

1. GREEN CHEMISTRY: PART-I

1.1 INTRODUCTION

Chemistry has contributed many essential materials to our society such as food products, fuel, fertilizers, agrochemicals, medicines, cosmetics, dyes, paints, polymers, liquid crystals, biomolecules, and nanoparticles.

Chemists have synthesized numerous novel products such as polymers, tough ceramics, nonlinear optical substances, electronic materials, drugs, genetic materials and novel energy sources.

The process of synthesis of the materials on industrial scale by chemical reactions requires large amount of different reactants, reagents, solvents, acids, bases and catalysts. The industrial scale synthesis of these materials not only forms desired products but also generates undesired and harmful by-products which are major contributors to air, water and soil pollution. The biggest challenge must be faced by chemists is creation of sustainable future and conservation of natural resources. So, the synthetic chemists have responsibility to minimize environmental pollution by decreasing the harmful, unwanted by-products released in the process of synthesis of materials. During the last three decades chemists have been focusing on minimization of chemical pollutants.

The term "Green Chemistry" was first coined by **Paul. T. Anastas** in 1991 in the programme of United States Environmental Protection Agency (USEPA). Anastas is considered as the "**Father of Green Chemistry**" for his contribution in synthesis of chemicals and designing chemical processes which are safe and environmentally benign. The main aim of the green chemistry is to make the synthesis of chemicals and designing of chemical processes should lower the negative effects on human beings and our environment. It conserves the environment by cleaning up and inventing novel chemical methods which are economically feasible and environmentally friendly.

Another term for green chemistry is **sustainable chemistry**. There is a difference in green chemistry and environmental chemistry in protection of environment from pollution. Green chemistry focuses on designing chemical methods which can reduce pollutants i.e., it makes efforts to decrease generation of pollutants at source. Environmental chemistry studies the effect of chemical pollutants released into the natural environment.

Green chemistry is one of the basic and powerful tools to fulfil the 17 Sustainable Development Goals (SDGs) created by the United Nations in 2015, aim at utilizing natural resources in sustainable, environmentally friendly manner and conserving natural resources for future generations.

1.2 DEFINITION OF GREEN CHEMISTRY

“The invention, design, and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances” - IUPAC.

“The branch of chemistry and chemical engineering which utilizes a set of principles to reduce or eliminate use of hazardous substances or the generation of toxic products is called as green chemistry.”

1.3 NEED FOR GREEN CHEMISTRY

- Chemistry plays an important role in production of very essential materials to human life, and it is very important to the development of the world. But the designing of materials has released very large amount of chemical pollutants in to the environment and has led to the environmental pollution.
- Globally there is growing pressure from people, NGOs and government on chemists and chemistry-based industries to prevent release of chemical pollutants into the environment.
- There is a requirement of greener and cleaner processes to design materials to achieve the goals of sustainable development.

1.4 GOALS OF GREEN CHEMISTRY

The principles and rules of green chemistry are framed with the intention of achieving the following goals.

- Make efforts to better use of existing resources for the progress of designing a chemical process.
- Decrease waste produced in any chemical preparation or treatment of chemicals.
- Substances should be produced by better processes that reduce negative effects on the environment.
- Replacement of toxic reagents, intermediates, solvents and products with other chemical substances which have properties with less impact on the environment.
- Decrease the energy needed to produce desired substances by using much faster processes or replacing the energy source with low cost equally efficient renewable energies.
- Reduce toxicity of specified chemical substances.
- Minimize the costs by eliminating unnecessary steps in the preparation of a substance.

- Encourage all required actions to produce and use chemicals which are suitable for fulfilling goals of sustainable development.

1.5 BASIC PRINCIPLES OF GREEN CHEMISTRY

P.T. Anastas and J. C. Warner published twelve (12) principles of green chemistry in 1998 to reduce the effects of chemical substances on human health and environment by designing green chemistry methods for the preparation of materials. The principles are:



Fig. 1.5 Twelve principles of green chemistry

GREEN CHEMISTRY & NANOTECHNOLOGY

1. **Prevention of Waste:** It is better to prevent generation of waste at source than treating of waste later it is formed. The first important responsibility of chemists is to develop novel chemical processes to reduce the production of toxic waste substances.
2. **Atom Economy:** It measures conversion efficiency of chemical reaction in terms of incorporation of all the chemical substances involved in the formation of desired product. It is defined as the ratio of the total mass of atoms in the desired product to the total mass of atoms in the reactants.

$$\begin{aligned}\% \text{ Atom Economy} &= \frac{\text{Mass of atoms in desired product}}{\text{Mass of atoms in all the reactants}} \times 100 \\ &= \frac{\text{Molar mass of desired product}}{\text{Molar mass of all the reactants}} \times 100\end{aligned}$$



Here, A, B = Reactants

D = Desired product

W = Waste

$$\% \text{ Atom economy} = \frac{\text{Mass of D}}{(\text{Mass of A} + \text{Mass of B})} \times 100$$

$$\% \text{ Atom economy} = \frac{\text{Mass of D}}{(\text{Mass of D} + \text{Mass of W})} \times 100$$

The choosing or designing of reactions which incorporate more number of reactants in desired product have high atom economy and generate low waste. Atom economy is theoretical concept and measures the efficiency of a reaction based on the balanced equation.

E.g., atom economy of Diels-Alder reaction is 100% since all the atoms in reactants are incorporated in the product, cycloadduct.

3. **Less Hazardous Chemical Syntheses:** Chemical reactions and synthetic methods designed should generate the chemicals that have little or no toxic effect on human health and other components in the environment.
4. **Designing Safer Chemicals:** The principle is closely related with previous one. Chemists should aim to generate chemical substances that fulfil their role and effective in its functioning with negligible toxicity to humans. To fulfil the goal of this principle requires understanding of chemistry along with toxicology and environmental sciences.

5. **Safer Solvents & Auxiliaries:** The solvents, separation agents and other agents are extensively used in the chemical reactions. Generally, they are very volatile and toxic. These should be replaced by safer green solvents such as water, supercritical water, supercritical carbon dioxide, ionic liquids, etc. The designing of solvent free reactions which use surfaces or interiors of clay, zeolites, silica and alumina can eliminate toxicity due to solvent.
6. **Design for Energy Efficiency:** The chemical transformation of reactants to products needs energy. It is better to reduce energy required for the formation of products by designing reactions which take place at room temperature and normal pressure.
7. **Use of Renewable Feedstocks:** The petrochemicals which are derived from crude oil, have been used as starting materials in many chemical transformations. But crude oil is non-renewable and can be exhausted. The synthesis can be made sustainable by replacing non-renewable resources by renewable raw materials and feedstocks derived from biological sources.
8. **Reduce Derivatives:** The unnecessary formation of derivatives in chemical synthesis should be reduced or avoided if possible. It requires more amount of solvents and reagents hence it generates more waste. Generally protecting groups are used in chemical reactions to prevent transformation of a particular functional group. It can be replaced by enzymes which selectively targets certain part of a molecule.
9. **Catalysis:** Catalysts are superior to stoichiometric reagents. Catalysts are used in small amounts, can accelerate the reaction, can reduce reaction temperature, can reduce waste, and can enhance selectivity of a reaction. It is very crucial in chemical production in chemical and other industries.
10. **Design for Degradation:** Chemists should design the chemical products which should be degradable by water, UV light or microorganisms after fulfilment of their function. The chemical products should not accumulate and stay in environment but should be broken down into smaller harmless chemical species.
11. **Real-Time Pollution Prevention:** The real time monitoring of a chemical process taking place in laboratory or industry can detect release of harmful chemical substances or pollutants into the environment before accident occurs.
12. **Safer Chemistry for Accident Prevention:** This principle focuses on safety to the workers and surrounding areas located around chemical industry. Chemists should design the reactions which use chemicals that are not explode, light on fire, ignite in air, etc., in the formation of products. It is better to avoid highly reactive explosive chemicals in formation of products in chemical industries to avoid accidents.

1.6 GREEN SYNTHESIS

The synthesis which involves using of green starting materials, green reagents, green solvents and green catalysts to design benign, sustainable and ecofriendly materials is called as green synthesis.

Atom economy measures the efficiency of a synthetic process. More efficient reactions have high atom economy due to incorporation of more number of atoms of reactants in the product and generate less waste. Inefficient reactions have low atom economy due to incorporation of less number of atoms in the product and generate more waste. Generally, the high economy chemical processes are preferred over low atom economy processes.

1.6.1 100% Atom Economy Reactions

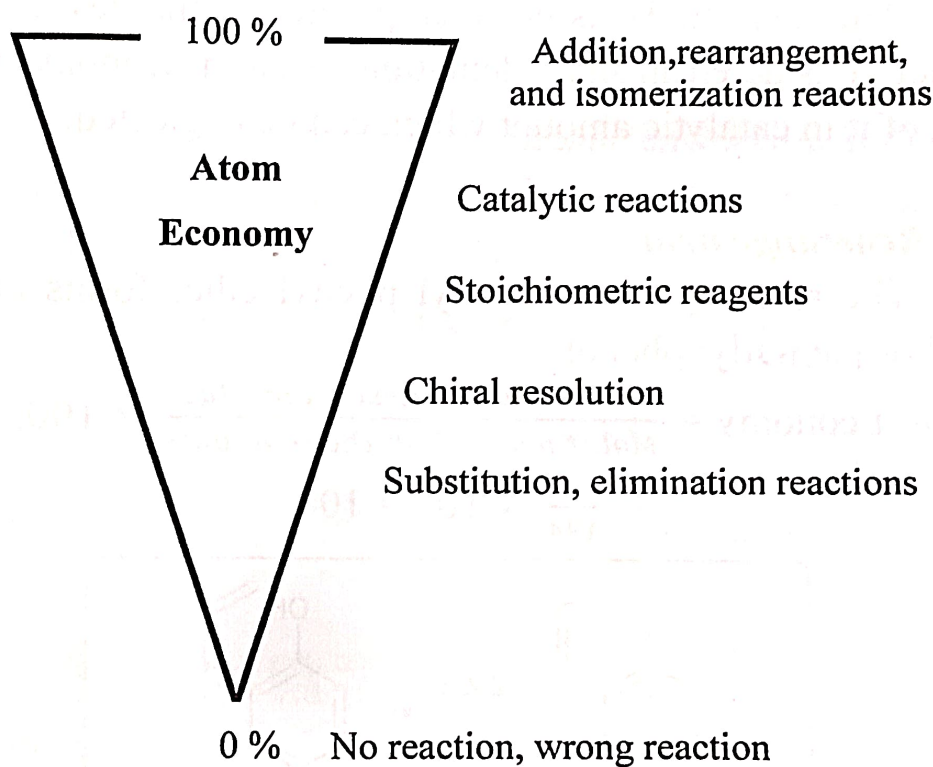


Fig. 1.6.1 Atom economy of reactions

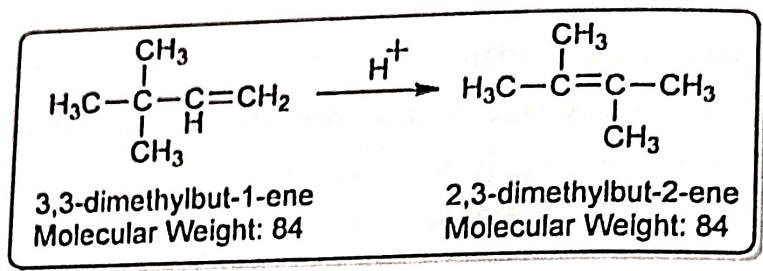
The ideal atom economy of a chemical process is 100 % where all the reactant atoms are found in the product. The addition, rearrangement, isomerization and pericyclic reactions have 100% atom economy since the reactions incorporate all the atoms of the reactants into the products.

1.6.1.1 Rearrangement Reaction

Rearrangement reactions involve reorganization of the atoms or groups of a molecule. Since all the reactant atoms are incorporated in the product, the atom economy of rearrangement reaction is 100%.

E.g., i) Acid catalyzed rearrangement of 3, 3-dimethyl-1-butene to 2,3-dimethyl-2-butene
 ii) Claisen Rearrangement.

i) Acid catalyzed rearrangement of 3,3-dimethyl-1-butene to 2,3-dimethyl-2-butene



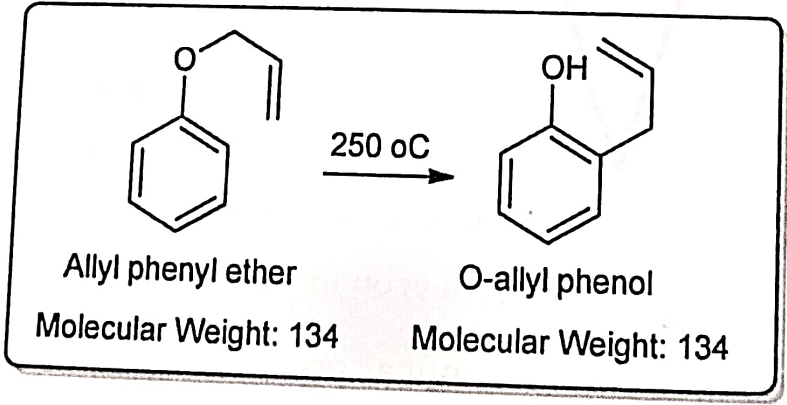
$$\begin{aligned}
 \% \text{ Atom Economy} &= \frac{\text{Molar mass of desired product}}{\text{Molar mass of all the reactants}} \times 100 \\
 &= \frac{84}{84} \times 100 = 100
 \end{aligned}$$

Although the H^+ is not incorporated in the desired product, it is not considered in the calculation of atom economy is due to taking of it in catalytic amount which can be neglected.

ii) Claisen Rearrangement

The rearrangement of allyl phenyl ether forms ortho-allyl phenol or para-allyl phenol.

$$\begin{aligned}
 \% \text{ Atom Economy} &= \frac{\text{Molar mass of desired product}}{\text{Molar mass of all the reactants}} \times 100 \\
 &= \frac{134}{134} \times 100 = 100
 \end{aligned}$$



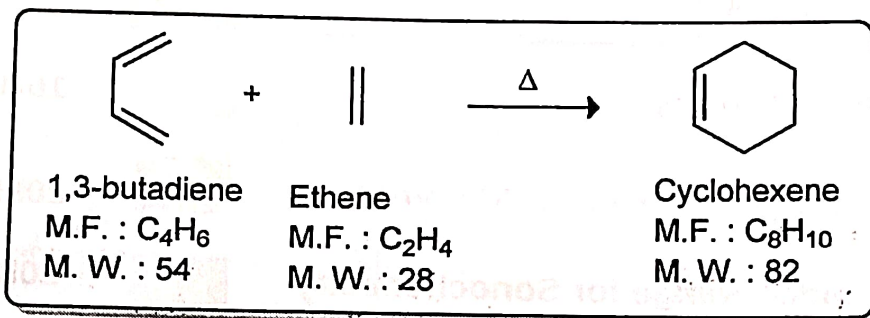
1.6.1.2 Addition Reaction

Addition reactions have 100% atom economy due to incorporation of all the reactant atoms in the desired product. Generally high atom economy addition reactions are preferred to low atom economy elimination and substitution reactions.

E.g., i) Diels-Alder reaction, ii) Addition of hydrogen halide to alkene

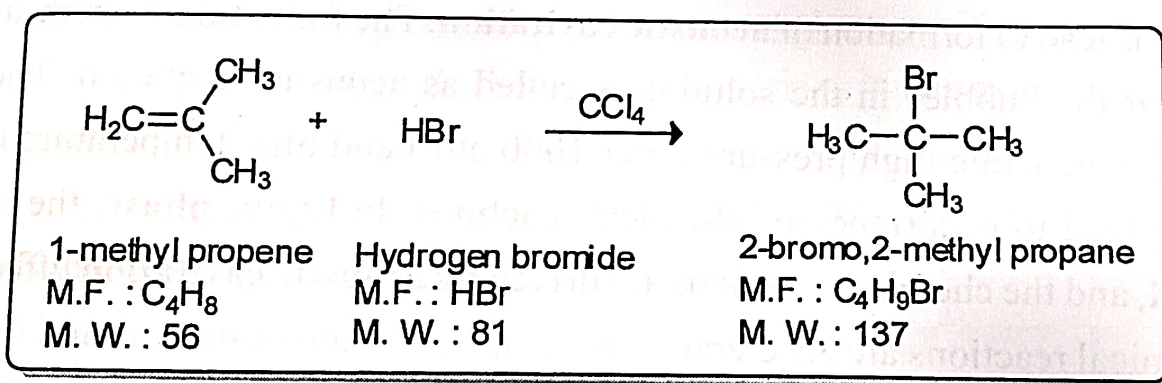
GREEN CHEMISTRY & NANOTECHNOLOGY

i) **Diels-Alder Reaction:** Diels-Alder reaction is a cycloaddition reaction between conjugated diene and dienophile which forms cyclohexene derivative. It incorporates all the atoms of the reactants into the desired product, so the atom economy of Diels-Alder reaction is 100%.



$$\begin{aligned}\% \text{ Atom Economy} &= \frac{\text{Molar mass of desired product}}{\text{Molar mass of all the reactants}} \times 100 \\ &= \frac{82}{(54+28)} \times 100 = \frac{82}{82} \times 100 = 100\end{aligned}$$

ii) **Addition of Hydrogen Halide to Alkene:** The addition of hydrogen bromide to methyl propene forms 2-bromo, 2-methyl propane. The reaction incorporates all the atoms of the reactants into the desired product, so the atom economy of the reaction is 100%.



$$\begin{aligned}\% \text{ Atom Economy} &= \frac{\text{Molar mass of desired product}}{\text{Molar mass of all the reactants}} \times 100 \\ &= \frac{137}{(56+81)} \times 100 = \frac{137}{137} \times 100 = 100\end{aligned}$$

1.6.2 Organic reactions by Sonication Methods

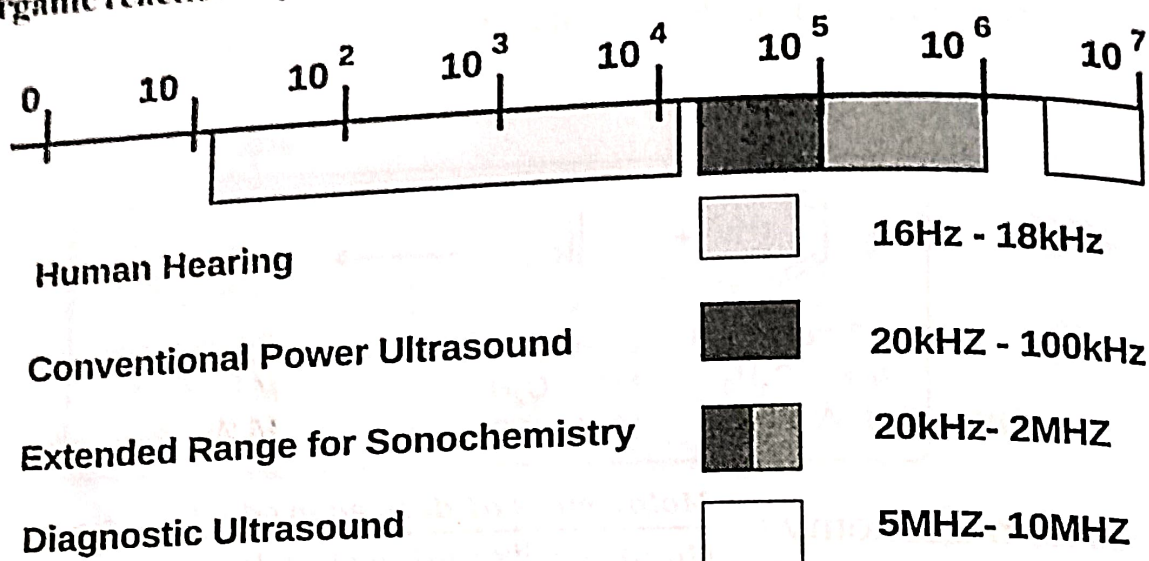


Fig. 1.6.2.a Sound frequency ranges

The sound waves of frequency greater than 20 kHz are called as ultrasonic waves. The frequency range of ultrasound is from 20 KHz to 10 MHz. The frequencies of ultrasound used in chemical reactions are about **20 KHz - 100 KHz**, which are significantly lower than that of medical applications (5 MHz – 10 MHz).

When sound waves are passed through liquid medium, series of compressions and rarefactions lead to formation of **acoustic cavitation**. The formation, growth, and implosive collapse of the bubbles in the solution is called as acoustic cavitation. The collapse of bubbles can generate high pressure (over 1000 atm) and high temperature (around 5000 K) which lead to occurrence of chemical reactions. In **liquid phase**, the molecules are **activated**, and the chemical reactions are driven by **acoustic cavitation** effect. Solid state sonochemical reactions are accelerated due to introduction of **defects** and increase in rate of **diffusion** of molecules.

Sonochemistry deals with the effect of ultrasound waves on chemical reactivity. It is a powerful green approach in organic synthesis. Chemical reactions which are induced by ultrasound are called as **sonochemical reactions**.

Generally, ultrasound accelerates a chemical reaction by more intimate mixing of reagents and enhances the efficiency and activity of an insoluble catalyst by increasing its surface area. The chemical reactions under ultrasound may also be accelerated because of generation highly reactive radical species during cavitation.

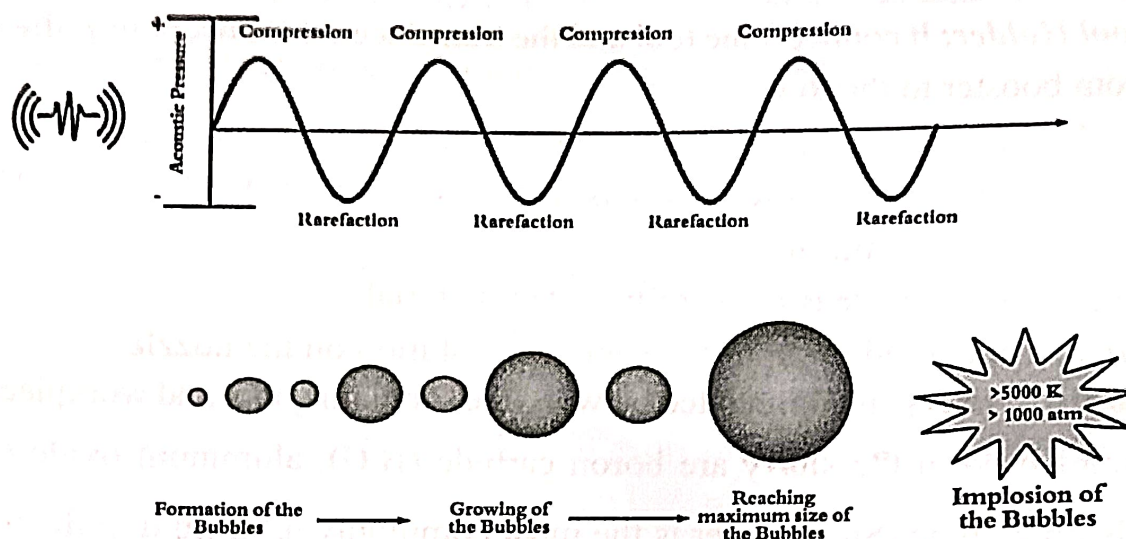


Fig. 1.6.2.b Sound propagation in a liquid showing cavitation bubble formation and collapse

Advantages of Sonochemical Synthesis

Sonochemical synthesis has several advantages over conventional synthetic methods. These are:

- It requires mild ambient temperatures and may protect thermally unstable reactants.
- The ultrasound enhances proper mixing and diffusion of reactants.
- The reactions have short reaction times.
- The reactions have high yield.
- It can generate unique and highly reactive high-energy intermediates.
- The energy efficiency of sonochemical reactions is about 100 times that of thermal or photochemical reactions.
- It can form physical extreme materials in molten or plasma state with minimum energy inputs.

1.6.2.1 Sonochemical Apparatus

An ultrasonic equipment consists of the following parts: Power source, piezoelectric transducer, booster, tool holder, tool, nozzle, abrasive slurry.

- **Piezoelectric Transducer:** It mainly consists of a cylinder which is made up of piezoelectric ceramic. It converts electrical or mechanical energy into sound energy and generates ultrasonic radiations by piezoelectric effect. They are mostly made of quartz or barium titanate.
- **Booster:** It amplifies the mechanical vibration generated by transducer and the amplified sound waves are supplied to tool holder (horn).

- **Tool Holder:** It connects the tool and the transducer. It transfers amplified vibration from booster to the tool.
- **Tool:** It must have high wear resistance and fatigue strength. The tool is made by tough, strong and ductile materials like brass, steel or stainless steel. Hammering is done by using this tool.
- **Nozzle:** The nozzle is made of tungsten material.
- **Pumps:** It is used to supply the abrasive solution on the nozzle.
- **Abrasive slurry:** It is circulated between the oscillating tool and workpiece. Abrasive grains used in the slurry are boron carbide (B_4C), aluminum oxide (Al_2O_3) and silicon carbide (SiC). Water is the most commonly used fluid in the formation of slurry.

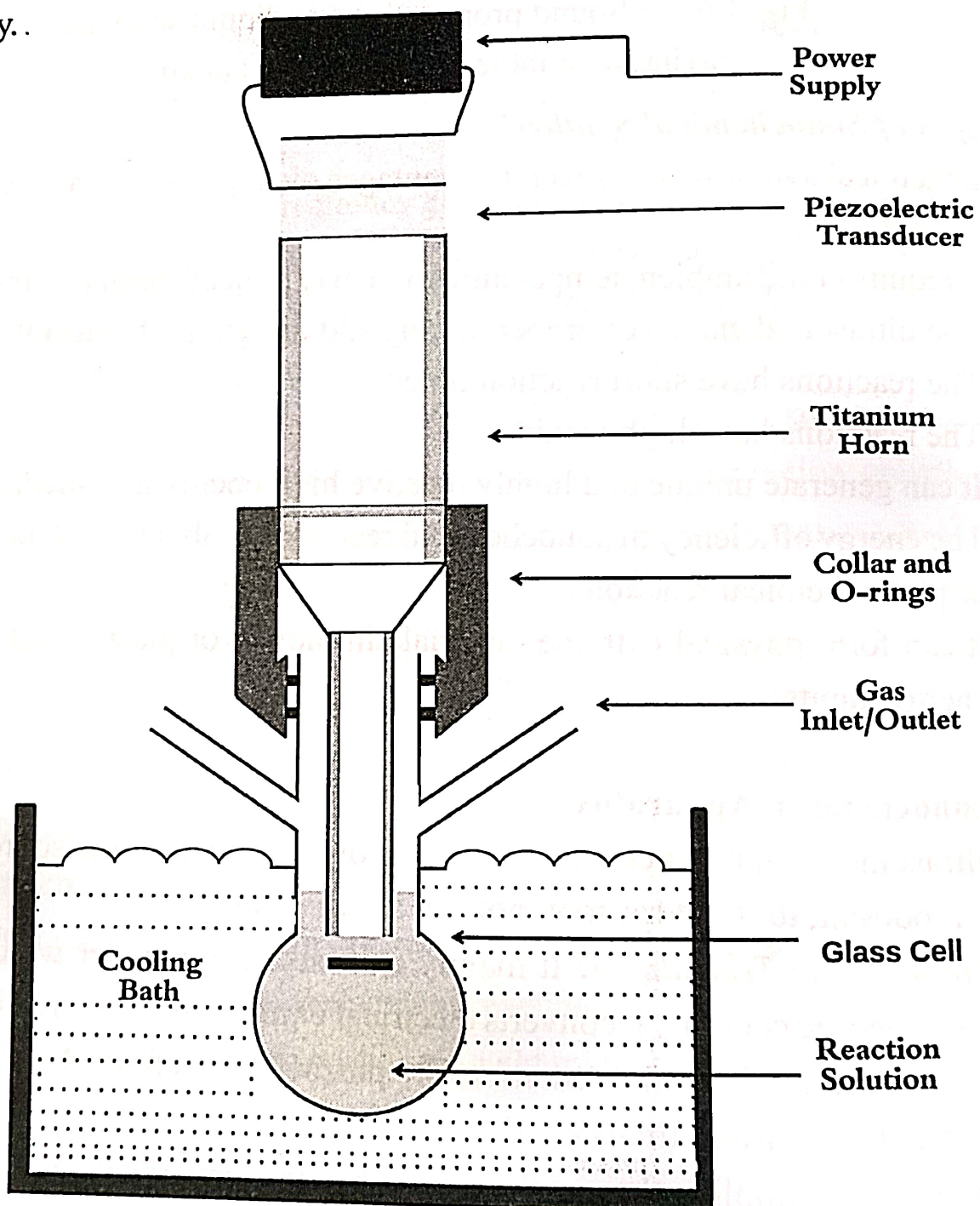
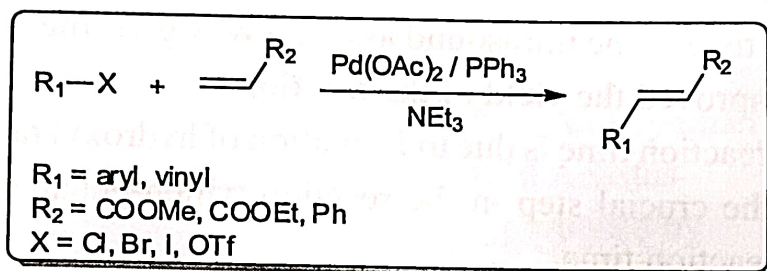


Fig. 1.6.2.1 Sonochemical Apparatus

1.6.2.2 Sonochemical Reactions

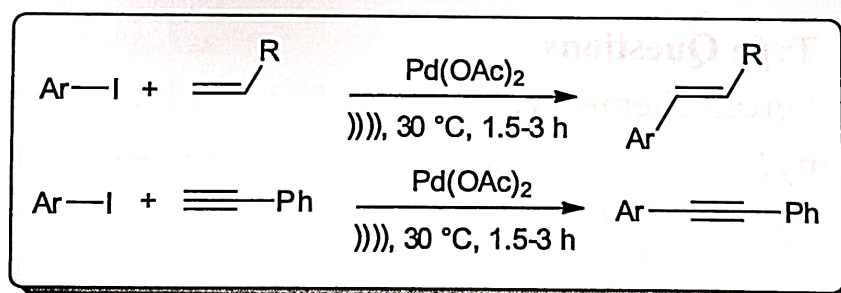
1.6.2.2.1 Heck Reaction

Conventional Heck Reaction: It is a palladium catalyzed C-C cross coupling between aryl halides or vinyl halides (or triflates) and activated alkene in the presence of base and ligand. It is carried out generally in polar aprotic solvents (DMF, NMP).



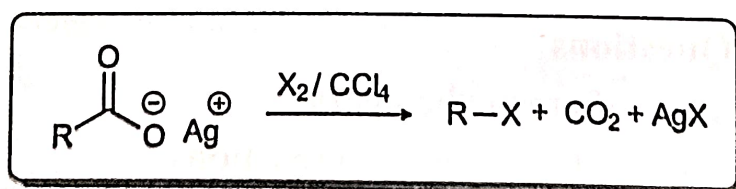
Sonochemical Heck Reaction: The ultrasound assisted Heck reactions are performed in ionic liquids. It has many advantages over the conventional method, these are:

- The conventional reactions take long reaction times (8-72 h) and occur at high temperature (80-140 °C). The ultrasound assisted reactions take short reaction times (1.5-3 h) and occur at ambient temperature (30 °C).
- The conventional reactions form mixture of E and Z alkenes, while the ultrasound assisted reactions completely form E alkene.
- The ultrasound assisted method doesn't require phosphine ligands.



1.6.2.2.2 Hunsdiecker Reaction

The decarboxylation of silver salts of carboxylic acids to alkyl halides by treating with halogen is known as Hunsdiecker reaction.



1.6.2.2.3 Wittig Reaction

The reaction of an aldehyde or ketone with phosphonium ylide forms an alkene and a phosphine oxide. It is known as Wittig reaction. The Wittig-Horner reaction is a modification of Wittig reaction which forms functionalized olefins such as acrylates or acrylonitriles from aldehydes.

Although good yields are obtained in the conventional Wittig-Horner reaction, it suffers from long reaction times. The ultrasound assisted Wittig-Horner reaction has short reaction time and it has improved the yield of the reaction.

The shortening of reaction time is due to formation of hydroxyl radical by sonolytic cleavage of water. It is the crucial step in the reaction which enhances the rate of the reaction and reduces the reaction time.

