starks extraction.

The onium salt removes hydroxide into the organic phase while equilibrating with the inorganic base in the aqueous phase.¹³ The reactive intermediate Q^+R^- is then produced when the onium hydroxide removes hydrogen from the acidic organic molecule. In the absence of PTC, the interfacial mechanism's proposed pathway calls for the initial creation of the generated metal carbanion species was then

extracted into the organic phase by interacting with the interface between the organic and aqueous phases in phase transfer catalyst.⁸² The Makosza interfacial mechanism is plausible since asymmetric PTCs often include organic structures that are chiral and very lipophilic yet reluctant to enter the aqueous phase shown in **Scheme 12**.¹⁰⁹

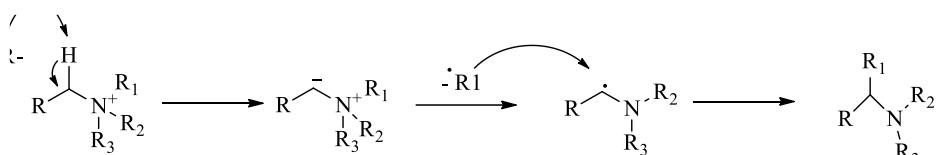
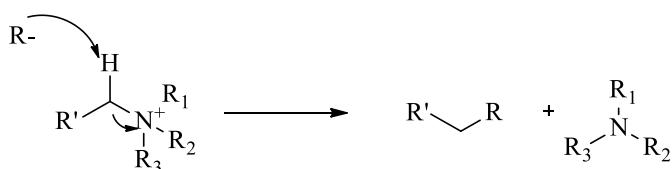
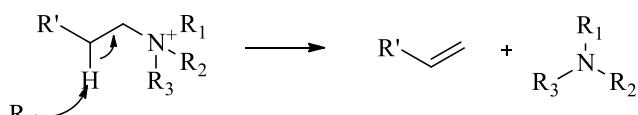
**Scheme 12:** Mechanisms of Makosza Interfacial.

The location of the contact and baseness of the inorganic salt how much onium carbanion there is that is readily available.¹¹⁰ A highly lipophilic PTC would have difficulty interacting with the interface, it should be emphasized, which would make using such a catalyst inadequate.¹¹¹, [92]

5.3. The Onium Carbanion's stability

The accumulating onium carbanion in the organic phase can start to break down in the absence of an

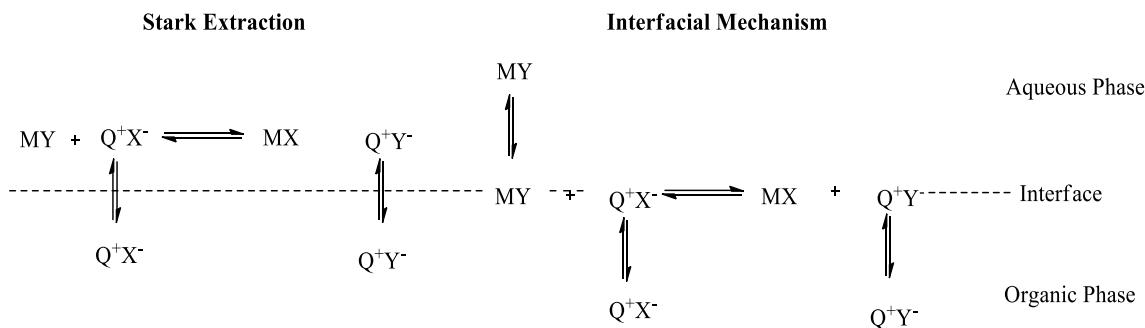
electrophilic reaction partner. Depending on the anion source, the onium carbanion created at PT conditions is unstable.¹¹³ Which is Stevens's rearrangement by Vial *et al.*(**Scheme 13**)¹¹⁴, nucleophilic substitution by Yang *et al.*(**Scheme 14**)¹¹⁵, and/or Hoffman elimination by Yandulov *et al.*(**Scheme 15**)¹¹⁶are known to be used. It is also possible that the strong inorganic base at the contact is influencing the direct breakdown of onium salt.

**Scheme 13:** Steven's Rearrangement.**Scheme 14:** Nucleophilic Substitution.**Scheme 15:** Hoffman elimination.

5. Anion addition via phase-transfer catalysed addition of metal salt

Active methylene or methane molecules are used to create the reactive onium carbanion from an inorganic base in the asymmetric PTC described above, and the carbanion species is then extracted the organic substance absorbs the onium salt as it passes through the interfacial area. So, ordinarily, both reagents stay in the organic phase.¹¹⁷ The anion is provided as the reaction partner in the second kind of asymmetric PTC as a solid and two reactants are firmly separated by the interface.^{118,119} An onium salt is used in this system to progressively transport from the aqueous phase into the organic phase of the anion. It has been suggested that both the Starks extraction method and the interfacial mechanism

might potential mechanisms for onium anion production.¹²⁰ In the asymmetric PTC, the interfacial mechanism appears to be active, just as it was in the example previously reported. Because of the relatively benign reaction circumstances, Side reactions like catalyst degradation are far less likely to occur.¹²¹ Interfacial mechanism and the Starks extraction procedure have both been presented as potential mechanisms for onium anion production. In 2012, Stark *et al.* Interfacial mechanism and the Starks extraction for onium anion production (**Scheme 16**).⁶⁵



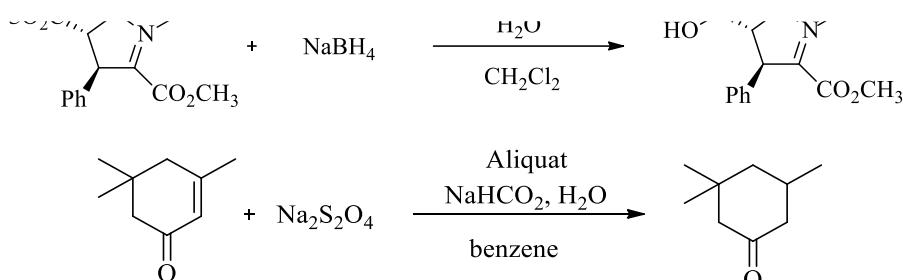
Scheme 16: Interfacial mechanism and the Starks extraction for onium anion production.

As a result of the anionic species' lack of prochirality, the biggest problem for these reactions. The distant electrically neutral reaction partner's enantiotropic face must be distinguished by the organic phase's chiral onium anion.¹²² The classic example of this group is the use of sodium hypochlorite or potassium permanganate as metal anion suppliers.

6. Anions react as salts of inorganic anions

Anions that are available as salts of inorganic anions can be employed in phase-transfer catalysis (PTC) to speed up reactions. In this situation, the PTC acts as a carrier to move the anionic species from one phase to another, often to an organic phase from an aqueous phase, in which it can engage in reaction with other reagents. BH⁴⁻ is the most dominant inorganic

anion utilized as a reducing agent.¹²³ The standard PTC catalysts—lipophilic TAA salts—can transfer this anion into a nonpolar solvent since it, in an aqueous solution of its sodium counterpart, is sufficiently stable. PTC is used to reduce carbonyl compounds that are insoluble in hydroxylic solvents. Under rare circumstances, it is even feasible to reduce an ester group.¹²⁴ By using sodium dithionite under PTC circumstances, α,β -unsaturated aldehydes, and ketones undergo a reduction of conjugated double bonds with exceptional selectivity.¹²⁵ In 2013, Kalplanek *et al.* were explained the PTC reaction of sodium dithionite, conjugated double bonds in unsaturated aldehydes and ketones are reduced (**Scheme 17**).¹²⁶

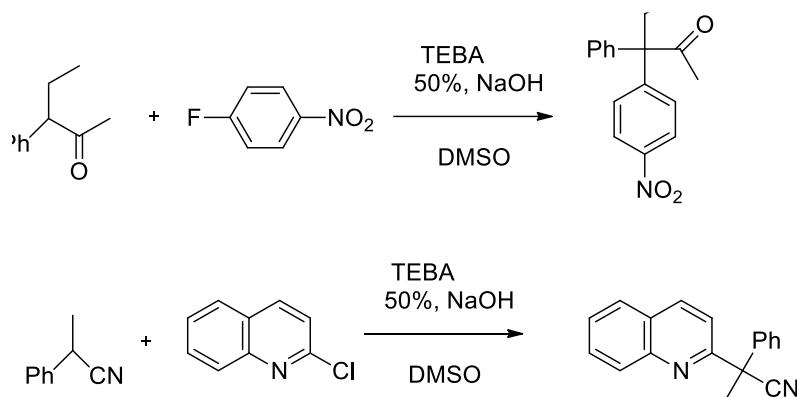


Scheme 17: Reaction of sodium dithionite under PTC conditions

7.1. Reactions catalysed by phase transfer and occurring in the presence of bases

Under PTC circumstances, the nucleophilic replacement in extremely electrophilic arenes (typically nitroarenes) involves the replacement of halogen atoms by carbanions successfully. But when the products don't work, only methylenic carbanions are compatible with the catalytic process. Possess an acidic hydrogen atom.¹²⁷ When nitroaryl substituents are introduced to methylenic carbanions ultimately, the products' C-H acids are considerably

stronger.^{128,129} As a result, they are quickly transformed into nitrobenzylic carbanions, which, when combined remain in the organic phase with the catalyst's lipophilic TAA cations. These carbanions cannot undergo any more reactions because of their limited nucleophilic activity.¹³⁰ The catalytic process is halted in this instance. In 2012, Chupakhin *et al.*, investigated the influence of PT, halogen atoms in nitroarenes are nucleophilically replaced by carbanions (**Scheme 18**).¹³¹



Scheme 18: Nucleophilic replacement of halogen atoms in nitroarenes by carbanions under the influence of PT

The presence of reactive the high effectiveness of PT-catalysed nucleophilic substitution of halogen atoms in nitroarenes by carbanions and the presence of anions in the organic phase in the form of TAA salts and low concentrations of the reactive species are probable contributing factors.¹³² This scenario suppresses potential competing processes during the organic phase.

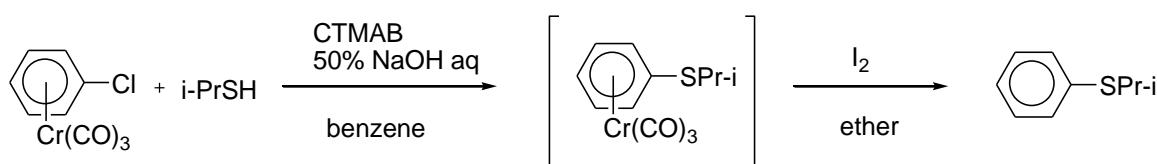
7. Organometallic chemistry- phase transfer catalysis

In the chemistry of organometallics and in reactions that are catalysed by organometallic compounds and complexes, a phase transfer

catalyst is frequently utilized. We will merely skim the major kinds of assessments because there have been so many of them for this topic.⁹⁰

8.1. Creation of complexes and compounds with organometallic elements under PT Catalysis

In 2023, Foster *et al.* explained the PTC technique, it is possible to effectively synthesize several organometallic compounds and complexes elaborated in **Scheme 19**.



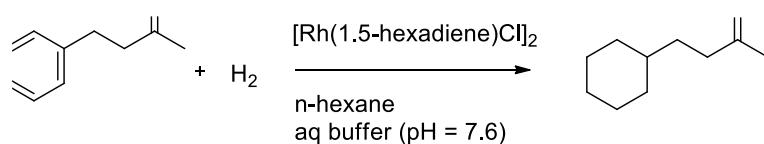
Scheme 19: Organometallic complexes and compounds under Phase transfer catalysis

The necessary transformations can take place by complexing organic molecules with organometallic moieties, which significantly changes their characteristics.¹³³ Under PTC circumstances, numerous changes involving organometallic complexes or substances are carried out. In halobenzene, this includes the fact that the replacement of the halogen by a nucleophile often requires harsh conditions. These reactions are made easier when these are transformed into chromium tricarbonyl

complexes.¹³⁴ For carrying out such a procedure using inorganic anions, alkoxides, etc., PTC is the preferred approach.

PTC is reduced and hydrogenated using carbonyls or complexes of CO and H₂

In 2022, Zhou and Wang *et al.*, investigate the process of phase transfer catalyst hydrogenation, CO and H₂ complexes are used (**Scheme 20**).^{135,136}



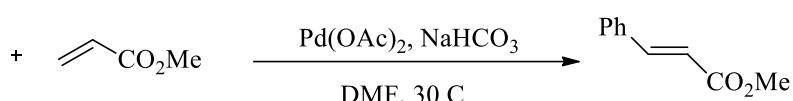
Scheme 20: Reaction of Phase transfer catalyst is hydrogenated by using CO and H₂ complexes.

In these processes, the hydrogenation catalyst and the organic substrate come into touch with each other through the two-phase system of the TAA salt.

8.2. The Heck reaction with PTC and its Reactions

For the production of organic compounds, Pd-catalysed processes such as the Heck reaction and

ethynylation of aryl or vinyl halides are highly useful.¹³⁷ Even if these reactions are successfully carried out in a homogenous media, in many instances, the employment of PTC in heterogeneous systems results in considerable benefits for yields, selectivity, and processes. In 2022 Chen *et al.*, explained heck reaction under PTC conditions (**Scheme 21**).¹³⁸

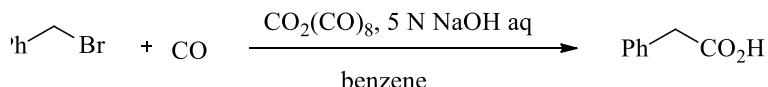


Scheme 21: Phase transfer catalyst with heck reactions.

8.3. Organic Halide Carbonylation by PTC and Metal Complexes

A versatile and effective way to produce carboxylic acids is by the organic halides are

carbonylated using transition metal catalysts. PTC provides exceptionally practical conditions for this reaction (**Scheme 22**).¹³⁹



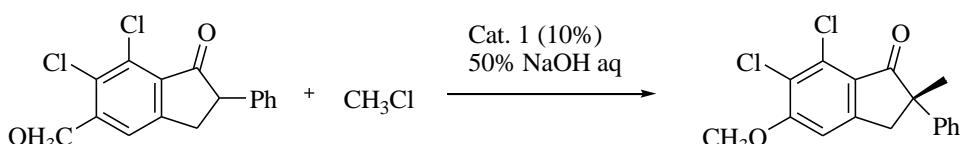
Scheme 22: Reaction of organic halide carbonylation and metal complexes.

The main advantage of PTC methodology in these reactions is that the product, a carboxylate anion, is continuously removed from the organic phase into the aqueous phase, ensuring a high turnover of the organic metal catalyst and also high selectivity of the monocarboxylation of dihalo- or polyhalo-molecules.¹⁴⁰

8.4. Reactions Catalysed by Enantioselective Phase Transfer

Realizing optically active catalysts supporting enantioselective synthesis would be of significant importance since new chiral centres are frequently

produced in PT-catalysed reactions.¹⁴¹ These options were particularly appealing since optically active tertiary amines, such as alkaloids, are widely accessible. A thorough search for these responses first turned up primarily negative findings.¹⁴² This issue was just recently satisfactorily resolved with the introduction of appropriate chiral TAA salts. In 2022, Pupo *et al.*, (**Scheme 23**) explained the reaction of catalysed by enantioselective phase transfer under PTC conditions.¹²²

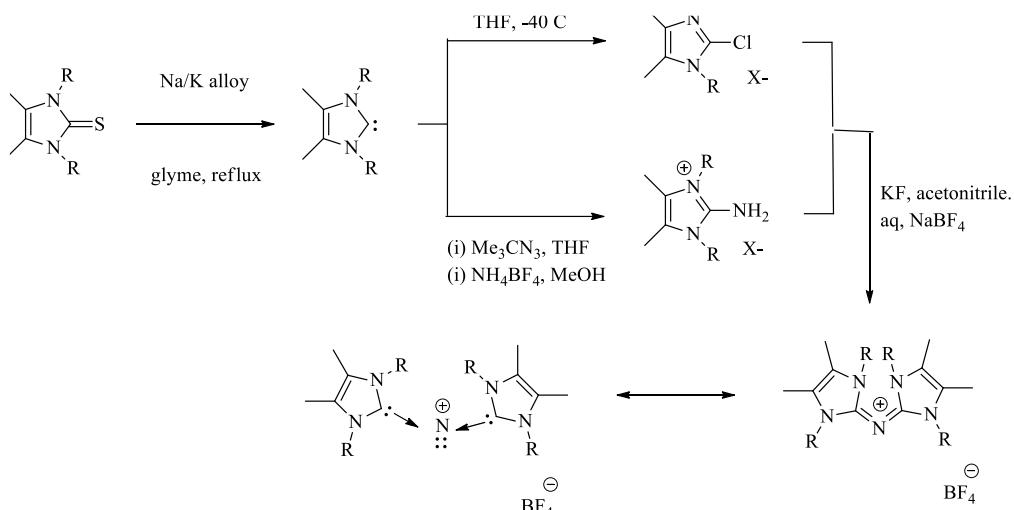


Scheme 23: Reactions of enantioselective in phase transfer catalyst.

Phase-transfer catalysts of the next generation: NL²⁺ systems

Currently, one of the most important tools for chemists is the phase-transfer catalyst (PTC) used to carry out chemical processes. PTCs give good yields of the desired product by accelerating different biphasic system responses. Most PTCs

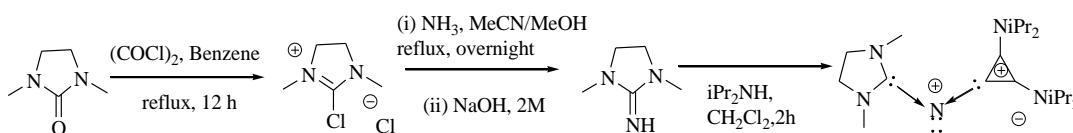
fall within the umbrella of the formula NR⁴⁺X. Recent reports of PTCs include various compounds with a new structure and the general formula NL²⁺ X. The electron density is provided by ligands that donate electrons to a nitrogen atom with a formal positive charge to produce the NL²⁺ species (**Scheme 24**).¹⁴³



Scheme 24: Synthetic process for creating the NL²⁺ species, imidazol-2-ylidene act as electron-donating ligands.

This family of divalent NI compounds is a class of substances because electronic structure investigations published support for the viability of L-N coordination (donor-acceptor) interactions in these species may be found in the literature. According to reports, these species have more

catalytic capability than conventional NR⁴⁺ systems. It has been discovered that certain NL²⁺ complexes are helpful in asymmetric phase-transfer catalysis (**Scheme 25**).¹⁴⁴

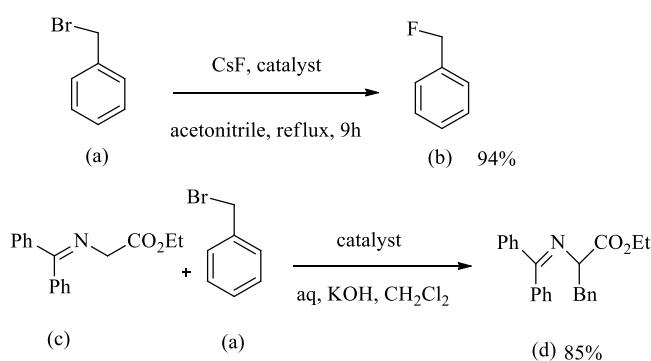


Scheme 25: Synthetic plan to create NL²⁺ species with NHC and CCC as electron-donating ligands

As a result, these systems provide a wealth of opportunities for investigating the novel mechanistic elements connected to their distinctive electrical structure as well as the catalytic characteristics. The synthesis, electrical, structural, and catalytic uses of NL²⁺-based PTCs are discussed in this work along with considering their bright possibilities for catalytic organic chemistry in the future.

A PTCs-based analysis of NL²⁺ systems-catalysed reactions

PTCs are employed in many different processes to achieve benefits including enantiopurity, greater yields, and use of less dangerous chemicals.¹⁴⁵ Only a few processes have used the catalysis of these new PTCs. In a heterogeneous solution, benzyl bromide (**a**) was successfully fluorinated using the PTC 16 to produce the fluorinated product (**b**) 94% of the time (**Scheme 26**).



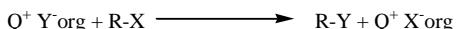
Scheme 26: Benzylation and fluorination reactions using an NL²⁺ system as a PTC.

The same response just traces of the product were produced when the reaction was carried out without the catalyst.^{144,146} In the same study, it was also looked into whether the NL²⁺ system 16 could catalysed reaction ii in Scheme 8 of the benzylation of the glycinate ester (**c**) in an alkaline biphasic system. In the presence of the catalyst, 85% of the product was produced, however without the catalyst, no product was seen. In 2018, Patel *et al.*, explained NL²⁺ systems as a phase transfer catalyst.¹⁴⁴

Green chemistry in PTC

In green chemistry, the general catalyst plays a significant part in the convenience of reaction execution, good yield, and the production of less dangerous by-products, among other things. Particularly, the usage of PTC is growing, which helps people utilize organic solvents less, resulting in less dangerous by-products and other

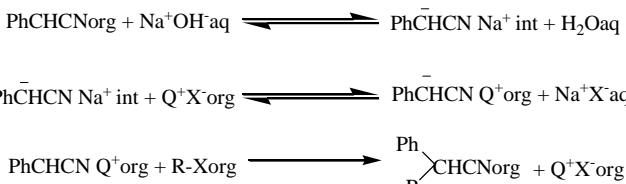
issues associated with organic solvents.^{147,148} The widespread use of PTC in aqueous systems enables greener, more advanced, environmentally friendly synthesis. PTC also allows for solvent-free synthesis. Phase-transfer Organic anions undergo catalysed reactions that are mechanistically more difficult.¹⁴⁹ In these situations, the organic phase includes the anion precursor, an electrophilic reactant, and finally, a solvent, whereas the inorganic phase contains the base, such as concentrated aqueous or solid NaOH, KOH, or solid K₂CO₃. [1,2] This technology is used for the alkylation of phenylacetonitrile (**Scheme 27**) by the interaction of its carbanion with an alkyl halide



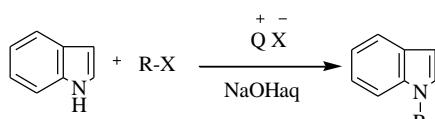
Scheme 27: The alkylation of phenylacetonitrile by the interaction of its carbanion with an alkyl halide

A catalytic quantity of tetraalkylammonium halide, typically 1% molar, causes an exothermic reaction that results in phenyl alkyl acetonitrile. The procedure is represented by **equation (2)** in

Scheme 28, where the subscripts "org," "aq," and "int" stands for the organic and aqueous phases, respectively, and the interfacial area.



Scheme 28: An exothermic reaction of phenyl alkyl acetonitrile.



Scheme 29: The N-alkylation of indole, CH acids, alcohols, and NH acids can also be effectively alkylated.

Future perspectives

Phase transfer catalysis is a powerful technique for speeding up the transfer of a reactant from one phase to another in organic chemistry. The process might be sped up using a phase transfer catalyst, enhance selectivity, and streamline the reaction process. Phase transfer catalysts are expected to become more crucial in the production of chemicals and organic synthesis in the future. This is because there is a rising need for chemical processes that are both sustainable and efficient. Phase transfer catalysis can have a

large positive impact on waste reduction and energy efficiency, two important sustainability-related factors.¹⁵⁰ Additionally, scientists are working hard to create new kinds of phase transfer catalysts that are more eco-friendly, efficient, and selective. For instance, there is rising interest in creating catalysts that are made from waste or renewable resources like biomass.¹⁵¹ Simple, inexpensive, and Useful mild bases include NaOH and K₂CO₃ in place of hazardous ones in any kind of chemical reaction, alkali metal amides, hydrides, and alkoxides are

produced that are conducted biphasic systems where a PTC is present. Additionally, PTC can be utilized in the synthesis process for the production of fine chemicals (such as agrochemicals, pharmaceuticals, dyes, and paper).¹⁵² In the manufacture concerning phenylacetic acid, a component used as an intermediary in the perfume industry, is also employed in the perfumery and fragrance industry.¹⁵³ Regarding medicinal products, such as the creation of several medications including ritaline, oxaladine, phenoperidine, dicyclonine, etc. The requirement to segregate the catalyst from the product's organic phase, particularly in commercial applications, is one of PTC's key drawbacks. Additionally, phase transfer catalysis is not just used in organic chemistry. It is also being used in fields like materials science and inorganic chemistry. Phase transfer catalysts, for instance, are being used to speed up the creation of nanoparticles, which have many uses in industries ranging from electronics to medicine¹⁵⁴ Overall, phase transfer catalysis has a promising future, and we may anticipate further development and innovation in this area as scientists try to create more effective, long-lasting, and adaptable catalysts for a variety of applications.

Conclusion

In summary, phase transfer catalysts (PTCs) serve a critical role in promoting chemical reactions between immiscible phases, such as between an aqueous phase and an organic phase. They achieve this by successfully transporting polar or charged species from one phase to another, enabling reactions that would otherwise be prevented by phase separation. PTCs may speed up reactions, boost yields, and enhance selectivity, making them useful instruments in a variety of chemical processes. PTC and micellar catalysis and reactions in micro emulsions are similar in that they both involve the catalytic action of TAA salts, which are frequently surface-active agents and have a significant impact on the size of the interfacial region. When organic molecules that are moderately and weakly acidic are deprotonated in nucleophilic substitution reactions and base-assisted reactions. When it comes to solving problems brought on by the immiscibility of reactants in various chemical processes, phase transfer catalysts are an invaluable tool. They have become crucial instruments in contemporary synthetic chemistry and have helped with the production of novel materials, medicines, and fine chemicals thanks to their capacity to allow mass transfer between phases and foster effective reactions. The

application of phase transfer catalysts is anticipated to remain a key area of interest as catalysis research develops in the fields of chemical synthesis and process development.

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