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A brief introduction to Green Chemistry

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Abstract: Incontrovertibly, chemistry not only plays an important role in our daily lives but also at the same time, chemical developments bring new environmental problems and harmful side effects. Green chemistry is defined as environmentally benign chemical synthesis. It is the utilization of a set of principles that reduces or eliminates the generation of hazardous substances in the process of manufacturing of chemical products and its uses. It is about waste minimization at source, use of catalysts in place of toxic excessive reagents. Use of solvent free recyclable resources is a noble practice to keep our environment free from hazards. The quest of green chemistry is the urgent need now a days. The green chemistry looks at prevention of pollution on the molecular scale. Today the green chemistry is an extremely important area of research as the use of chemical products is increasing sharply in our world. Through the use of green chemistry we can produce eco-friendly dyes, foods, design safer chemicals and safer solvents and auxiliaries etc. The adaptation of twelve principles of green chemistry developed by Paul T. Anastas and J. C. Warner is an important measure to keep our environment safe. The most applicative principle of green chemistry is - "It is better to prevent waste than to treat or clean up waste after it is formed." Green chemistry is not a solution to all environmental problems but the most fundamental approach to prevent pollution.

Keywords: Green Chemistry, Sustainable Chemistry, Recyclable, Bio-catalysis

1. Introduction

Green chemistry is also called „Sustainable Chemistry‟ is an area of chemistry and chemical engineering focused on the designing the products and processes that minimize the use and generation of hazardous substances. Green chemistry is sustainable in the sense that it serves the desires of today‟s generation without endangering the possibilities of future generations. The ecological term sustainability is always found in connection with Green Chemistry. It is also used in economic contexts. Green chemistry is more basically defined as the development and production of chemical products and the establishment of procedures that can replace the generation of dangerous products. It is well established issue that there is an increasing necessity for more environmentally acceptable process in chemical industry.

This trend is known as „Green Chemistry" [1-9]. Green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green Chemistry needs a standard shift from traditional concepts of process efficiency, that focus largely on chemical yield, to one that assigns economic value to eliminate waste at source and avoiding the use of toxic or hazardous substances. The term „Green Chemistry" was coined by Paul T. Anastas of the US Environmental Protection Agency (EPA) [3].

A realistic working definition of green chemistry can be formulated as follows [10]. Green chemistry efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solventsin the manufacture and application of chemical products. Anastas has pointed out that the guiding principle of Green Chemistry is the design of environmentally benign products and processes [4]. This concept is incorporated in the twelve principles of Green Chemistry [1, 4], which can be paraphrased as

1. Prevention

Green chemistry mainly concentrates on the processes by which the chemical products are produced. The ultimate goal of this principle is to design a green process when chemical products are produced so that one can eliminate waste at source. Thus it is better to prevent waste than to treat waste after it is created.

2. Atom Economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. Thus chemists must not only attempt to achieve maximum percent yield, but also design syntheses that maximize the incorporation of the atoms of the reactants into the desired product.

3. Less Hazardous Chemical Synthesis

Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing Safer Chemicals

Chemical products should be designed to preserve efficacy of the function while reducing toxicity. Minimizing toxicity and simultaneously maintaining function and efficacy may be one of the most demanding aspects of designing safer products and processes. To achieve this goal we need the understanding of not only chemistry but also of the principles of toxicology and environmental science. Highly reactive chemicals are often used by chemists to manufacture products because they are quite valuable at affecting molecular transformations. However, they are also more likely to react with unintentional biological targets, human and ecological, resulting in unwanted adverse effects.

5. Safer Solvents and Auxiliaries

The use of auxiliary substances (solvents, separation agents, etc.) should not be made unnecessarily whenever possible and, when used should be innocuous. Solvents and separation agents provide for mass and energy transfer and without this, many reactions will not proceed. Solvents are the major contributors to the overall toxicity profile and because of that create the majority of the materials of concern associated with a process. They contribute the greatest concern for process safety issues because they are inflammable and volatile.

Solvents and mass separation agents of all kinds subject a lot to the chemistry not to mention the chemical process and the overall "greenness" of the reaction. If a solvent is needed then water should preferred [11].

Waterisnon-toxic,non-inflammable,abundantly available and inexpensive. Moreover, owing to its highly polar character one can expect novel reactivities and selectivities for organometallic catalysis in water. In addition, this provides an opportunity to overcome a serious inadequacy of homogeneous catalysts, namely the immense recovery and recycling of the catalyst. Thus, performing the reaction in an aqueous biphase system, whereby the catalyst resides in the water phase and the product is dissolved in the organic phase [12, 13], allows recovery and recycling of the catalyst by simple phase separation method.

6. Design for Energy Efficiency

Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7. Use of Renewable Feedstocks

A raw material or feedstock should be renewable rather than depleting whenever technically and economically possible. The concept of creating all our future fuels, chemicals and materials from feed stocks that never deplete is an interesting concept which at first glance seems impracticable. Mankind currently removes fossil fuels, coal, oil and natural gas from the ground and extracts minerals for profit until they are exhausted. In particular, our fossil fuels for carbon-based chemicals and materials are being rapidly depleted in a predictable manner with the expected rise of global populations and expanding energy intensive economies on several continents.

8. Reduce Derivatives

Unnecessary derivatization (blocking group, protection/de-protection, temporary modification of physical/chemical processes) should be avoided whenever possible. This is an important principle of green chemistry i.e. to reduce the use of derivatives and protecting groups in the synthesis of target molecules. One of the most excellent ways of doing this is the use of enzymes. Enzymes are very much specific and they can often react with one site of themolecule and leave the rest of the molecule alone and hence protecting groups are often not required.

9. Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents. The primary objective of green chemistry is the minimization of waste in the manufacture of chemicals and associated products. The concept of atom economy is followed here i.e., synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

An enlightening example is given by the synthesis of hydroquinone. Traditionally it was produced by oxidation of aniline with stoichiometric amounts of manganese dioxide to give benzoquinone, followed by reduction with iron and hydrochloric acid named as Béchamp reduction. The aniline was derived from benzenevianitration and Béchamp reduction. This traditional and old-fashioned process has now been replaced by a more modern and greener route involving autoxidation of p-diisopropylbenzene, followed by acid catalysed rearrangement of the bis-hydroperoxide.

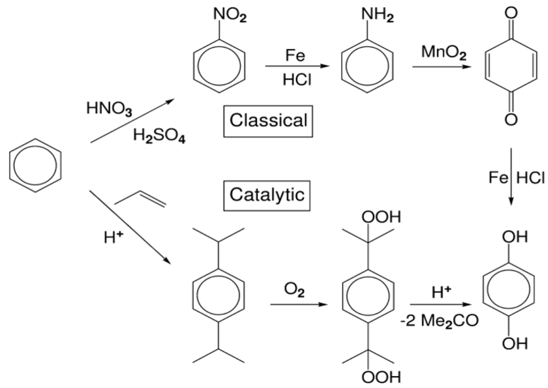


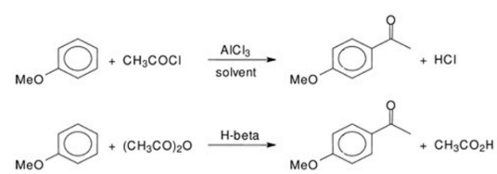
Fig. Two routes to hydroquinone

Another important point is to be mentioned here is that a major source of waste in the chemical industry is resulting from the extensive use of liquid mineral acids l i k e HF, H_2SO_4 etc. and a variety of Lewis acids and they cannot easily be recycled and in general end up through a hydrolytic work-up, as waste streams containing large amounts of inorganic salts. Their wide spread replacement by recyclable solid acids would afford a dramatic reduction in waste. Solid acids, such as zeolites, acidic clays and related materials, have many advantages. They are often truly catalytic and can easily be separated from liquid reaction mixtures, avoiding the need for hydrolytic work-up, and recycled. Moreover, solid acid are non-corrosive and easier (safer) to handle than mineral acids such as H_2SO_4 or HF.

A prominent example is Friedel-Crafts acylation which is widely applied reaction in the fine chemicals industry. Friedel-Crafts acylations generally require more than oneequivalent of Lewis acid such as $AlCl_3$ or BF_3. In classical Friedel-Crafts acylation acetyl chloride is used in combination with 1.1 equivalents of $AlCl_3$ in a chlorinated hydrocarbon solvent and generated 4.5 kg of aqueous effluent, containing $AlCl_3$, HCl, solvent residues and acetic acid, per kg of product.

The commercialization of the first zeolite-catalysed Friedel-Crafts acylation by RhônePoulenc (now Rhodia) may be considered as a benchmark in this area. Zeolite beta is employed as a catalyst, in fixed-bed operation, for the acetylation of anisole with acetic and hydride, to give p-methoxyacetophenone. The Rhodia process generates 0.035 kg of aqueous effluent i.e., more than 100 times less, in compared to the traditional process. It is also consisting of 99% water, 0.8% acetic acid and <0.2% other organics, and requires no solvent. Besides, a product of higher purity is obtained, in higher yield (>95% vs. 85–95% in traditional process), the catalyst is recyclable and the number of unit operations is reduced from twelve to two. Hence, the Rhodia process is not only environmentally superior tothe traditional process, it is economically also favorable.

Fig. Zeolite-catalysed vs. classical Friedel-Crafts acylation



In the context of green chemistry biocatalysis has many attractive features. Mild reaction conditions (physiological pH and temperature), enzyme as an environmentally compatible catalyst and water as solvent combined with high activities and chemo-, regioand stereo selectivities in multifunctional molecules. In addition, the use of enzymes generally circumvents the need for functional group activation and avoids protection and de-protection steps required in traditional organic syntheses. This affords processes which are shorter, generate less waste and are therefore both environmentally and economically more attractive than conventionalroutes.

Replacement of conventional process by bio-catalysis is provided by the synthesisof6amino penicillanic acid (6-APA), a key raw material for semi-synthetic penicillin and cephalosporin antibiotics, by hydrolysis of penicillinG.

10. Design for Degradation

Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.

11. Real-time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time inprocess monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention

Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires. This principle is known as the “Safety Principle”. It is the rational outcome of many of the other principles. The primary focus of Green Chemistry is clearly to make the environment safer. Materials and processes that are safer for the environment also are likely to be safer for the human beings.

Conclusion:

In conclusion some important points are mentioned yet again. The starting materials used for the chemical industry must be renewable and less toxic for the environment. Chemists should use less toxic solvents and they must concentrate to design of safer chemicals and products. Catalytic reagents should be used instead of stoichiometric reagents.Chemists must divert their efforts to use less dangerous raw materials and reagents for the synthetic routes of the production of chemical products. They should use catalysts and new synthetic techniques. Conventionalprocess should be replacedbybio-catalysis.It is obvious that the challenge for the future chemical industry is based on safer products and processes designed by utilizing new ideas in fundamental research. Great efforts should take on to design an ideal process that starts from non-polluting materials. Green Chemistrynot a solution to all environmental problems but the most fundamental approach to preventing pollution.

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