

LITTLE FLOWER COLLEGE GURUVAYUR  
DEPARTMENT OF CHEMISTRY

**TOPIC : USE OF QUATERNARY SALTS AS PTC**

Presented by

Princy K.Johnson

# Use of Quaternary Salts as Phase Transfer Catalyst

1. Simple Tetraalkyl –Onium salts as PTC

2. Special Quaternary salts as PTC

- Heterocyclic quaternary salts
- Bis-(quaternary ammonium salt) as PTC
- Cluster quaternary salts
- Ethoxylated quaternary salts
- Crown –quaternary salts
- Quaternary salts containing a  $\beta$ -hydroxyl group
- Betaines as PTC
- Quaternary salts containing siloxane groups

# Simple tetra alkyl –onium salts as PTC

- The most commonly used PTC are quaternary ammonium and phosphonium ions
- Of these tetrabutyl ammonium salts ,trioctylmethylammonium chloride,benzyltriethyl ammonium chloride are most frequently reported ones.
- The use quaternary salt as PTC will include some features
  - ❖ Distribution of catalyst and reactive species into the organic phase
  - ❖ Consideration of use of an anion –activating or an accessible quaternary salt
  - ❖ Stability of quaternary salt under reaction conditions
  - ❖ The effect of catalyst structure

## 1. Distribution of Q<sup>+</sup>Y<sup>-</sup> into the organic phase

- Tetramethyl ammonium cation plus simple anions such as Cl<sup>-</sup>, Br<sup>-</sup>, CN<sup>-</sup>, AcO<sup>-</sup> etc are not easily distributed so they are not good PTC
- Tetraethylammonium and propyl ammonium salts are poor catalyst for transferring small anions
- Tetrabutyl ammonium salts are frequently used as PTC not because they offer the highest reactivity, but because they are readily available in high purity, relatively inexpensive, and they can easily be removed from organic reaction products by extraction into water
- Quaternary ammonium cations, having pentyl to decyl groups easily extract anions into almost all organic phases
- Higher tetraalkylammonium salts and higher groups can easily extract the monovalent anion but their reaction rate decreases due to their high organophilic nature.

## 2. Anion vs accessible nature of –onium salts

Bulky quaternary salts activate anions by increasing the distance separating cation from anion in the ion pair

Quaternary ammonium cations having three or four large alkyl groups to achieve useful reaction rates

These catalysts are referred to as anion-activating structures.

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Quaternary ammonium salts having one large group and three small groups such as hexadecyltrimethyl ammonium salt are considered to be highly accessible because the openness of the structure.

The accessible quaternary ammonium salts reside easily in the interface and therefore able to lower the interfacial tension between the organic and the aqueous phase .this allows the organic phase to be displaced as smaller droplets into the aqueous phase

It increasing the total surface area and increasing the net total number of anions transferred into the organic phase.

### 3. Stability of the quaternary salt catalyst during PTC reactions

- If polyethers are used as catalysts, then raising temperature may decrease the stability and activity of the catalyst.
- Quaternary ammonium or other -onium salts usually decomposes at high temperatures about 120-150 °C for neutral salts, but at low temperatures for system containing conc. Na or KOH.
- Poly ethyleneglycol and crownethers are more resistant to thermal decomposition under basic conditions, but are sensitive to acidic conditions.



# The catalyst structure

Normal PTC alkylation of phenols by reactive alkylating agents and aqueous NaOH is almost selective for O-alkylation

However, bulky quaternary ammonium salts immobilized on silica gel or alumina provide an aqueous or polar environments giving a high yield of C-alkylation products.

# 2.SPECIAL QUATERNARY SALTS

## 1.Simple heterocyclic quaternary salts

Some saturated heterocyclic quaternary salts are more stable than conventional tetraalkyl ammonium quaternary salts.

- 4-aminopyridinium derivatives –used for anhydrous reaction with solid sodium phenoxide.
- Hexaalkyl guanidinium derivatives – used for aromatic displacement reactions.
- Heterocyclic quaternary ammonium salts based on the morpholine and piperidine-used for oxidation of p-xylene.

## 2. bis(quaternary ammonium salts )

- They are selective catalyst
- Alkylation using bis-[2N-benzyl-N,N-diethylammonium)ethyl]ether dichloride gives 70% monoalkylated product and 22% dialkylated product.
- Bis(pentaalkyl guanidinium) alkane salts used for aromatic displacement reactions.

### 3.Cluster quaternary salts

They are formed by clustering quaternary ammonium cations around a polyvalent anionic species.

They providing a highly polar ionic center which can easily accommodate additional ionic species.

