Journal of Advances and Scholarly Researches in Allied Education
Vol. 13, Issue No. 1, April-2017, ISSN 2230-7540

A Study on Phase Transfer Catalysis and Its Scope

Pooja[1]* Dr. Piyush Kumar Pathak[2]

[1] Research Scholar, CTU, Ahmadabad

[2] Associate Professor, Department of Chemistry, CTU, Ahmadabad

Abstract – Catalysts and catalytic promoters played a very important role not only in the chemical process but also in all biochemical processes. The term "Catalysis" is known for its importance in process efficiency and product selectivity, starting from small-scale reactions to large scale industrial processes. Currently, catalysts are extensively exploited in all areas of chemical industries including petroleum, petrochemical fertilizers, polymers, fine chemicals, drugs and drug intermediates. Therefore, it is considered that the importance of catalysts in modern chemical industry is unaccountable and inevitable. Because, the catalytic materials has a tremendous economic impact and in turn reflected in growth of the concerned industries/laboratories.

Key Words: Phase, Catalysis, Chemical

- X -

INTRODUCTION

The catalysts are broadly classified into two categories viz., homogeneous catalyst and heterogeneous catalyst. A catalyst when present in the same phase as the reactants is called homogeneous catalyst. The catalyst which on the other hand, when present in the different phase from the reactants is said to be heterogeneous catalyst. In homogeneous catalysis, catalysts are spread throughout the reaction medium on a molecular scale and may be finally incorporated into the reaction products.

The major limitation of the process is difficulty in separation of the catalyst at the end of the reaction. In heterogeneous catalysis, the catalysts are in a different phase, generally solid phase to that of reactants which could be liquid or gas phase. The catalysts are insoluble and can be separated merely by filtrations at the end of the reaction. Further, they can be employed to perform the high temperature reactions.

Generally, it is well known that in all kinds of chemical reactions, collision is the essential condition for the progress of the reaction in heterogeneous system to get the desired product. However, in the early period, the main problem faced by chemists was to conduct the reactions effectively between water soluble ionic reactants and organic soluble reactants. Normally, these types of immiscible reagents react very slowly6 due to the intrinsically low solubility of the reagents located in two different phases. This important problem has been solved traditionally by applying high agitation speed7 or by employing cosolvents8. The increase of agitation speed is also involved the electrical and mechanical energy loss. Similarly, the additions of protic cosolvents like alcohols are led to decrease the rate of the reaction due to the formation of hydrogen bond with reactants, and also the work-up procedure becomes intricate.

Liquid-liquid phase transfer catalysis consisting of two phases, an organic phase containing a liquid reagent (RX) immiscible with water and an aqueous phase containing a nucleophilic reagent (Nú) and the quaternary onium catalyst (Q+X −). The general mechanism proposed by Starks involves two steps, viz., the transfer of nucleophile from aqueous phase to the organic phase via the intermediable of the positively charged moiety (Q+) of the onium salt either preferentially or totally portioned in the organic phase and the reaction of oleophilic water insoluble reagent (R-X) with the transferred water soluble nucleophile whose reactivity is magnified by oleophilic environment. Therefore, the success of the reaction is not strictly dependent on the partitioning of the onium salt between organic and aqueous phase, but depends on the capability of the salt interacting with hydrophilic anion in order to transfer this in the organic phase and of making the transferred anions available in highly reactive form in the lipophilic phase.

PHASE TRANSFER CATALYSIS AND ITS SCOPE

When sodium cyanide was mixed with octyl chloride no product was observed even after prolonged time even though the former one is soluble in water. But on introduction of catalytic amount of quaternary ammonium chloride, an exchange occurs in the aqueous phase between Na^+CN^- and $Bu_4 N^+ Cl^-$. The ion-pair $Bu_4 N^+CN^-$ due to presence of 16 carbons of the quaternary ammonium ion, it transfers into organic phase where the reaction takes place.

According to the interfacial mechanism, a molecule of an organic substrate, for example phenyl acetonitrile in the organic phase located near the interface is deprotonated by the hydroxide ion which is also available near the interface but within the aqueous phase. An ion-pair $[Na^+ R^-]$ is thus formed at the boundary and as such is insoluble in both phases. The anchored $[Na^+ R^-]$ remains at the interface until the catalyst cation organic phase in the form of a new ion pair $[Q^+R^-]$. The quaternary counter ion X^- is simultaneously liberated into the aqueous phase. Finally, $[Q^+R^-]$ reacts with alkyl halide substrate RY to give the product i.e. R-R ' and the $[Q^+Y^-]$ thus formed may reenter into another cycle of catalytic process.

Solid-liquid PTC consists of reaction occurring between an organic reagent soluble in a solvent and a solid substrate insoluble in this solvent. Co-extraction of water in liquid- liquid PTC has created a negative influence on certain reactions and can even fully suppress them23-26 . The employment of SL-PTC can make this problem less burdensome. The most important role of a complexant M^+Y^- such as crown ethers27, 28, cryptands29 or chelant30 in solid-liquid PTC is to bind the cation of a salt, as a result solubilizing the salt in liquid phase along with increasing the nucleophilicity of anion. To cite an example, potassium permanganate is added into a benzene medium containing an olefin. Under these conditions, the crystals of potassium permanganate remain at the bottom of flask, the solvent remains colourless and the reaction does not occur. If a catalytic amount of 18-crown 6 is added to the reaction mixture, then the solvent immediately turns purple which means the permanganate dissolved in the system and the olefin gets smoothly oxidized. The complexants first used were crown ethers prepared by Pedersen27 which showed high complexing abilities of alkali and alkaline earth cations. Solid-liquid phase transfer catalysis using complexants is still hampered by high cost of catalysts like crown ethers or cryptants. In some cases, the presence of water is strictly avoided when the reactions are conducted with a quaternary onium catalyst under solid-liquid conditions.

Reaction occurs in the immobilized liquid phase with continuous transfer of products and reactants between gas and liquid phases. Crown ethers, cryptants, phosphonium salts and polyethylene glycols (PEG) were used as PTCs because they increase the anion transfer into organic phase and thus enhances the activities. Even though the efficiency of PEGs is lesser than that of other PTCs, they are more pertinent in gas-liquid PTC because they are not toxic and the cost is very less. They form complex with alkaline metal cations and therefore can solubilize the related solid reagents into supported liquid phase, making them more readily available for reactions. Numerous reactions had been carried out by following the GL-PTC technique.

Similar to quaternary onium salts, the activity of macrocyclic ethers is high and is dependent on the structure. The known examples like crown ethers and cryptands (PTC catalysts) were first prepared by Pederson and Lehn et al. These catalysts have a tendency to complex with various ions and molecules and are one of the most important achievements in modern organic chemistry. The steady increasing interest of macrocyclic PTCs can be attributed to their unique properties viz., specific complexation of metal salts, ionic or neutral, organic and inorganic molecules; the ability to transfer ionic reagents from aqueous or solid phases to organic phases.

Open chain polyethers and single chain polyethers are used in displacement reactions and borohydride reductions. They are more stable than quaternary ammonium salts, but lower activity. It is very often used to carry out rare organic reactions. When a larger quantity of catalyst is used, it has not caused any problems.

DISCUSSION

Phase transfer catalysis has been a very fascinating area of current research interest to the chemists all over the world. It has been well recognized as a general and versatile technique applicable not only in organic chemistry56 but also a broadly useful tool in several other areas of chemistry viz., inorganic chemistry57, electrochemistry58, photochemistry59, heterocyclic chemistry60, industrial chemistry61, medicinal chemistry62 and especially in polymer chemistry63. The field of PTC has grown-up spectacularly over the past few decades, paving many new applications in the chemical, fine chemical and pharmaceutical industries. PTC finds applications in a variety of reactions. Primary applications are in nucleophilic substitution reactions64 and in reactions in the presence of bases involving the deprotonation of moderately and weakly acidic organic compounds. Typical reactions where PTCs employs as catalysts include, alkylation65, displacements reactions64, oxidation66, transition metal co-catalyzed reactions67 (carbonylation, reduction and hydrogenation), condensations68, carbene reactions15, additions69, polymerization70 , dehydrohalogenation71 , and so on, which are often part of a multi-step synthetic process for the manufacture of fine chemicals. The following examples explain some of the important reactions catalyzed by phase transfer catalysts exclusively in organic chemistry.

Dihalocyclopropanes are valuable compounds for the synthesis of cyclopropane derivatives and other pharmaceutically valuable products which can be obtained by the addition of dihalocarbenes to the double bond of olefins. Dihalocarbenes are very useful intermediate neutral molecules having divalent carbon atoms with two unshared electrons. They are normally synthesized by the reactions of strong bases with organic polyhalides of compounds which have no hydrogen on β-carbons, and therefore cannot undergo the usual β-elimination reactions. The base abstract the protons from the halogen attached carbon atom (α-elimination) resulting in the formation of trihalocarbanions (-CX3) which then loses halide ions to form carbenes. Doering et al72 have stated that dihalocarbenes can be added easily to various olefins in the presence of t-butoxide in t-butyl alcohol to form cyclopropane derivatives in high yields. In these reactions, normally, dihalocarbene undergoes hydrolysis easily in the presence of water; hence, vigorous anhydrous conditions are required which in turn results in low yield of addition product. On the other hand, when PTC is added, the obtained yield of addition product is increased to 60-70 percent.

C-alkylation is one of the most widely studied PTC reactions which provide pharmaceutically valuable products or intermediates for the synthesis of perfumes, fragrances and plant production agents 82 . This is very important for the preparation of organic compounds to build up the carbon skeleton in organic reactions. The C-H covalent bond is very strong and it is not easily dissociated into a proton and carbanion in hydrocarbons. Hence, to deprotonate the C-H bond very strong base is used to inactivate hydrocarbons. On the other hand, the C-H bond must be activated by strong electronwithdrawing groups to stabilize the carbanion to be formed. PTC is a facile and convenient technique for alkylation of a large number of carbanions.

In the same way, phase transfer catalyzed N-alkylations of nitrogen heterocycles viz., pyrrole, carbazole, imidazole, and benzotriazole were documented in literature. Nalkylation of other relatively strong NH acids such as sulfonamides, imides, or cyanamide as well as less acidic diarylamines, amides, etc., also belongs to this category of processes. Purines were commonly N-alkylated under PTC conditions. 3,7-dimethyl-1H-purine2,6(3H,7H)-dione 6-Chloro-9H-purine79 was reacted with 1-bromopropane in the presence of PTC and NaOH at 70oC and produced 3,7-dimethyl-1-propyl-1H-purine-2,6(3H,7H)- dione 104 with 100% yield. Chloropyrazole and piperazine derivatives were N-alkylated with dibromobutane using DMF and tetrabutylammonium salts and the desired product was obtained in 95 % yield108.

CONCLUSION

Acetanilide was alkylated by a variety of alkylating agents with various leaving groups (including iodide) in the presence of BTEAC, 50 % aqueous NaOH and benzene to yield the N-alkylated product109 . Benzamide110 was dialkylated under SolidLiquid PTC conditions and dibutyl benzamide was obtained in 98 % yield in the presence of NaOH/K2CO3, Bu4N +HSO4 - and toluene. The polymerization employing water soluble initiators such as K2S2O8, (NH4)2S2O8, KHSO4 etc., along with phase transfer catalysts is a relatively new area of research and has become an attractive and fascinating field of research to the chemists in view of enhanced reaction rates and polymerization at lower temperatures. Further, water soluble initiators such as potassium peroxydisulphates (PDS) and ammonium peroxydisulphates offer some advantages over the conventional organic soluble initiators like benzoyl peroxide (BPO) α, αand ’-azabisisobutyronitrile (AIBN). They are more stable and also eliminate the storage and handling problems normally associated with organic soluble initiators.

REFERENCES

1. J.J. Berzelius (2016). Ann. Chim. Phys., 61, pp. 146.

2. H.U. Blaser, A. Indolese, A. Schnyder (2010). Curr. Sci., 78, pp. 1336.

3. R.A. Sheldon, Ven Bekkum (2011). Fine Chemicals through Heterogeneous Catalysis, Wiley-VCH, Wilhelm, New York.

4. J.P. Mikkola, P. Virtanen, H. Karhu, T. Salmi, D.Y. Murzina (2016). Green Chem., 8, pp. 197.

5. K. Anderson, P. Goodrich, C. Hardacre, D.W. Rooney (2013). Green Chem., 5, pp. 448.

6. C.M. Starks (2011). J. Am. Chem. Soc., 93, pp. 195.

7. F.M. Menger (2010). J. Am. Chem. Soc., 92, pp. 5965.

8. A. Bhattacharya (2015). Ind. Eng. Chem. Res., 35, pp. 645.

9. T. Balakrishnan, S. Hari Babu, A. Perumal (2010). J. Polym. Sci.: Part A: Polym. Chem. 28, pp. 1421.

10. J. Dockx (2013). Synthesis, 441.

Corresponding Author

Pooja*

Research Scholar, CTU, Ahmadabad