LITTLE FLOWER COLLEGE GURUVAYUR DEPARTMENT OF CHEMISTRY

TOPIC: PHASE TRANSFER CATALYSIS

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Phase-Transfer Catalyst

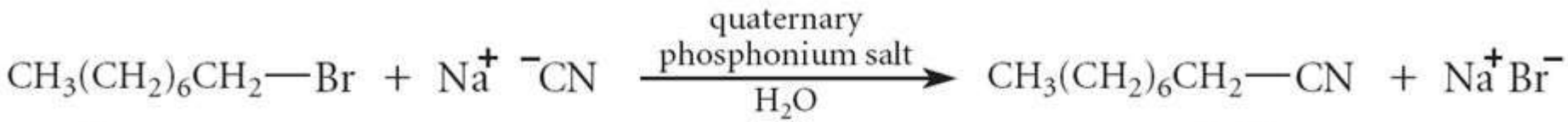
A phase-transfer catalyst or PTC is a catalyst that facilitates the migration of a reactant from one phase into another phase where reaction occurs

Phase-transfer catalysis is a special form of heterogeneous catalysis

Ionic reactants are insoluble in an organic phase in the absence of the phase-transfer catalyst but they are soluble in aq. phase

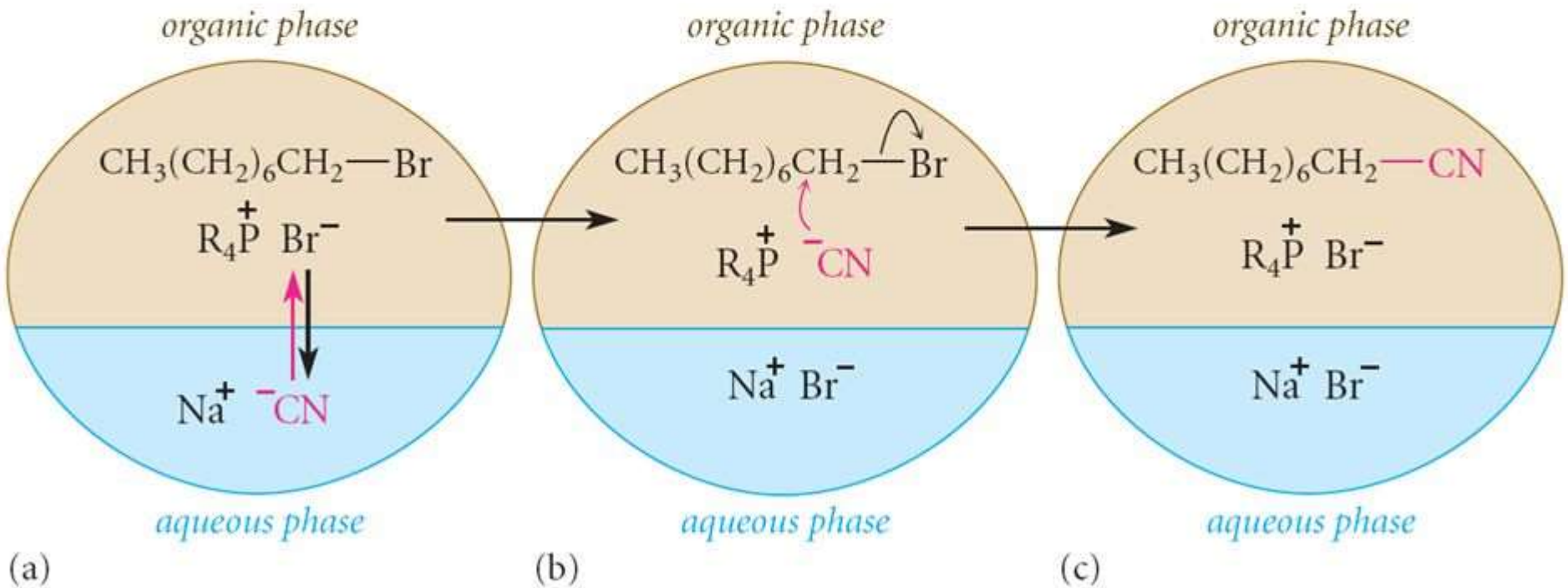
Phase-transfer catalysts are especially useful in green chemistry—by allowing the use of water, the need for organic solvents is reduced

Phase-Transfer Catalysis



$CH_3(CH_2)_6CH_2—Br + Na^+ {}^-CN \rightarrow CH_3(CH_2)_6CH_2—CN + Na^+Br^-$

1-bromooctane **nonanenitrile**



TYPES OF PHASE-TRANSFER CATALYSTS

There are many types of phase transfer catalysts, such as quaternary ammonium and phosphonium salts, crown ethers, cryptands, etc.

Among these, the quaternary ammonium salts are the cheapest and hence the most widely used in the industry.

PRINCIPLE

The principle of PTC is based on the ability of certain phase-transfer agents (the PT catalysts) to facilitate the transport of one reagent from one phase into another (immiscible) phase wherein the other reagent exists

reaction is made possible by bringing together the reagents which are originally in different phases

it is also necessary that the transferred species is in an active state for effective PT catalytic action, and that it is regenerated during the organic reaction

Theories of catalysis

1) Intermediate Compound formation theory (Homogenous catalyst reaction)
2) Adsorption theory (Heterogenous catalyst reaction)

1) Intermediate compound formulation theory:

According to this theory one of the reactants combines with catalyst to form intermediate product, which carries out the reaction,

E.g. $A + C = AC$

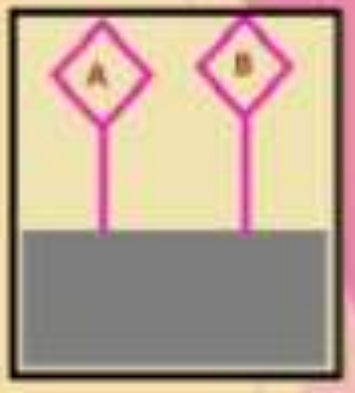
$AC + B = AB + C$

$A + B + C = AB + C$

where A and B are reactants, C is the catalyst and AC is the intermediate product.

2) **Adsorption Theory:**

In general adsorption theory applies to heterogeneous catalytic reactions. The catalyst functions by the adsorption of the reacting molecules on its surface. The adsorption reaction undergoes four types of steps.



(i) Adsorption of reactant molecule:

The reactant molecules A and B strike the surface of the catalyst.

The reaction molecules held up by the partial chemical bond.

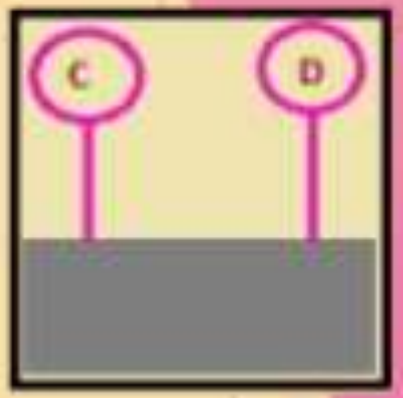
ii) Formation of intermediate complex:

The reactant molecule adjacent one another join to form an intermediate complex (A-B). The intermediate complex is unstable.

(iii) Decomposition of intermediate complex:

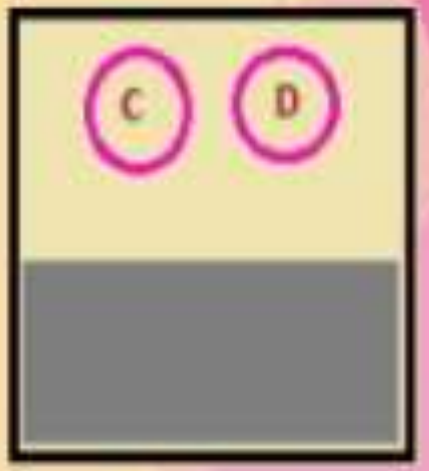
The intermediate complex breaks to form the products C and D.

The product molecules hold to the catalyst surface by partial chemical bond.



(iv) **Release of product:**

The product particles are released from the surface.



MECHANISMS OF PTC

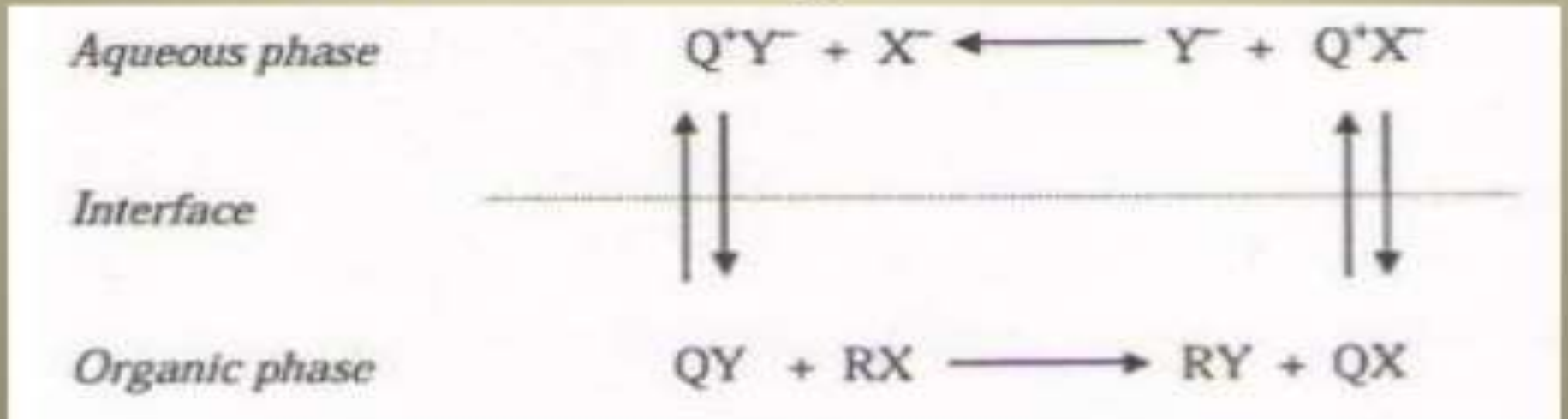
A quaternary ammonium halide dissolved in the aqueous phase (Q^+X^-) undergoes anion exchange with the anion of the reactant dissolved in the aqueous solution

The ion-pair formed (Q^+X^-) can cross the liquid-liquid interface due to its lipophilic nature and diffuses from the interface into the organic phase, this step being the phase-transfer

In the organic phase, the anion of the ion-pair being quite nucleophilic undergoes a nucleophilic substitution reaction with the organic reagent forming the desired product (RY)

The catalyst subsequently returns to the aqueous phase and the cycle continues.

An overview of PTC reactions is given in the scheme bellow:



Types of phase transfer catalyst

- Quaternary 'Onium' salts such as ammonium, phosphonium , antimonium and tertiary sulphonium salts.

Some of the PTC's normally used are:-

1) Aliquat 336 : $N^+CH_3(C_8H_{17})_3\ Cl^-$

Methyl trioctylammonium chloride

2) Benzyl trimethylammonium chloride or bromide (TMBA)

$N^+(CH_3)_3\ CH_2\ C_6H_5\ X^-$

3) Benzyl triethylammonium chloride

$N^+(C_2H_5)_3\ CH_2\ C_6H_5\ X^-$

4) Cetyl trimethylammonium chloride or bromide (CTMAB)

$N^+\ (CH_3)_3\ (CH_2)_{15}\ CH_3\ X^-$

Advantages of PTC

1. Do not require vigorous conditions and the reaction are fast.
2. Do not require expensive aprotic solvents.
3. Do not require high temperature ; the reaction usually occur at low temperature.
4. There is no need for anhydrous conditions since water is used as one of the phases.
5. With the help of PTC , the anion is available in organic solvent and so its nucleophilicity increases.

APPLICATIONS OF PTC

PTC finds applications in a variety of reactions

- PTC is widely exploited industrially
- Applications involving the use of a co-catalyst include co-catalysis by surfactants, alcohols and other weak acids in hydroxide transfer reactions, use of iodide, or reactions carried out with dual PI catalysts have been also reported
- In nucleophilic substitution reactions and in reactions in the presence of bases involving the deprotonation of moderately and weakly acidic organic compounds
- PTC has made possible the use of cheaper and easily available alternative raw materials like potassium carbonate and aqueous NaOH solution, thereby obviating the need of severe anhydrous conditions, expensive solvents, and dangerous bases such as metal hydrides and organometallic reagents
- When any kind of chemical reactions are carried out in the presence of a PT catalyst in biphasic systems, simple, cheap and mild bases like NaOH and K2CO3 can be used instead of toxic alkali metal alkoxides, amides, and hydrides
- Perfumery and Fragrance Industry like Synthesis of phenylacetic acid, an intermediate in the perfumery industry

- In the field of Pharmaceuticals like Synthesis of various drugs like dicyclonine, phenoperidine, oxaladine, ritaline, etc.
- Polymeric bonded PTC for the determination of cyanide, iodide, nitrite, sulphide and thiocyanate, led to easy layer separation and PTC-free injection of the sample into the chromatograph
- However, the main disadvantages of PTC, especially in commercial applications, are the need to separate the catalyst from the product organic phase
- PTC can also be used for the synthesis process for fine chemicals manufacture industries
- Polyester polymers
  for example are prepared from acid chlorides and bisphenol-A
- Phosphothioate -based pesticides are generated by PTC-catalyzed alkylation of phosphothioates
- One of the more complex applications of PTC involves asymmetric alkylations, which are catalyzed by chiral quaternary ammonium salts derived from cinchona alkaloids

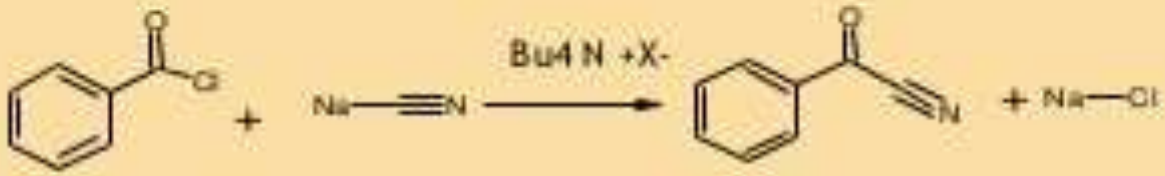
Applications of phase transfer Catalysis

1) Nitriles From Alkyl Halides :-

R-X + NaCN —PTC→ RCN + NaX

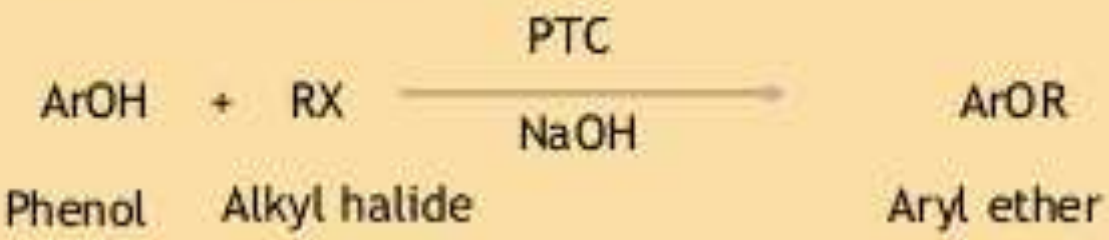
Organic Aqueous Nitrile

2) Benzoyl Cyanides from Benzoyl Chloride:-

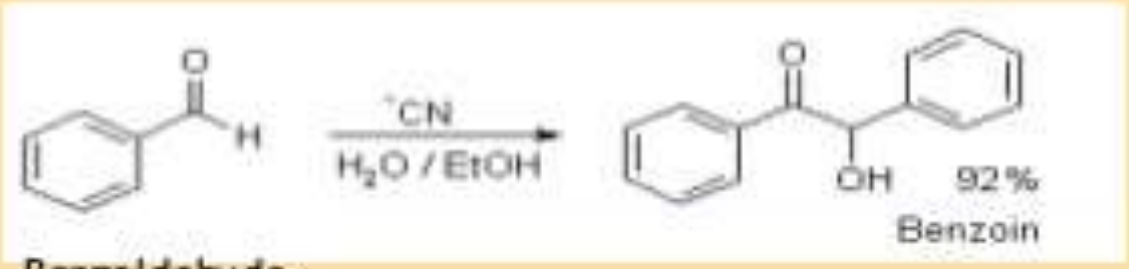


Benzoyl chlolride — Sodium cyanide — Benzoyl cyanide

3) Aryl Ethers/Thioethers :-



4) Benzoin Condensation :-



Benzaldehyde

4) **Esterification** :-Carboxylic acids can be esterified with alkyl halides in the presence of triethylamine.

$$RCO_2Na + RX \xrightarrow{PTC} RCO_2R + Na\,X$$

Carboxylic acid as sod. salt — Alkyl halide — Ester

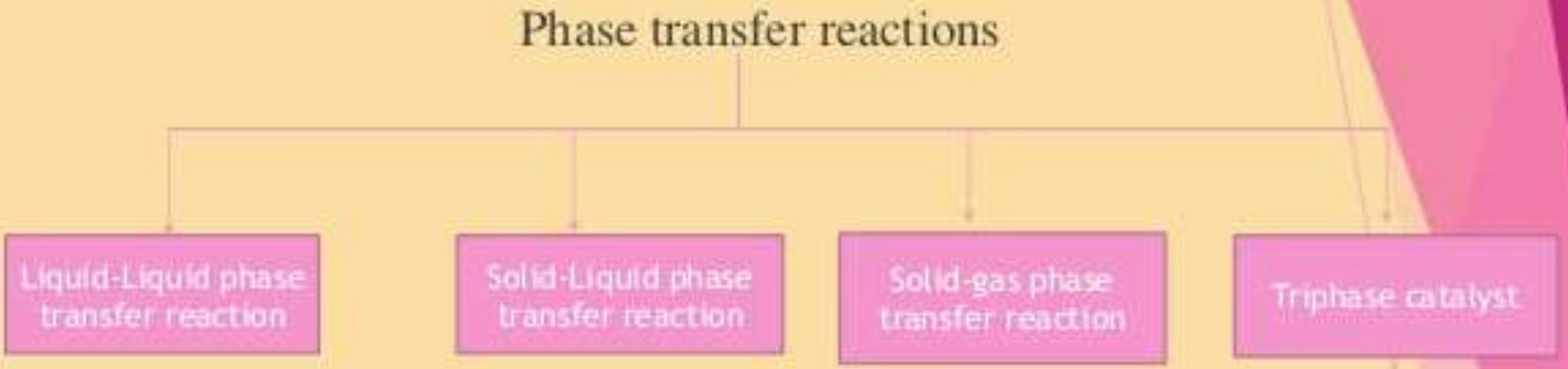
5)In the field of Pharmaceuticals like Synthesis of various drugs like dicyclomine, phenoperidine ,oxaladine ,ritaline ,etc.

6) **Williamson Ether Synthesis :-**

$$C_8H_{17}OH + C_4H_9Cl \longrightarrow C_8H_{17}OC_4H_9 + C_8H_{17}OC_8H_{17}$$

Alcohol — Alkyl halide — Ether — By-product

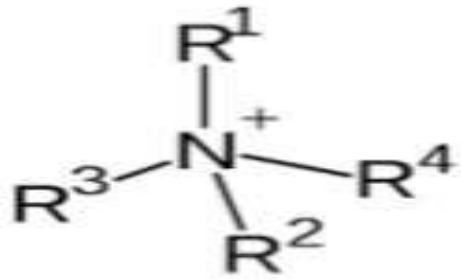
Types of phase transfer catalysed reactions



- Insolubilized ammonium and phosphonium salts
- Insolubilized crown ethers and cryptands
- Insolubilized cosolvents

Quaternary Ammonium Compound

Quaternary ammonium compounds (QACs or Quats) share the common quaternary ammonium cation as shown in figure. The substituents R1, R2, R3 and R4 varied in order to effect the properties of the molecule. In pure form the QACs will also contain an negative particle such as chloride, bromide or methosulfate. When in solution, like in a sewage system, the substances will be dissociated and the anion the QACs were once associated with will be irrelevant.



Quaternary ammonium compounds are positively charged polyatomic ions of the structure NR4+, R being an alkyl group or an aryl group.

In organic synthesis, quaternary ammonium salts are employed as phase transfer catalysts (PTCs). Such catalysts accelerate reactions between reagents dissolved in immiscible solvents. The highly reactive reagent dichlorocarbene is generated via PTC by reaction of chloroform and sodium hydroxide.

QACs are widely used as ingredients in industrial applications and find widespread use in household products, including fabric softeners, detergents, disinfectants, preservatives, and a range of personal care products.

Current concern that the increased use of such biocides in consumer products might contribute to the emergence of antibiotic resistance has led us to examine the effects of a QAC-containing domestic cleaning fluid on the population dynamics and antimicrobial susceptibility of domestic sink drain biofilm communities. QAC susceptibilities of numerically dominant, culturable drain bacteria were determined in vitro before and after repeated QAC exposure.

Quaternary ammonium compounds (QACs) are amphoteric surfactants that are widely used for the control of bacterial growth in clinical and industrial environments. Broad-spectrum antimicrobial activity and surfactant properties have made QACs such as benzalkonium chloride the favored hygienic adjuncts in disinfectant cleansing formulations, and they have been increasingly deployed in domestic cleaning products over the last decade

Majorly QACs are used as a raw material in pharmaceutical company, they are used to produce