

The Basic Principle of Phase-Transfer Catalysis, Some Mechanistic Aspects and Important Applications

Senthamizh Selvi, R¹, Nanthini, R² and Sukanyaa, G³

Abstract - Phase-transfer catalysis (PTC) has been widely used for the synthesis of organic compounds for more than three decades. Phase transfer catalysis (PTC) uses catalytic amounts of phase transfer agents which facilitate interphase transfer of species, making reactions between reagents in two immiscible phases possible. PTC is used widely in the synthesis of various organic chemicals in both liquid-liquid and solid-liquid systems. The scope and mechanistic features of PTC have been the aim of numerous studies. The use of PTC combined with other rate enhancement techniques like sonochemistry, microwaves, electroorganic synthesis, and photochemistry, is being increasingly explored. Applications in this area in the manufacture of organic intermediates and fine chemicals seem almost unlimited.

Intex Terms - Phase-transfer catalysis, important applications

1. INTRODUCTION

Since its introduction around 1965, phase transfer catalysis (PTC) has become a firmly established technique in synthetic organic chemistry[1]. Many reviews on synthetic methods using phase transfer catalysts have been published (Brandstrom, 1977; Dehmlow and Dehmlow, 1993; Weber & Gokel, 1977; Starks, 1994; Freedman, 1986). One of the major concerns in using a phase transfer catalyst (PTC) in soluble form is its separation from the reaction mixture. For efficient use of the catalyst and to meet product purity requirements, synthetic techniques using PTCs involve an additional separation for catalyst isolation and product purification[2-4].

There are many desirable reactions which cannot be brought about because of the reactants are inaccessible to each other. The crucial difficulty of bringing together a water soluble nucleophilic reagent and an organic water insoluble electrophilic reagent has been traditionally solved by the addition of a solvent that is both water-like and organic-like (such as ethanol, which derives its hydrophilic nature from its hydroxyl group and its lipophilicity from the ethyl group)[5]. The transfer rate is very high by increasing the area of the interface[6]. Phase-Transfer Catalysis (PTC) is a well-known method of promoting reactions between reagents with opposite solubility preferences. In such systems each reactant is dissolved in the appropriate solvent. Commonly, the two solvents are immiscible to one another, and then a phase-transfer catalyst is added to facilitate the transport of one reactant into the other phase. By means of the catalytic step, the enhanced reactivity between the ionic species leads to increase of the rate of the desired reaction. The foundations of PTC were laid in the late 1960s and early 1970s from the studies of Makosza(1975), Starks(1971), and Brandstrom(1977). Starks is believed to have coined the phrase phase transfer catalysis, and although some would tend to disagree with calling the PT cycle a catalytic process in the true sense of the word catalysis, the terminology has been well established and stays, especially since only catalytic amounts of the phase-transfer agents are required for effective phase-transfer action.

2 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.

1. *Senthamizh Selvi R*
Easwari Engineering College,
Department of Chemistry,
Ramapuram, Chennai-600 089, India
2. *Nanthini.R*
Postgraduate and Research Department of
Chemistry, Pachaiyappa's College,
Chennai-600 030, India.
3. *Sukanyaa G*
Queen Mary's College for Women (Autonomous),
Chennai-600 005, India
Email: senthamizh1980@gmail.com

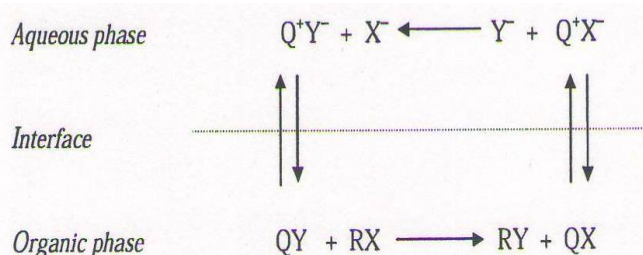
3 PRINCIPLE OF PHASE-TRANSFER CATALYSIS

The principle of phase transfer catalysis (PTC) is brought forth well by Reuben and Sjöberg (1981). 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. Thus, reaction is made possible by bringing together the reagents which are originally in different phases. However, 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[7].

4 MECHANISMS OF PTC

The mechanism of PTC reaction was first proposed in 1971[8]. According to Starks' original work, 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^+Y^-) 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 below:



A prerequisite for a substance to function as a PT-Catalyst is to form ion-pairs soluble in the organic phase and to be transferred in a highly active state[9,10]. Other mechanisms that can be considered as phase-transfer catalytic are:

4.1 PTC of uncharged species: complexation and transfer of uncharged protic species or metal salts into the organic medium as complexes of the phase-transfer agent[11].

4.2 Electron-transfer catalysis for Redox systems[12-15].

4.3 Metal ion-transfer from aqueous solutions into water-immiscible ionic liquids containing neutral complexing agents[16].

4.4 Pyrolytic alkylation process, whereby thermal decomposition of a quaternary ammonium salt yields a volatile alkyl derivative in the heated injector of a gas chromatography[17].

5 APPLICATIONS OF PTC

PTC finds applications in a variety of reactions.

- Applications involving the use of a co-catalyst include co-catalysis by surfactants (Dolling, 1986), alcohols and other weak acids in hydroxide transfer reactions (Dehmlow et al., 1985, 1988), use of iodide (traditionally considered a catalyst poison, Hwu et al., 1992; Yeh et al., 1988), or reactions carried out with dual PI' catalysts (Szabo et al., 1987; Tsanov et al., 1995; Savelova and Vakhitova, 1995; Jagdale et al., 1996) 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 K_2CO_3 can be used instead of toxic alkali metal alkoxides, amides, and hydrides.
- PTC can also be used for the synthesis process for fine chemicals manufacture. (agro-chemicals, pharmaceutical, dyes, paper, and so on) industries (Lindbloom and Elander, 1980; Reuben and Sjöberg, 1981; Freedman, 1986; Starks, 1990; Sharma, 1997).
- Perfumery and Fragrance Industry like Synthesis of phenylacetic acid, an intermediate in the perfumery industry (Cassar et al. 1976).
- In the field of Pharmaceuticals like Synthesis of various drugs like dicyclonine, phenoperidine, oxaladine, ritaline, etc. (Lindbloom and Elander 1980).
- 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[18-20].
- However, the main disadvantages of PTC, especially in commercial applications, are the need to separate the catalyst from the product organic phase.

6 CONCLUSIONS

In recent years, a lot of research has gone into developing new techniques for reaction rate enhancement. Usually, these techniques are more chemistry-intensive than what traditionally chemical engineers have been used to. The present paper has thus concentrated on the methods of modelling PTC reactions, using both soluble and immobilized forms of the catalyst.

7 REFERENCES

- [1] W.P.Weber and G.W.Gokel, *Phase Transfer Catalysis in Organic Synthesis*, Springer-Verlag Berlin Heidelberg, 1977.
- [2] Sridhar Desikan and L.K.Doraiswamy, *Chemical Engineering Science*, 55, pp.6119-6127, 2000.
- [3] A.Brandstrom, *Advances in Physical Organic Chemistry*, 15, 267, 1997.
- [4] C.M.Starks, *Phase Transfer Catalysis*, New York: Chapman & Hall. 1994.
- [5] D.H.Wang and H.S.Weng, "Preliminary Study on the Role Played by the Third Liquid Phase in Phase Transfer Catalysis" *Chemical Engineering Science*, 43, 209, 1988.
- [6] C.A.Bunton, In: *Surfactant Science Series*; M.Gratzel, Kalyanasundaram Eds, Marcel Dekker, Inc.: New York, 38, 1991.
- [7] A.Brandstorm, "Principles of Phase Transfer Catalysis by Quaternary Ammonium Salts," *Advances in Phy. Org. Chem.*, 15, 267, 1977.
- [8] C.M.Starks, *J.A.C.S.*, 93, 195, 1971.
- [9] C.De Rooter, R.Otten, U.Brinkman and R.Frei, *J. Chromatography*, 436, 429, 1988.
- [10] H.J.Glatzer and L.K.Doraiswamy, *Chemical Engineering Sciences*, 55, 5149, 2000.
- [11] Y.Sasson and R.Neumann, In: *Handbook of Phase Transfer Catalysis*, Blackie Academic, Glasgow, 1997.
- [12] G.Rothenberg, G.Barak and Y.Sasson, *Tetrahedron*, 55, 6301, 1999.
- [13] T.Endo, Y.Saotome and M.Okawara, *J.A.C.S.*, 106, 1124, 1984.
- [14] K.K.Park, C.H.Oh and W.K.Joung, *Tetrahedron Letters*, 34, 7445, 1993.
- [15] M.P.Jensen, J.A.Dzielawa, P.Rickert and M.L.Dietz, *J.A.C.S.*, 124, 10664, 2002.
- [16] M.Rompa, E.Kremer, B.Zygmunt, *Analytical Bioanalytical Chemistry*, 377, 590, 2003.
- [17] S.H.Chen, H.L. Wu, M.Tanaka, T.Shono and K.Funazo, *J. Chromatography, Part- A*, 507, 257, 1990.
- [18] S.Chen, S.Wu, H.Kou and H.Wu, *Analytical Toxicology*, 18, 319, 1994.
- [19] S.Jacobsson, A.Larson, A.Arbin, A.Hagman, *J. Chromatography*, 477, 329, 1988.
- [20] H.D.Meiring, A.P.G.Den Engelsman, J.M. de Jong, *J. Chromatography, Part-A*, 644, 357, 1993.