

## ❖ Phase Transfer Catalysis

The phase-transfer catalysis may simply be defined as a special form of heterogeneous catalysis that supports the movement of a reactant from one phase into another phase where the reaction occurs.

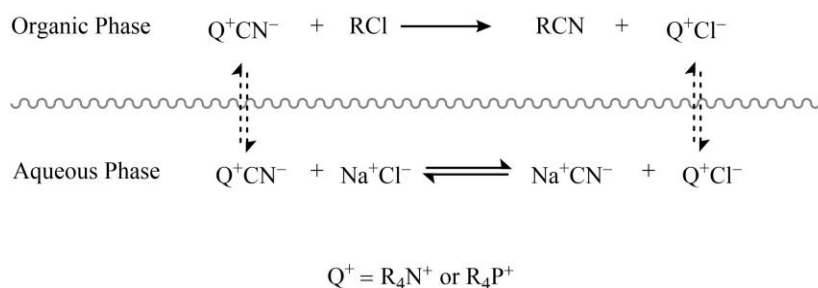
Ionic reactants are often soluble in an aqueous phase but insoluble in an organic phase in the absence of the phase-transfer catalyst (PTC). The function of a phase transfer catalyst resembles detergent to solubilize the salts into the organic-phase. In other words, the phase-transfer catalysis accelerates the reaction rate. By using this type of catalysis, we can get faster rates with better yields, fewer byproducts, eliminate the need for dangerous or expensive solvents that will dissolve all the reactants in one phase, eliminate the need for expensive raw materials and minimize waste-related complications. In this section, we will discuss the prominent mechanisms and applications of phase transfer catalysis.

### ➤ Mechanisms of Phase Transfer Catalysis

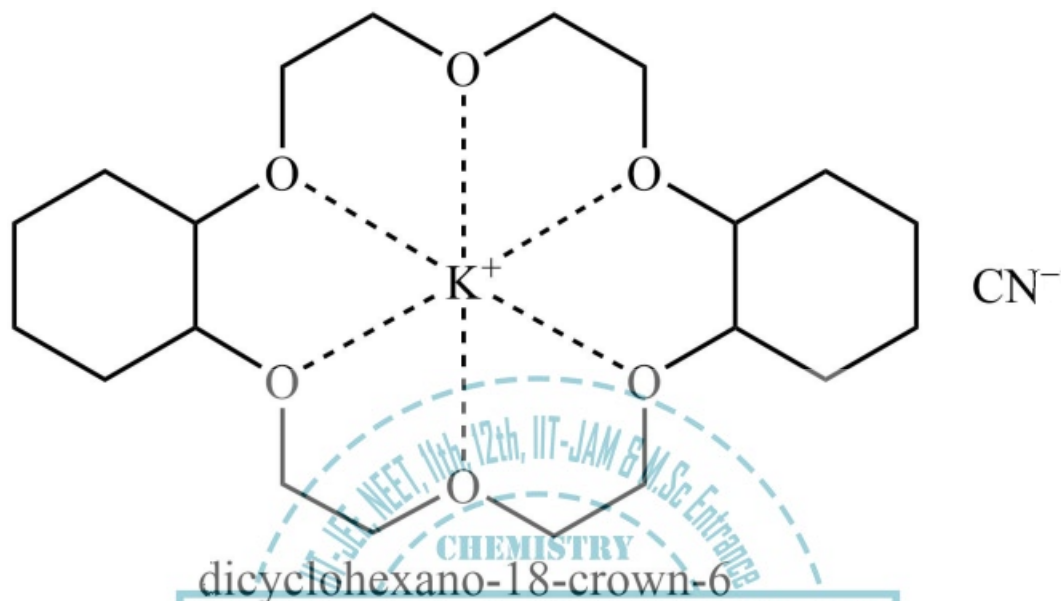
The mechanism of phase-transfer catalysis can primarily be divided into two categories where the acting routes are different but the final effects are similar. In other words, the anion is made to enter into the organic phase and permitted to be fairly free to react with the substrate in both types.

**1. Quaternary phosphonium or ammonium salts:** This mechanism can be understood by taking the example of the reaction between sodium cyanide and 1-chlorooctane where no substitution product (1-chlorooctane) is formed even after heating (with constant stirring) the mixture for weeks. However, even we add a very small amount of a suitable “quaternary ammonium salt”, sufficient amount of 1-chlorooctane is obtained in less than two hours.

The reason for no reaction when “quaternary ammonium salt” is absent is that  $\text{CN}^-$  ions cannot pass from aqueous phase to organic phase in sufficient concentration all alone, leaving behind  $\text{Na}^+$  ions because this would disturb the electrical neutrality of both phases; and  $\text{Na}^+$  ions have no motivation go into organic phase since highly hydrated in the aqueous medium. However, “quaternary ammonium or phosphonium salts” are added, the quaternary ammonium ( $\text{R}_4\text{N}^+$ ) and quaternary phosphonium ions ( $\text{R}_4\text{P}^+$ ) are produced which do have the ability to pass through the interface between two phases. This is because ‘R’ groups in  $\text{R}_4\text{N}^+$  and  $\text{R}_4\text{P}^+$  are quite bulky causes poor solvation in the aqueous phase. Therefore, when they cross the phases’ interface, they also carry  $\text{CN}^-$  ions with them to keep the electrical neutrality of both phases. Once the  $\text{CN}^-$  ions reach sufficient concentration, they start reacting with  $\text{RCl}$  to yield  $\text{RCN}$  and halide anions ( $\text{Cl}^-$ ). The whole process can be depicted as given below.



**2. Crown Ethers and Other Types of Cryptands:** It is quite a well-known fact that some cryptands have the ability to surround certain cations. For instance, when KCN salt is mixed with dicyclohexano-18-crown-6, a new salt is obtained which has the same anion much larger cation as shown below.



This new cation has a much smaller positive charge density than  $K^+$ ; and therefore, it gets very poorly hydrated. Furthermore, the new cryptate salt is quite soluble in many solvents including organic-types; therefore, we can add this new salt directly to the organic phase without the need for an aqueous phase. Many cryptands have been employed to make salts with  $OAc^-$ ,  $F^-$ ,  $I^-$ ,  $Br^-$ , and  $CN^-$  to enhance the rates of nucleophilic substitution reactions.

Finally, we can conclude that “quaternary phosphonium or ammonium salts” as well as “cryptands” are quite capable of moving the anion from aqueous to organic phase; however, it has been found that even if sodium and potassium salts were soluble in the organic phase, they don’t very fast nucleophilic substitution because they exist as ion pairs with corresponding anions, and are not free to attack the substrate efficiently. On the other hand,  $R_4N^+$  or  $R_4P^+$  and cryptate cations ions don’t pair with anions very effectively, letting them, free to attack the substrate.

#### ➤ Applications of Phase Transfer Catalysis

Although the application domain is quite large, some of the main applications of phase transfer catalysis in synthetic organic chemistry are given below.

- i) Phase transfer catalysis is widely used in industries for commercial production.
- ii) Phase transfer catalysis is used in the alkylation of phosphothioates to produce pesticides.
- iii) Chiral quaternary ammonium salts are used as phase transfer catalysts for the asymmetric alkylations.

- iv) Phase transfer catalysis is not bound to systems with hydrophobic and hydrophilic reactants and is employed in liquid-solid and liquid-gas reactions sometimes.
- v) Phase-transfer catalysts are especially valuable in green chemistry by allowing the use of water, and therefore, the requirement for organic solvents is lowered.



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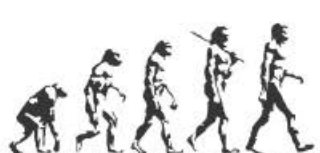
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**MANDEEP DALAL**



*First Edition*

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