

NEW ASPECT AND PERSPECTIVE OF GREEN CHEMISTRY FOR SUSTAINABLE ERA

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ABSTRACT

Green chemistry is placed in the frontier areas of research to design the processes that reduce or eliminate the use and generation of hazardous substances. It is accepted that most of today's industry is unsustainable by design so there is an urgent need for more environmentally acceptable processes in the chemical industries. Green chemistry launch new technologies that are cleaner and economically competitive rather than accepting waste generation and disposal as unavoidable. Green chemistry provides 12 green paths for different synthetic routes using non- hazardous solvents and environmental- friendly chemicals.

Keywords : Photochemistry, Electrochemistry, Sonochemistry, Microwavechemistry Atom economy.

INTRODUCTION

Green Chemistry is defined as environmentally benign chemical synthesis which is based on non regulatory and economically driven approach to achieving the goals of environmental protection by generation of non-hazardous substances. It describes an area of research arising from scientific discoveries to reduce pollution and covers the following areas:

- Development of environmentally improved routes to synthesize products.
- Use of sustainable resources, biotechnology, alternative and innovative technology for industrial processes.
- Design of new green chemicals

The modern civilization it is unimaginable to improve and maintain our current standard of living, without the myriad product of industrial organic synthesis Society has come to depend on the products of the chemical industry and pharmaceutical

industry.^{1, 2,3}

Chemists envisioned chemistry as the solution to a host of society's needs. Indeed, they created many things which improve the quality of life on earth like dyes, plastic, cosmetics and other materials. At the same time chemistry brought about medical revolution through antibiotics which cure infection disease. But there are some adverse outcome due to discovery of drugs, insecticides, herbicides, fertilizers etc. because these cause a cancerous grip on air, water, soil and noise pollution on earth that grabbed this world like an octopus, e.g. DDT which accumulated in birds, and causes egg shell thinning and nesting failures results in decline of that species. Refrigerant like CFCs (chloroflorocarbons) depletes the ozone layer remarkably which protects our earth from harmful UV rays of sun.^{4,5} According to the WHO report, about 10 to 15 % of the total population of India is suffering from common cold, bronchitis, asthma, hay fever; these diseases are airborne and spread the infection from several hundred kilometers under favorable conditions.^{6,7}

EMERGING GREEN TECHNOLOGY

Green chemistry involves modified engineering, practices, bioremediation, ecofriendly reaction media and concept of atom economy leading to almost zero waste. It differentiates the grey synthetic processes with that of green natural processes having strategic objectives with social and environmental benefits.⁹ Green strategies include the replacement of organic solvent by water, elimination of a solvent, if possible, the substitution of substances which are less or non- toxic to replace toxic heavy metals, development of solid support reagents and catalysts for synthesis, launching of ecofriendly methods for organic synthesis, designing of products, which can be recycled or safely disposable and use of dry media reactions and many other important aspects. Green products should be synthesized by environment friendly techniques.¹⁰ Emerging techniques, in the overall development of "Green Chemistry" can be categorized in the following parts:

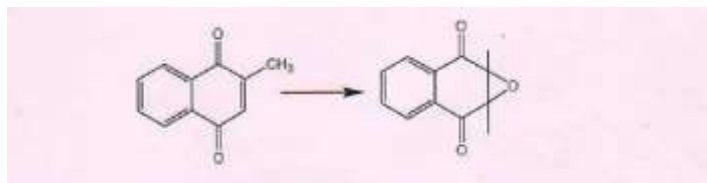
(1) Photochemistry

Photochemistry is the study of reactions that are brought about by visible or Ultra- Violet light. Most common example of photochemical reaction is photosynthesis in the plants by means of sunlight.¹¹ According to Stak - Einstein law when a photon is absorbed by a molecule or atom it must transfer all its energy to atom or molecule and promoted to higher energy state.¹²

Some examples of reactions that furnish by light

- Solar energy is used for isomerisation, catalytic cyclisation and purification of water.¹³
- Dithianes, benzyl ethers and related other compounds have been cleaved by the use of visible light with a dye.¹⁴
- Visible light was used in cyclization to produce substituted pyridines with almost no by products in combination with water.¹⁵
- In zeolites, oxidation of hydrocarbons with blue light gives improved selectivity.¹⁶

- In the presence of titanium dioxide, Photo oxidation of cyclohexane gave 85.4% cyclohexanone, 2.6% cyclohexane and 12% carbondioxide.¹⁷
- 1, 4-benzoquinone and aldehyde are used to produce Acylhydroquinones using Sun light. This process produces no by product salt, in contract to the usual acylation with an acid chloride.¹⁸
- Photo redox reactions can be carried out with semiconductors and irradiation of nitrobenzene in the presence of zinc oxide particles in alcohol produce phenyl hydroxyl amine in 73% yield.¹⁹



(2) Electrochemistry

Electrochemistry deals with the study of relationship between electrical and chemical energy and interconversion of one form of energy into another.

Application of electrochemistry

- The large volume application of electrochemistry in organic chemistry appears to be the hydrodimerization of acrylonitrile to form adiponitrilide (200000 tons / year) which is then reduced to the hexamethylenediamine or hydrolysed to adipic acid for the preparation of Nylon 66.²⁰
- It can be used to regenerate an expensive or toxic reagent.
- Electrochemistry is used to generate sodium hypiodite and sodium hydroxide continuously for the epoxidation of 2- methylnaphthoquinone and its yield is 100% and no waste is produced.²¹
- Electricity can be used in oxidation and reductions of reagents for example, when iodine is reduced to hydroiodic acid, no waste products are formed.²²
- Naphthalene can be oxidized to naphthoquinone with 98% selectivity using a small amount of cerium (III) that reoxidized to cerium (IV) electrically.²³
- Electrically Substituted aromatic compounds can be oxidized to the corresponding phenols with a platinum electrode in trifluoroacetic acid, triethylamine and methylene chloride.²⁴
- Hydrogenation of edible oils using a cell of electricity with a Nafion memberane with a ruthenium anode on one side and a platinum or palladium black cathode on the other produced less of the undesirable trans-isomers than conventional hydrogenations.²⁵
- Electrochemistry also provides a way to produce radicals and anions.²⁶
- The electrochemical hydrogenation of water immiscible olefins and acetylenes is enhanced by ultrasonication.²⁷

- Tetramethyl adipic acid is synthesized by direct carbon-carbon bond formation between the saturated primary carbon atom of pivalic acid using a sonoelectrical fenton process.²⁸
- Reduction of carboxylic acids, nitro compounds, nitrile, oxidation of aromatics and methyl aromatics has been widely reported.²⁹

(3) Sonochemistry

Ultrasound is defined as a frequency of sound, which is beyond human hearing i.e. above 16 KHz. Chemical reactivity of a system increases on irradiating it with power ultrasound. The study of effects of ultrasound on chemical reactivity is termed as sonochemistry. Some important applications of ultrasound in chemical synthesis are given as³⁰:



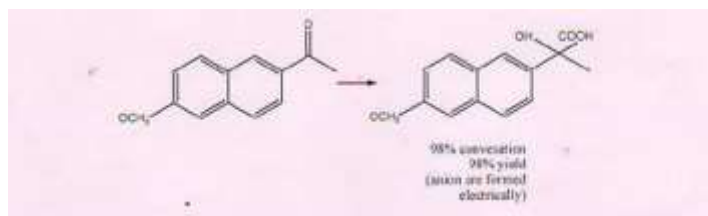
Other examples of sonochemistry based organic synthesis are addition reaction, oxidation, reduction, hydroboration, coupling reactions etc. have been reported.³⁰⁻³⁵ An improved synthesis of chalcones and ionic liquid under ultrasound irradiation has been reported.³⁶ The yields of chalcones were 52- 97% and 83-98% respectively with pulverized KOH and KF-Al₂O₃ catalysts in alcoholic solvent.³⁷ Ultrasound technique is also useful in treatment of various pollutants. Sonochemical degradation of toxic halogenated organic compounds and volatile pollutants in natural ground water have been reported.³⁸

(4) Microwave Chemistry

Microwaves region lies between infrared radiation and radio frequency of electromagnetic spectrum. The wave length ranges from 1cm to 1m. Frequencies of microwaves are similar to frequency of radar and telecommunication devices.^{39, 40}

Mechanism for microwave heating

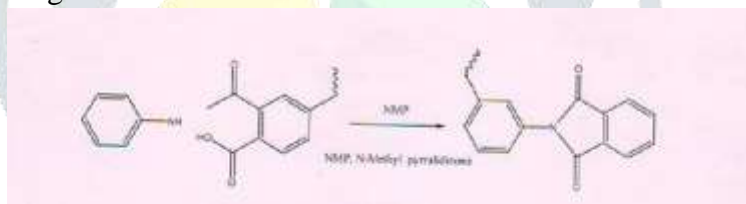
- Dipole rotation- Dipole rotation is an interaction between molecules and electric field in which polar molecules try to align with electric field. The strong agitation due to reorientation of molecules causes intense internal heating.⁴¹
- Ionic conductance- Irradiated sample is serves as electric conductor. The charge are moved through material under the influence of electric charge which cause polarization.⁴²



Applications

- Various types of reactions are conducted in microwave oven as 2,3-Dimethyl indole was obtained with 67% yield from phenylhydrazine and butane -2- one at 220 °C in min.⁴³

- Hydrolysis of benzyl chloride into benzyl alcohol takes 3 minute in microwave while same reaction takes 35 minute by conventional method.⁴⁴
- Various types of oxidation⁴⁵⁻⁴⁷ can be carried out in MW, e.g. with the use of organic solvent some organic reactions can be carried out in microwave like esterification of alcohol⁴⁸, esterification of benzyl ethers using LuBr_3 ⁴⁹, Fries rearrangement⁵⁰, orthoester claisen rearrangement⁵¹, Diels-Alder reaction, decarboxylation⁵², Chalcones synthesis and aziridine synthesis.^{52, 53}
- Hydrogenation of β -lactams using a hydrogen donor and Pd as catalyst has been described by Bose and co-workers.⁵⁴
- Hantzsch dihydropyridine synthesis and oxidation of β , β -disubstituted enamines over $\text{KMnO}_4/\text{Al}_2\text{O}_3$ is also reported to occur in MW within shorter time and high yield as compared to older method.^{55- 57}
- Thiadiazepines synthesis and carbohydrate glycosylations can be carried out in MW by using solvent.^{58, 59}
- Under solvent free condition, aromatic, aldoximes were converted to the corresponding nitriles in the presence of a molecular sieve type modified zeolite, Ersorb, in microwaveoven.⁶⁰
- The reaction of activated aryl halides with secondary amines in the presence of basic Al_2O_3 synthesized N-aryl amines under microwave irradiation in solvent free conditions is reported.
- A fast solvent procedure under microwave irradiation for the synthesis of melamine's is also developed using silica gel supported reagent.⁶²



(5) Atom economy

Atom economy is a smarter and advance version of percentage yield has discovered by the green chemistry⁶³. The aim of atom economy is to conduct chemical reaction where all the atoms that go into process come out either incorporated in the products or marketable side products. An atom economy is the ratio of formula weight of atoms utilized to the formula weight of all reactants in the reaction. For example

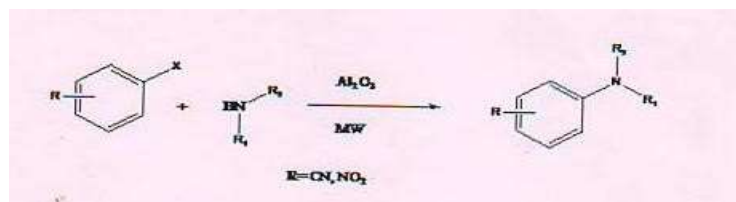
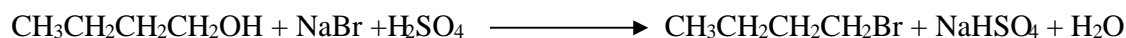


Fig. 6

% Atom economy = Formula weight of atoms utilized x 100 / Formula weight of all Reactants = $137 \times 100 / 275 = 50 \%$

Quantification of the waste generated in chemicals manufacturing was based on Environment factors (E factor). This attract the attention of chemical and pharmaceutical companies on the need for a paradigm shift from a concept of process efficiency, which was exclusively based on chemical yield, to one that is motivated by elimination of waste and maximization of raw materials utilization. The E factor has been widely adopted by the chemical industry and the pharmaceutical industry.

(6) Solvent

Solvents are used as a medium for many types of reactions but all solvent are not ecofriendly. Therefore, non-ecofriendly solvent requires to be omitted in used.⁶⁸ The organic chemists using different solvents for the various steps in multistep syntheses make recycling difficult. It was revealed that solvents were a major contributor to the E factors of pharmaceutical manufacturing processes. It has been estimated that ca 85% of the total mass comprises solvents involved in pharmaceutical manufacture^{69,70}. That's why pharmaceutical companies are focusing on their effort of minimizing solvent use or replacement of many traditional organic solvents, such as chlorinated and aromatic hydrocarbons, by more environmental friendly alternatives. The use of ethanol have the added advantage of being readily biodegradable and ethyl lactate produced by combining two natural products, is being promoted as an environmentally attractive solvent for chemical reactions. The problem with solvents is not in their use but in the inherent inefficiencies associated with their containment, recovery and reuse. The subject of alternative reaction media is also an important issue. It is important from both an environmental and an economic viewpoint: recovery and reuse of the catalyst. An insoluble solid, which is heterogeneous catalyst, is easily separated by centrifugation or filtration while a homogeneous catalyst presents more problems. The serious shortcoming of homogeneous catalysis is the separation of the catalyst from the reaction products and its quantitative recovery in an active form.

There is a definite need for systems that combine the advantages of high activity and selectivity of homogeneous catalysts with the easy recovery and recycling characteristic of their heterogeneous counterparts. This can be achieved by employing a different type of heterogeneous system, such as liquid – liquid biphasic catalysis, where the catalyst is dissolved in one liquid phase and the reactants and products are in a second liquid phase and then the catalyst is recovered and recycled by simple phase separation. In continuous reaction, the catalyst solution remains in the reactor and is reused with a fresh batch of reactants without further treatment. Various non conventional reaction media have been intensively studied including water, supercritical CO₂, fluoruous biphasic, and ionic liquids alone or in liquid – liquid biphasic combinations. The use of water and supercritical carbon dioxide as reaction media fits with the current trend

toward the use of biomass - based raw materials which are renewable and ultimately derived from carbon dioxide and water.

Water has many benefits as it is nontoxic, Green chemistry methods are simple, clean, fast and economic. These methods are very efficient tool for recovery and saving energy. They have wide application in the field of pharmacy such as qualitative and quantitative analysis, organic and medicinal compound synthesis, hydro distillation, drying, loss on drying determination etc. Chemist could find a very short response time and better yield as compare to gray methods. Therefore, it is concluded that green chemistry technique are cost effective and ecofriendly.

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