Bachelor of Science
(B.Sc.- PCM)

GREEN METHODS IN CHEMISTRY
(DBSPSE301T24)

Self-Learning Material
(SEM-III)

Jaipur National University
Centre for Distance and Online Education

Established by Government of Rajasthan
Approved by UGC under Sec 2(f) of UGC ACT 1956
&
NAAC A+ Accredited

Jaipur National University

Course Code: DBSPSE301T24
Green Methods in Chemistry

TABLE OF CONTENT

EXPERT COMMITTEE

Prof. R. S. Lokhende
Department of Life Sciences
Jaipur National University, Jaipur

Prof. Purnima Nag
Department of Basic Sciences
Jaipur National University, Jaipur

COURSE COORDINATOR

Dr. Urvija Garg
Department of Life Sciences
Jaipur National University, Jaipur

UNIT PREPARATION

Unit Writers	Assisting & Proof Reading	Editor
Dr. Azhar Ullah Khan Department of Life Sciences JNU, Jaipur Unit: 1-3 Ms Annu Yadav Department of Life Sciences JNU, Jaipur Unit: 4-6	Dr. Sunil K Sharma Department of Life Sciences JNU, Jaipur	Prof. Ruby Singh Department of Life Sciences JNU, Jaipur

COURSE INTRODUCTION

This course provides a comprehensive introduction to Green Chemistry, exploring its principles, applications, and emerging trends. Students will gain a thorough understanding of the fundamental concepts of Green Chemistry and how they are applied to real-world scenarios. The course emphasizes the importance of sustainable practices in chemistry and introduces innovative methods for minimizing environmental impact.

The content is divided in six chapters including Introduction to the concept of Green Chemistry, including its definition, importance, and goals. Explore how Green Chemistry integrates into broader environmental and sustainability frameworks.

Exploration of cutting-edge technologies and research in Green Chemistry, including nanotechnology, biocatalysis, and renewable energy sources.

Course Outcomes: After the completion of the course, the students will be able to:

1. Understand and apply the principles of Green Chemistry to reduce environmental impacts in chemical processes.
2. Analyze and evaluate real-world case studies to identify successful Green Chemistry practices and their benefits.
3. Utilize advanced techniques such as microwave and ultrasound-assisted reactions to improve process efficiency and sustainability.
4. Implement strategies for pollution prevention and apply green solvents and reagents in practical scenarios.
5. Apply advanced techniques such as microwave and ultrasound-assisted reactions to enhance process efficiency and sustainability.
6. Anticipate and prepare for future trends and challenges in Green Chemistry, contributing to ongoing innovation in the field.

Acknowledgements:
The content we have utilized is solely educational in nature. The copyright proprietors of the materials reproduced in this book have been tracked down as much as possible. The editors apologize for any violation that may have happened, and they will be happy to rectify any such material in later versions of this book.

Chapter:1

Introduction of Green Chemistry

Objective

- Develop chemical processes that reduce or eliminate hazardous substances and waste.
- Design chemicals and processes that prioritize human health and safety.

1.1 Introduction

The concept of "green chemistry," coined by Paul Anastas in 1991, underscores a pivotal shift in chemical science. Historically and presently, chemistry has often been associated with the release of pollutants, the production of non-biodegradable materials, and environmental harm, affecting both ecosystems and human health. Recognizing these challenges, there is now a pressing need to redirect chemical science away from exploiting finite resources and generating excessive waste.

Instead, there is a growing imperative to harness chemistry in ways that meet human needs sustainably, without compromising the Earth's delicate support systems upon which all life depends. Fortunately, both the practice of chemical science and industry are steadily pivoting towards environmental stewardship and resource efficiency. This transformation aims to maximize the benefits of chemistry while significantly reducing or eliminating its detrimental impacts.

This progressive approach, known as green chemistry, champions the design and implementation of chemical processes and products that prioritize safety, minimize waste, and utilize renewable resources. By embracing these principles, the field of chemistry can contribute positively to a sustainable future, safeguarding the environment for current and future generations.

There is a misconception that green chemistry implies chemicals are entirely benign, which isn't entirely accurate because no chemical can be perfectly harmless. Green chemistry, instead, focuses on shifting chemical usage from more harmful (malign) to less harmful (benign) pathways.

For instance, common salt is essential for life but excessive consumption can lead to hypertension. Similarly, carbohydrates provide vital energy for daily life, yet overconsumption can pose health risks. Therefore, green chemistry aims to adopt processes and use chemicals in ways that minimize their negative impacts.

As the saying goes, "The dose makes the poison." This principle is central to homeopathy, where extremely small amounts of potentially toxic substances are used, and paradoxically, they can treat various serious illnesses. Interestingly, the efficacy of these homeopathic remedies often increases with dilution.

In essence, green chemistry promotes the transformation of chemical practices towards methods that are less harmful and more sustainable, acknowledging that all chemicals, even in small quantities, can have significant effects.

Definition of Green Chemistry: Green chemistry is the design, development, and implementation of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.

It aims to promote sustainability by minimizing the environmental impact of chemical practices, enhancing safety for humans and ecosystems, and conserving resources throughout the lifecycle of products. Key principles of green chemistry include the use of renewable feedstock's, the design of less toxic chemicals and processes, the maximization of atom efficiency, and the reduction of energy consumption and waste generation. Overall, green chemistry strives to integrate economic viability with environmental and social responsibility, ensuring that chemical innovations contribute positively to a sustainable future.

Green chemistry, also known as **sustainable or circular chemistry**, is a specialized field within chemistry and chemical engineering. It centers on designing products and processes with the primary goal of reducing or eliminating the use and creation of harmful substances. Where **environmental chemistry** examines the impacts of pollutants on the natural world, green chemistry directs its focus towards mitigating the environmental footprint of chemical activities. This encompasses strategies to minimize the depletion of nonrenewable resources and innovative technologies aimed at pollution prevention.

1.2. Need of Green Chemistry

Green chemistry is essential for several compelling reasons:

Environmental Impact: Traditional chemical processes often generate hazardous waste, consume large amounts of energy, and release harmful pollutants into the environment. Green chemistry aims to minimize these impacts by designing processes that are inherently safer and more sustainable.

Resource Conservation: Many chemical processes rely on finite resources, such as fossil fuels and rare earth metals. Green chemistry promotes the efficient use of resources, including renewable feedstock's and recyclable materials, reducing dependence on scarce resources.

Health and Safety: Chemical substances used in industry and consumer products can pose risks to human health and the environment. Green chemistry emphasizes the design of chemicals and processes that are less toxic and safer throughout their lifecycle.

Regulatory Compliance: Increasingly stringent regulations and public awareness regarding environmental and health impacts require industries to adopt cleaner and more sustainable practices. Green chemistry provides solutions to meet these regulatory requirements while maintaining competitiveness.

Innovation and Economic Benefits: Developing greener technologies often leads to innovation and new opportunities for economic growth. Companies that embrace green chemistry principles can reduce costs through improved efficiency, waste reduction, and enhanced product quality.

Global Sustainability: As global populations and industrial activities grow, the demand for chemicals and materials increases. Green chemistry offers pathways to meet these demands without compromising the ability of future generations to meet their own needs, aligning economic growth with environmental and social responsibility.

1.3 Goal of Green Chemistry

The primary goal of green chemistry is to design and develop chemical processes and products that minimize the use and generation of hazardous substances. This discipline aims to achieve sustainable outcomes by:

1. **Reducing Environmental Impact**: Green chemistry seeks to prevent pollution at the source by minimizing waste and eliminating the use of toxic substances. By designing processes that produce fewer hazardous by-products and emissions, it aims to mitigate environmental harm.

2. **Conserving Resources**: It promotes the efficient use of raw materials, energy, and water throughout the lifecycle of chemical products. This includes using renewable resources, optimizing reaction conditions to reduce energy consumption, and enhancing resource efficiency.

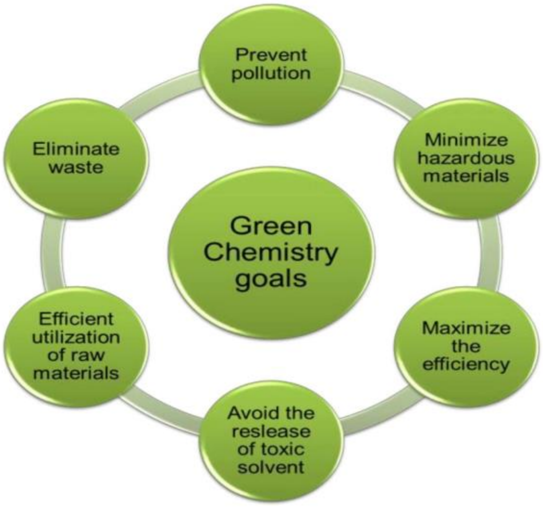
3. **Enhancing Safety**: Green chemistry prioritizes the safety of chemical processes and products for humans and the environment. By minimizing the use of hazardous chemicals and designing inherently safer chemicals and processes, it aims to reduce risks to health and ecosystems.

4. **Promoting Innovation**: It fosters innovation in chemical design and manufacturing processes to achieve sustainable solutions. By integrating principles such as atom economy, catalysis, and renewable feedstocks, green chemistry encourages the development of new technologies and products that are both economically viable and environmentally benign.

5. **Supporting Sustainability**: Ultimately, green chemistry aligns chemical practices with broader sustainability goals. It aims to ensure that chemical industries contribute positively to

global sustainability efforts, including reducing greenhouse gas emissions, conserving biodiversity, and promoting circular economy principles.

Hence, the goal of green chemistry is to transform the field of chemistry towards practices that meet current societal needs without compromising the ability of future generations to meet their own needs. It strives to harmonize economic growth with environmental stewardship and social responsibility, paving the way for a sustainable and equitable future.

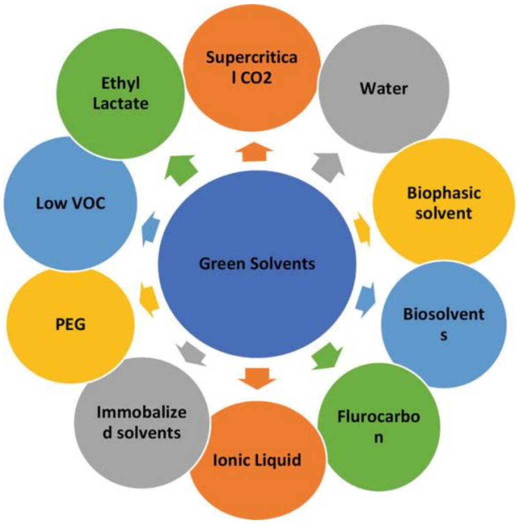


1.3 Tools of Green Chemistry

Chemists and innovators face a formidable challenge: to create new products, processes, and services in organic synthesis that meet the demands of society, affordability, and environmental sustainability. Meeting these goals requires a fresh approach focused on minimizing the materials and energy needed for chemical processes and products, reducing or eliminating the release of hazardous chemicals into the environment, maximizing the use of renewable resources, and enhancing the durability and recyclability of products.Organic chemists encounter specific challenges in this endeavor, such as pioneering novel synthetic pathways using green chemistry methodologies. These include the adoption of green solvents, catalysis in organic synthesis that is environmentally benign, synthesis in dry media conditions, catalyst-free reactions, and promoting energy-efficient synthesis techniques.

This proactive approach aims to revolutionize organic synthesis by integrating principles that not only advance scientific discovery but also prioritize sustainability and environmental stewardship.

- **Green solvents** are recognized for their favorable attributes, including low toxicity, limited water solubility, easy biodegradability in environmental settings, high boiling points, minimal volatility, mild odor, reduced health risks to workers, and recyclability post-use. Chemists employ various green solvents such as water, ionic liquids, supercritical fluids, and polyethylene glycols. The adoption of these green solvents has significantly advanced the development of environmentally sustainable reactions.



- **Green catalysis** in organic synthesis is a cornerstone of green chemistry, focusing on designing and deploying new catalysts and catalytic systems that simultaneously achieve environmental protection and economic benefits. Catalysis offers numerous advantages in green chemistry, including reduced energy requirements, catalytic efficiency compared to stoichiometric methods, enhanced selectivity, minimized use of processing and separation agents, and the ability to utilize less hazardous materials.

Catalysis is broadly classified into two branches: homogeneous catalysis, where the catalyst and the reaction mixture are in the same phase (typically liquid phase), and heterogeneous catalysis, where the catalyst is in a different phase (solid/liquid or solid/gas/liquid/gas). Homogeneous molecular catalysts offer distinct advantages when operating under optimal conditions, as their active sites are well-separated spatially, akin to enzymatic catalysis.

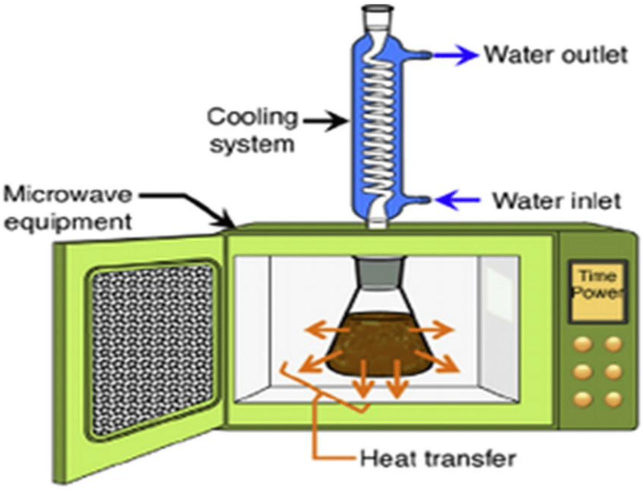
- **Heterogeneous catalysis**, on the other hand, addresses green chemistry goals by facilitating easy phase separation of products and catalysts. It involves bi-functional phenomena where reactants are activated between support and active phases, thereby obviating the need for separation via distillation or extraction. Environmentally beneficial catalysts like clays and zeolites have the potential to replace more hazardous catalysts currently in use, further advancing the principles of green chemistry.

- **A dry media reaction**, also known as a solid-state or solventless reaction, occurs in a chemical system where no solvent is present. In these reactions, the reactants are used either alone or incorporated into materials like clays, zeolites, silica, alumina, or other catalytic substances.

- **Solvent-free reactions** offer clear advantages, including reduced pollution and economic benefits due to simplified experimental procedures, streamlined workup processes, and time savings. These methods contribute to more efficient and environmentally friendly chemical synthesis practices.

- **Alternative energy tool in chemical synthesis**

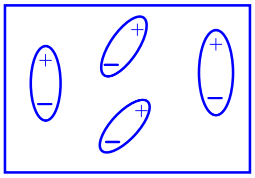
Microwave (MW) radiation, a form of electromagnetic radiation, serves as a prevalent heating source in organic synthesis. Its energy is sufficient to energize the reaction mixture, enabling it to surmount energy barriers and expedite reaction completion in a shorter duration.



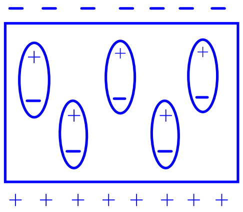
Scientific microwave oven

Theory of Microwave Heating- *Dipolar Polarization*

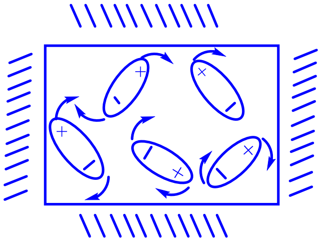
For MW heating to occur the matrix should be dipolar or ionic.Polar solvents e.g. water, DMF, CH_2Cl_2 with a dipole moment, i.e. high dielectric constant are MW-active whereas non-polar solvents like toluene, diethyl ether, benzene are MW-inactive.



Without constraint



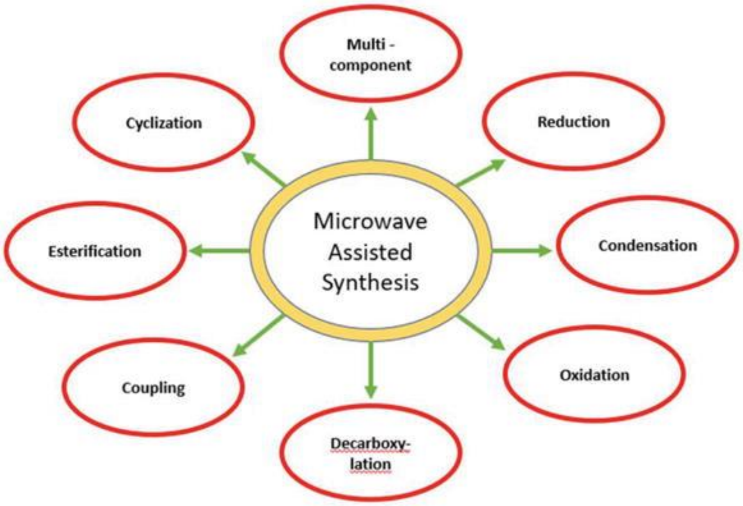
Submitted to continous electric current



Alternative electric current

In the presence of an electric field - dipole moment tend to align parallel to the applied field by rotation. If the electric field oscillates, the dipole realigns and rotates in respond to the alternate electric field. The molecules are extremely agitated, the molecular friction and collisions give rise to dipolar heating, ~10 ^{0}C per second.

•Note - gases are not microwave active because the rotating molecules are far apart



Various types of Microwave assisted synthesis.

- **Ultrasound irradiations in organic synthesis**

Sonochemistry is recognized as a beneficial approach for conducting organic reactions without the need for solvents. Key advantages of sonochemical techniques include high yields, low energy consumption, minimal waste generation, and the absence of solvent usage. Ultrasound application in chemical reactions within solutions operates on the principle of acoustic cavitation. This phenomenon involves mechanical activation that disrupts the molecular attractive forces in the liquid phase. The study of special effects of ultra sound on chemical synthesis is termed as sonochemistry.

1.4 Limitations of Green Chemistry

While green chemistry offers substantial benefits, it also has its limitations and challenges:

1. **Cost and Economic Viability**: Implementing green chemistry practices and technologies may initially involve higher costs due to the development of new processes, materials, and infrastructure. Companies may hesitate to invest in green alternatives if they perceive them as less economically competitive in the short term.

2. **Technological Barriers**: Developing green chemistry methodologies and replacing conventional processes can pose technical challenges. New catalysts, solvents, and technologies may require extensive research and development to achieve efficiency and scalability comparable to traditional methods.

3. **Education and Training**: Adopting green chemistry requires a shift in mindset and expertise among chemists, engineers, and industry professionals. Training and education in green chemistry principles and practices are crucial but may be lacking or insufficient in some contexts.

4. **Performance and Functionality**: Green alternatives must meet or exceed the performance standards of conventional chemicals and processes. If green products or technologies do not perform as effectively or do not meet regulatory requirements, adoption may be limited.

5. **Regulatory and Policy Frameworks**: Existing regulations and policies may not fully support or incentivize the adoption of green chemistry innovations. Regulatory hurdles, such as lengthy approval processes for new materials or technologies, can impede progress.

6. **Scale-Up and Integration**: Scaling up green chemistry processes from laboratory to industrial scale can be challenging. Factors such as consistency, reliability, and compatibility with existing infrastructure need to be addressed for widespread adoption.

7. **Consumer Awareness and Demand**: Green chemistry products and processes may not yet be widely recognized or demanded by consumers compared to traditional options. Increasing awareness and understanding of the benefits of green chemistry among consumers can drive market demand.

Addressing these limitations requires collaborative efforts among researchers, industries, policymakers, and consumers to overcome barriers and accelerate the adoption of sustainable and environmentally friendly practices in chemistry.

Summary: Green chemistry focuses on designing chemical processes and products to minimize or eliminate hazardous substances, addressing environmental concerns such as pollution and resource depletion. It is driven by the need to meet regulatory requirements, respond to consumer demand for eco-friendly solutions, and enhance sustainability in chemical practices. The advantages of green chemistry include environmental protection through reduced pollution and resource conservation, improved health and safety by using less toxic substances, and fostering innovation and economic competitiveness in sustainable industries. However, challenges such as higher initial costs, technological complexities in scaling up processes, performance disparities compared to conventional methods, and regulatory and market barriers may hinder its widespread adoption and implementation.

Keywords

Green chemistry: Designing chemical processes and products to minimize hazardous substances and environmental impact while conserving resources.

Need: Addressing environmental concerns, regulatory compliance, and consumer demand for sustainable solutions.

Advantages: Reduced pollution, enhanced resource efficiency, improved health and safety, fostering innovation.

Limitations: Initial costs, technological complexities, performance disparities, regulatory and market barriers.

MCQ

1. **What is the primary goal of green chemistry?**

A. Maximizing waste generation
B. Minimizing hazardous substances
C. Ignoring environmental impact
D. Using nonrenewable resources

Answer: B.

2. **Why is green chemistry necessary?**

A. To increase pollution levels
B. To comply with regulatory requirements
C. To maximize resource depletion
D. To use toxic chemicals

Answer: B.

3. Which of the following is an advantage of green chemistry?

A. Increased pollution
B. Reduced resource efficiency
C. Improved health and safety
D. Limited innovation

Answer: C.

4. What is a limitation of green chemistry?

A. High initial costs
B. Low regulatory barriers
C. Simple technological advancements
D. All of these

Answer D

Short answer questions

1. Define green chemistry
2. Why we need green chemistry.
3. Write the name of tools of green chemistry
4. Give the limitations of green chemistry

Chapter: 2

Principles of Green chemistry

Objectives

- Understand how to design chemical processes and products that minimize environmental impact, conserve resources, and support sustainable development goals.
- Learn to develop chemicals and processes that prioritize human health and safety by reducing exposure to hazardous substances.

2.1. Introduction In 1998, Paul Anastas (then leading the Green Chemistry Program at the US EPA) and John C. Warner (formerly of Polaroid Corporation) introduced a set of principles aimed at guiding green chemistry practices. These twelve principles encompass strategies to minimize environmental and health impacts associated with chemical production. They emphasize: Paul Anastas is known as the **Father of green chemistry**

- Optimizing process design to maximize the conversion of raw materials into final products.
- Utilizing renewable feedstocks and energy sources.
- Preferring safe and environmentally benign substances, including solvents.
- Designing processes for energy efficiency.
- Minimizing or eliminating waste production, representing the ideal approach to waste management.

2.2 Twelve Principles of Green Chemistry

Principle1: Waste prevention

The principle emphasizes that preventing waste is preferable to treating or cleaning it up after it has formed. Therefore, chemical processes should be optimized to minimize waste generation. The environmental factor (E factor) serves as a metric for quantifying the amount of waste generated during a production process, calculated by dividing the mass of waste by the mass of the product obtained. A lower E factor indicates more efficient results. Other methods for assessing waste include comparing the mass of raw materials used to that of the final product.

The Environmental (Mass) Efficiency Factor, or E-factor, is computed as follows:

E-Factor = Total Waste (kg) / Product (kg) equals the E-factor.

Principle 2: Atom Economy

It is among the cornerstones and most significant concepts of green chemistry. The theory behind the atom economy was formulated by B.M. Trost. The quantity of reactants that go straight into the intended result is known as the "atom economy."

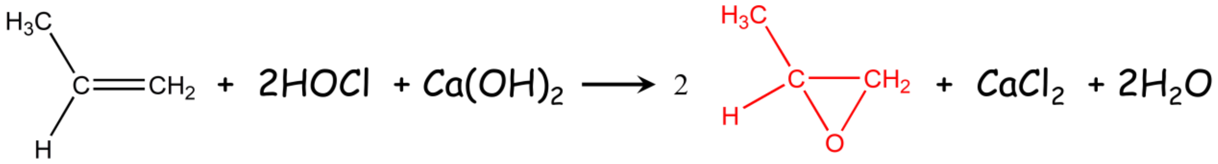
It is commonly known as the percentage of atoms utilized. The identical idea, as follows, has also been developed by R. A. Sheldon.

“Synthetic methods should be formulated to maximize the incorporation of all materials used in the process into the final product, minimizing waste generation”

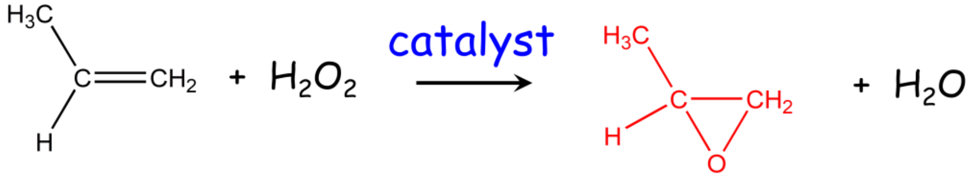
$$\text{Atom economy} = \frac{\text{Mass of desired product}}{\text{Total mass of all products (or reactants)}} \times 100\%$$

The greater the value of the atom economy, the better is the reaction to convert all the reactant atoms to the desired product ⇒ Less waste

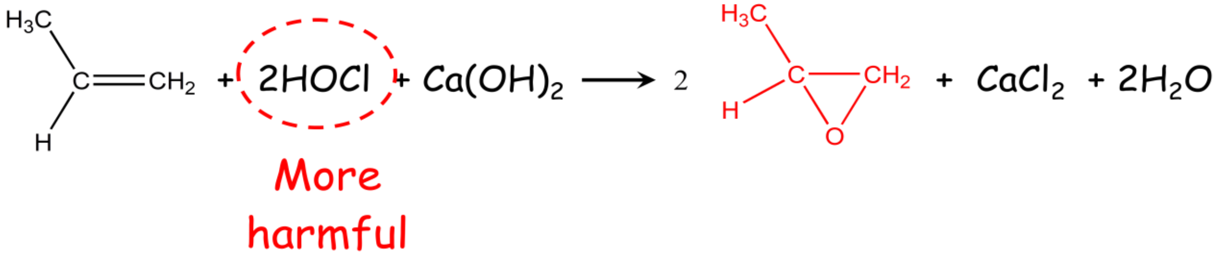
Examples of reactions with their atom economy

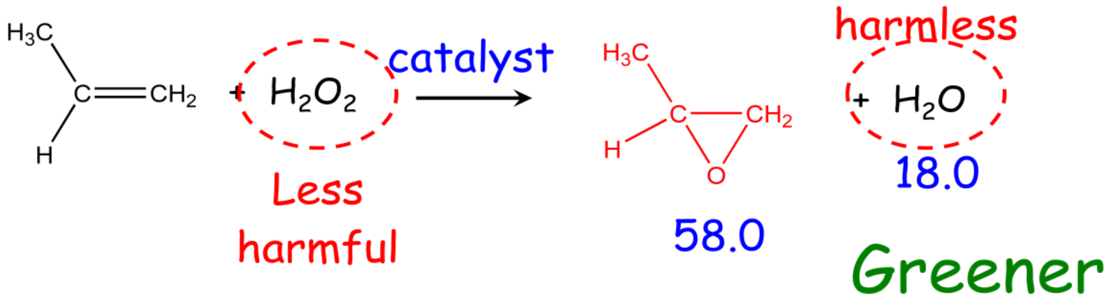


$$AE = \frac{2\times 58.0}{2\times 58.0 + 111.0 + 2\times 18.0}\times 100\% \quad = 44.1\%$$



$$AE = \frac{58.0}{58.0 + 18.0}\times 100\% \quad = 76.3\%$$





Principle3: Safersyntheses (Synthetic processes should be developed to employ and produce less toxic or non-toxic compounds whenever possible).

Chemists earlier used the chemicals entity as necessary. The green method eliminates the need for everything and favors safer chemicals or reagents. When there are safer substitutes, it is preferable to avoid using and producing harmful substances. It may be problematic to produce harmful wastes in synthesis going forward, which emphasizes the need for safe disposal.If these wastes or primary products are poisonous, workers may be harmed and must be protected, which raises the expense of pollution. The production of polystyrene foam sheet packaging material is a notable example of the employment of safe chemicals; in this case, CO_2 is used as the blooming agent instead of dangerous chlorofluorocarbons, which deplete the ozone layer and contribute to global warming.

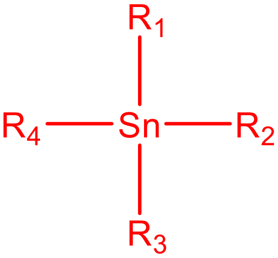
Principle4: SaferProducts

The principle states: "Chemical products should be designed to maintain their efficacy while minimizing toxicity." Achieving this requires deeper understanding of toxicity, knowledge that is often not covered in standard chemistry courses for students.

Advances in chemistry and related sciences have improved our understanding of how chemical structures influence product properties. For instance, this knowledge informs the color of dyes and paints, the amphiphilicity crucial for detergent action, the tensile strength of different fibers, and the non-flammability properties of various fabrics.

To design non-toxic chemicals, it is crucial to understand why certain chemicals exhibit toxicity while others do not, and why some organisms are more susceptible to specific toxic substances than others. Predicting the potential toxicity of a chemical beforehand is essential. Additionally, the dosage of chemicals significantly influences their toxic effects; substances may be harmless in small amounts but toxic above a certain threshold, similar to drug overdoses. Some chemicals accumulate in body fat, necessitating knowledge of their partition coefficient (distribution between lipid and water). Sorting through these factors, among others, is challenging but achievable through gradual progress.

Example; For example, chemicals called organotin compounds(Anti-biofouling agent) were used in large ships to prevent accumulation of barnacles and marine plants traditionally.



The accumulation of barnacleson the ship may increase the resistance to its movement. ‘However, organotin compounds are highly toxic to the surrounding marine life. Then, Rohm and Haas Company developed a non-toxic alternative called Sea-NineTM. It degrades quickly in the marine environment and is not toxic to the surrounding marine life’.

Principle5: Safersolvents/auxiliaries

Auxillary chemicals (solvents, separation agents) should be avoided or used sparingly be harmless. In synthetic processes, chemists typically utilize any organic solvent of their choice. These solvents are typically volatile organic solvents (VOCs), which pose a serious threat to the environment since they can cause smog and low-level ozone to form through the oxidation of free radicals in the air. Additionally, they are extremely combustible and have negative effects on humans, such as allergic skin reactions, headaches, and eye irritation. The usage of green alternative solvents has become required as a result of these realities. However, using solvents should be avoided if at all possible. It is essential, advised to use solvents of this type that are inert, have lowtoxicity, simple to recycle without tainting subsequent goods. The chosen solvent shouldn't be harmful to people's health or the environment. Examples of halogenated solvents that have been linked to cancer include $CHCl_3$ and CCl_4, which can be avoided by using greener alternatives like liquid CO_2, ionic liquids, or water.Immobilized solvents have been used in place of conventional volatile organic compounds to circumvent their issues. These solvents don't harm the environment, retain their solvency, and are non-volatile.

Principle6: Energy efficiency

Reaction energy requirements should be as low as feasible to avoid negative effects on the environment and the economy. Synthetic procedures ought to be used at room temperature and pressure wherever feasible. The least amount of energy needed for the chemical reactions must be utilized. Since thermal energy is not directed directly at a bond or the molecules undergoing the reaction, it is non-specific and is instead utilized in conjunction with other, more targeted energy sources. Thermal energy is the most widely employed conventional energy source in reactions. These green energy sources include ultrasonic, microwave, and photochemical energy sources. According to this idea, the reactions' energy consumption must be kept to a minimum. There are several approaches to increase the energy efficiency of processes:

a) Reduce heat and energy losses using well-maintained equipment and good insulation.
b) Reactants of this type should typically be used for lower temperatures and/or less energy requirement.
c) It promotes the development of catalysts of this kind that allow processes to operate at lower pressures and temperatures, thereby consuming less energy.

Principle7: Renewable Feed-stocks

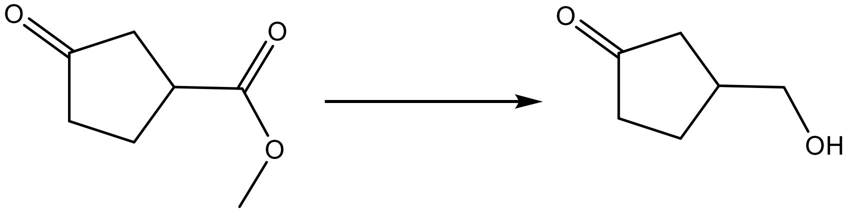
The principle states: "Raw materials or feedstocks should be renewable rather than depleting, whenever technically and economically feasible." Fossil fuels are depletable resources, whereas renewable feedstocks primarily consist of biological materials like plant-based resources.

This principle is closely linked to sustainability, emphasizing the need to ensure resources are available for future generations as we utilize them. Transitioning from petroleum hydrocarbons, which pose environmental challenges, is imperative. For instance, converting petroleum hydrocarbons often involves oxidation catalyzed by toxic metals such as chromium. This illustrates how green chemistry principles are interconnected and cannot be viewed in isolation. Utilizing biological feedstocks holds promise and must meet the requirement of renewability.

Principle 8: Derivative Reduction

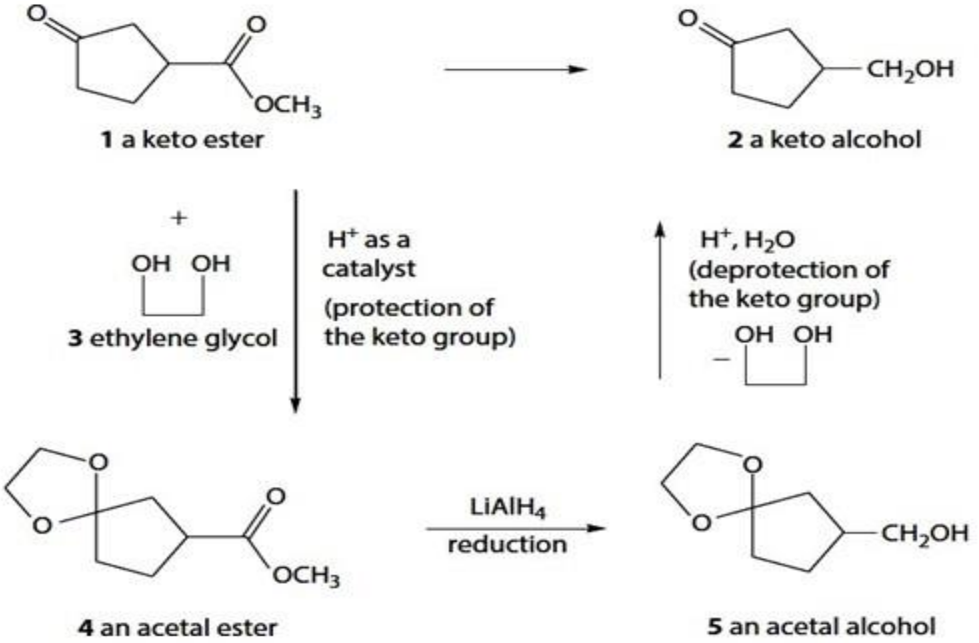
The principle states: "Avoid unnecessary derivatization, such as blocking groups, protection/ deprotection, and temporary modifications of physical/chemical processes, whenever feasible."

The derivatization principle is demonstrated with an example from early organic chemistry. Starting with compound 1 containing keto and ester groups, the goal is to produce compound 2 where the ester group is transformed into an alcohol while retaining the keto group.



1 A keto ester **1 a keto alcohol**

Chemists illustrate the derivatization principle with an example from organic chemistry. Starting with compound 1 containing keto and ester groups, the objective is to produce compound 2 where the ester group is converted to an alcohol while preserving the ketogroup. To achieve this, compound 1 is reacted with ethylene glycol (3) under acidic conditions to form compound 4, where the keto group is protected as an acetal (5), while the ester group remains unchanged. Subsequently, the ester group in compound 5 is reduced to yield alcohol 6 using lithium aluminum hydride ($LiAlH_4$), leaving the acetal group intact. Finally, the acetal group is removed through acid hydrolysis, resulting in the desired product 2.



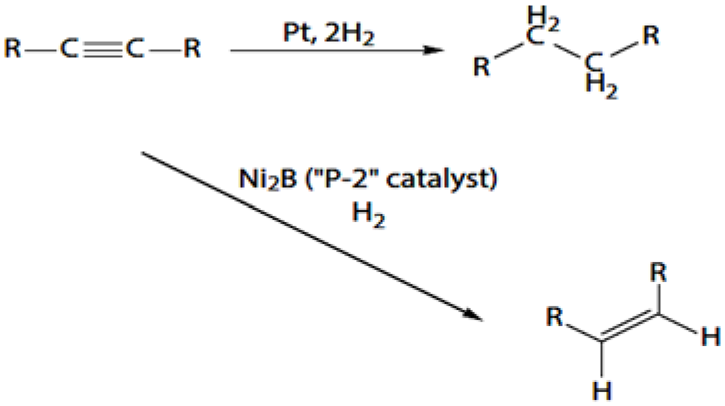
This process demonstrates the sequence of protection, reduction, and deprotection, where the keto group is initially protected to prevent undesired reduction, and later deprotected to expose the ketone functionality.

In this example, for a novice organic chemistry student, the process of protection and deprotection was deemed necessary. However, upon closer examination of the reaction sequence, it becomes evident that there is a poor atom economy due to the waste of ethylene glycol. Alternatively, recycling ethylene glycol would involve extracting it from the aqueous waste and purifying it for reuse, which might not be economically feasible.

Principle 9: Catalysis (Selective catalytic reagents are preferable than stoichiometric reagents.)

The catalytic reagent can be fully recovered because it remains unchanged. All catalysts, including enzymes, reduce the reaction's activation energy, accelerating it millions of times without causing any changes to the reaction. Nonetheless, the specificity of biocatalysts' stereochemistry and chemical selectivity set them apart from all other catalysts. Given the rate of reaction, catalytic specificity, reduced cost, and other advantages over non-biological catalysts, biocatalysts are superior; nonetheless, they have poor stability and lack heat sensitivity. Because they are biodegradable, biocatalysts require less energy. Catachol is a traditional example use as catalytic reagents, catechol synthesis starts with benzene, takes several steps, and has extreme reaction conditions that result in undesirable byproducts. Nevertheless, the biocatalytic approach uses Escherchia coli to synthesize catechol from glucose in a single step, is commercially feasible, and produces no byproducts.

Catalytic selectivity is valuable in numerous fundamental chemical reactions familiar to students. An example is depicted in the figure below.



Selectivity in hydrogenation of unsaturated hydrocarbons

Principle10: Degradability

Chemical products synthesized their useful to environment and decompose into harmless degradation products. The synthesized moieties must be able to transform into final products that are not harmful. In general, a lot of synthetic products are created that do not break down when they are finished using them. Therefore, it is necessary to create a product that degrades naturally; otherwise, it would linger in the environment, be ingested by plants or animals, and build up inside their biosystems, which would be harmful to the affected species. For instance, the organochlorine class of insecticides, which includes DDT, is not biodegradable and poses serious health risks. As a result, a product should be made so that it breaks down in the environment into harmless materials. Groups and other characteristics can now be included into molecules to speed up their breakdown. The biodegradable, functional groups that are vulnerable to hydrolysis, photolysis, or other potential modifications have been employed.

Principle 11. Real time analysis for pollution control

It is necessary to create analytical technologies that will enable the reduction and prevention of hazardous waste formation. In order to evaluate the risks that are present in the process stream, one needs precise and trustworthy sensors, monitors, and procedures. It is possible to monitor a process for the production of dangerous byproducts and side reactions using a variety of ways.

Principle 12. Inherently safer chemistry to control accidents: When selecting substances for a chemical process, care should be taken to reduce the risk of chemical accidents such as leaks, explosions, and fires. According to this theory, less of these chemicals should be used in chemical reactions that have the potential to go wrong (explosion, fire, and hazardous vapor). As far as possible, accidents, fires, and explosions should be prevented. Because solvents are used so frequently in organic chemistry labs, it is thought that these volatile organic compounds (VOCs) can catch fire easily. It is important to remember that accidents like the Bhopal gas tragedy shouldn't occur when studying chemistry.

Summary: The 12 principles of green chemistry provide a comprehensive framework for developing sustainable chemical practices. These principles advocate for minimizing environmental impact, reducing waste, and enhancing safety throughout the lifecycle of chemical products and processes. They emphasize prevention of waste generation, maximizing atom economy by efficiently using raw materials, and selecting safer chemicals and solvents. Energy efficiency is promoted through optimized processes, while renewable feedstocks are preferred to diminish reliance on finite resources. Reduction of unnecessary derivatization steps and utilization of catalysis further minimize waste and enhance efficiency. Chemical products should be designed for degradation after use to prevent persistent environmental harm. Real-time pollution monitoring and safer design strategies mitigate risks of accidents and hazardous conditions. Collectively, these principles guide the chemical industry towards sustainable practices that support environmental stewardship and ensure the well-being of current and future generations.

Keywords

Green Chemistry: safe and environmental friendly chemistry.

Atom Economy: Maximize the incorporation of all materials used in a chemical process into the final product.

Prevention: Design processes to prevent waste generation by using efficient methods and minimizing by-products.

Catalysis: Use catalytic processes to increase efficiency, reduce waste, and minimize energy requirements.

MCQ

1. Which principle of green chemistry emphasizes designing processes to prevent waste generation?

A. Atom Economy	B. Prevention
C. Renewable Feedstocks	D. Design for Degradation

Answer: B.

2. The principle of maximizing atom economy aims to:
A. Minimize waste generation
B. Use renewable feedstocks
C. Design safer chemicals
D. Enhance energy efficiency

Answer: A.

3. Which principle advocates for using safer chemicals and solvents whenever possible?
A. Safer Solvents and Auxiliaries
B. Design Safer Chemicals
C. Use of Renewable Feedstocks
D. Real-time Analysis for Pollution Prevention

Answer: B.

4. Catalysis in green chemistry primarily aims to:
A. Maximize atom economy
B. Reduce derivatives
C. Design for degradation
D. Increase efficiency and reduce waste

Answer: D.

5. Which principle encourages the use of renewable resources as raw materials?
A. Use of Renewable Feedstocks
B. Real-time Analysis for Pollution Prevention
C. Safer Chemistry for Accident Prevention
D. Design for Energy Efficiency

Answer: A.

Short Answer Questions

1. Explain the principle of "Prevention" in green chemistry.
2. What does "Atom Economy" mean in the context of green chemistry?
3. How does green chemistry promote the use of "Renewable Feedstocks"?
4. What is meant by "Design for Degradation"?
5. Discuss the principle of "Safer Chemistry for Accident Prevention".

Chapter: 3

Green Chemistry in Real World Cases

Objectives:

- Green chemistry seeks to minimize pollution by preventing waste generation rather than treating it after it's formed.
- Green chemistry prioritizes the safety of chemical products and processes for workers, consumers, and the environment.
- Fosters innovation in chemical design and manufacturing methods and Developing plastics from renewable resources like corn
- Development of Fully Recyclable Carpet and catalytic processes that require less energy and produce fewer by-products

3.1 Introduction

Green chemistry, also known as sustainable chemistry, focuses on designing chemical products and processes that minimize environmental impact and are sustainable. Here are some real-world cases that highlight the application and importance of green chemistry:

1. **Benign by Design**: This concept emphasizes designing chemicals that have minimal environmental impact from the outset. For example, pharmaceutical companies have started designing drugs that degrade into harmless substances after use, reducing environmental pollution.

2. **Catalysis**: Green chemistry promotes the use of catalytic processes to reduce energy consumption and waste generation. For instance, catalytic converters in cars help reduce harmful emissions by converting pollutants into less harmful substances.

1.

3. **Bio-based Feedstocks**: Using renewable raw materials such as biomass instead of fossil fuels can reduce the environmental footprint of chemical production. This approach is increasingly applied in producing biofuels, bioplastics, and biochemicals.

2. **Waste Minimization**: Developing processes that generate less waste or utilize waste as a resource is a key principle of green chemistry. An example is the conversion of

agricultural waste into biofuels or using industrial by-products as raw materials for other processes.

3.

4. **Safer Solvents and Materials**: Green chemistry advocates for the use of safer solvents and materials that are less toxic and have lower environmental impact. For instance, replacing volatile organic solvents with water-based alternatives in various industrial processes.

5. **Energy Efficiency**: Improving energy efficiency in chemical processes through better design and optimized conditions is another aspect of green chemistry. This reduces energy consumption and associated greenhouse gas emissions.

6. **Life Cycle Assessment (LCA)**: Green chemistry considers the entire life cycle of a product, from raw material extraction to disposal. LCA helps identify environmental hotspots and opportunities for improvement throughout the product's life cycle.

7. **Regulatory Drivers**: Governments and regulatory bodies increasingly promote green chemistry through policies and incentives aimed at reducing environmental impact. This encourages industries to adopt greener practices and technologies.

3.2 Surfactants for carbon dioxide – replacing smog producing and ozone depletingsolvents with $CO_2$for precision cleaning and dry cleaning of garments.

Using surfactants with carbon dioxide (CO_2) as a solvent represents an innovative approach in the field of precision cleaning and dry cleaning of garments. This method replaces traditional solvents that contribute to smog formation and ozone depletion with a more environmentally friendly alternative. Here’s an overview of how surfactants can be utilized in CO2-based cleaning processes:

3.2.1 CO_2 as a Solvent:

Carbon dioxide in its supercritical state ($scCO_2$) or as a near-critical fluid is an attractive solvent due to several key properties:

- **Environmental Benefits**: CO_2 is non-toxic, non-flammable, and readily available as a byproduct of various industrial processes. Its use as a solvent reduces the emission of volatile organic compounds (VOCs) and greenhouse gases compared to traditional solvents.

- **Efficiency**: CO_2 has tunable solvent properties depending on pressure and temperature, making it suitable for a wide range of applications from cleaning to extraction and beyond.

3.2.2 Surfactants in CO_2 Cleaning:replacing smog producing and ozone depleting solvents with $CO_2$for precision cleaning and dry cleaning of garments**.**

Surfactants play a crucial role in various industrial applications, including those involving carbon dioxide (CO_2). Carbon dioxide, due to its unique chemical properties, can be challenging to handle and utilize effectively in industrial processes. Surfactants, also known as surface-active agents, are compounds that lower the surface tension between two substances, allowing them to mix more easily.

Dry cleaning using carbon dioxide (CO_2) has found widespread application across various industries and technical fields such as aerospace, automotive, electronics, medical, manufacturing, research (both basic and applied), and optics. This versatile method utilizes different CO_2 cleaning techniques capable of removing a wide range of contaminants including gross contamination, paint, overlayers, grease, fingerprints, particles as small as nano meters, hydrocarbon and organic residues, and even radioactive residues. Materials suitable for CO_2 cleaning encompass metals, polymers, ceramics, and glasses. However, a key limitation is that the contamination must be accessible on the surface rather than embedded within the material.

Carbon dioxide cleaning encompasses several distinct methods tailored for parts cleaning, leveraging different phases of CO_2. These methods include:

- Solid dry ice pellets,
- Liquid CO_2,
- CO_2 snow (a hybrid approach),
- Supercritical CO_2.

Each method offers unique advantages depending on the specific cleaning requirements and the nature of the contaminants to be removed. These technologies underscore the versatility and effectiveness of CO_2 as a cleaning agent in modern industrial and technical applications, contributing to enhanced efficiency, reduced environmental impact, and improved cleanliness standards across diverse sectors.

3.2.3 Carbon dioxide (CO_2) is increasingly favored as an alternative solvent for dry cleaning due to several key reasons:

- Firstly, CO_2 is a preferred choice over Volatile Organic Compounds (VOCs) and Halogenated Organic Compounds (HOCs) because it is non-toxic, nonflammable, and chemically inert. This reduces health risks for workers and minimizes environmental impact compared to traditional solvents that can be harmful and contribute to air pollution.

- Secondly, CO_2 is readily available as a byproduct from various industrial processes, such as the production of ammonia and natural gas extraction. This makes it a cost-effective option as it can be obtained without additional resource-intensive production.

- Furthermore, the used CO_2 can be easily recovered, purified, and reused in the cleaning process, enhancing its sustainability and reducing overall operational costs. This closed-loop system minimizes waste and conserves resources, aligning with principles of environmental stewardship and sustainable practices.
- In summary, CO_2 stands out as an alternative solvent for dry cleaning due to its safety, availability, and recyclability, offering a cleaner and moresustainable approach to industrial cleaning processes across various sectors.

3.2.4 Solubilityof substances in CO_2

The solubility of substances in carbon dioxide (CO_2) is influenced by its non-polar nature, where the dipoles of its two bonds cancel each other out. As a result, CO_2 dissolves smaller non-polar molecules effectively, including hydrocarbons with fewer than 20 carbon atoms, as well as other non-polar organic compounds such as aldehydes, esters, and ketones.

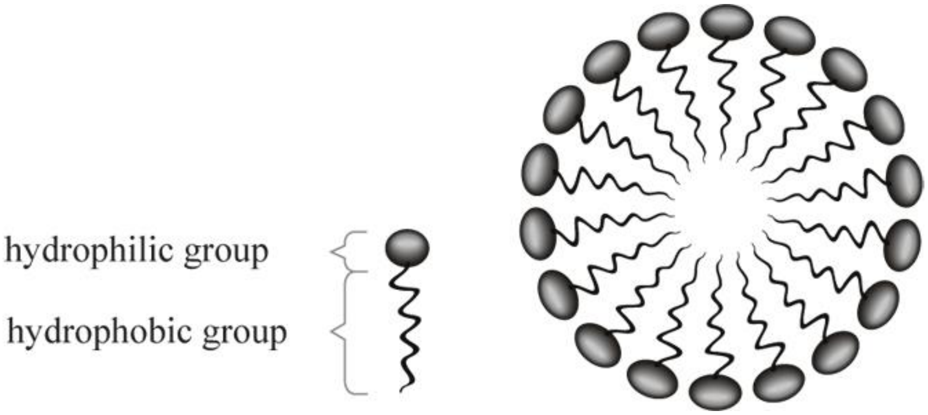
However, $CO_2$is unable to dissolve larger molecules such as oils, waxes, grease, polymers, and proteins, nor does it dissolve polar molecules due to its non-polar characteristics. This selective solubility makes CO_2 particularly suitable for cleaning processes targeting specific types of contaminants while leaving others unaffected.

3.2.5 What are surfactants

Surfactants, short for surface-active agents, are chemical compounds that are amphiphilic in nature, meaning they have both hydrophilic (water-loving) and hydrophobic (water-repelling) parts. This dual nature allows surfactants to lower the surface tension between two substances, such as between a liquid and a solid or between two immiscible liquids.

Surfactants are molecules characterized by having both a polar and a non-polar portion. This dual nature enables surfactants to interact effectively with both polar and non-polar substances. They enhance the solubility of substances that are typically insoluble in a given solvent.

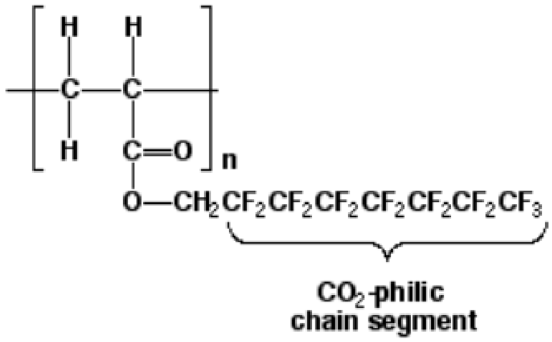
In aqueous solutions, surfactant molecules tend to aggregate into spherical structures known as micelles. In these micelles, the non-polar ends of the surfactant molecules are oriented towards the center, shielded from the surrounding water molecules, while the polar ends are exposed on the outer surface. This arrangement stabilizes the micelle in water and allows surfactants to effectively encapsulate non-polar substances within the micelle core, thereby facilitating their dispersion and solubilization in the aqueous environment.



Micellesstructure

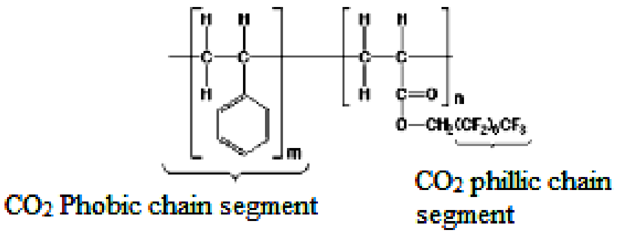
A Surfactant for Liquid or Supercritical Fluid CO_2:

In 1994, Joseph M. DeSimone from the University of North Carolina and North Carolina State University made a significant discovery. He found that polymers, like the one depicted below, exhibit solubility in liquid or supercritical CO_2 due to their ability to incorporate both CO_2-loving (CO_2-philic) and CO_2-repelling (CO_2-phobic) functionalities. This discovery opened up new possibilities for using CO_2 as a solvent in various applications, leveraging the unique properties of polymers to interact effectively with carbon dioxide in its different phases.

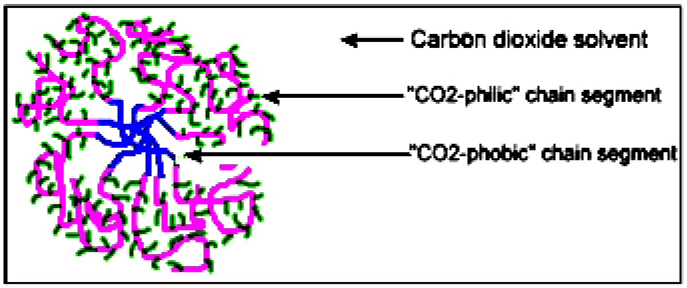


- **Block Copolymers utilize to build Surfactant for CO_2**:

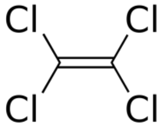
DeSimone synthesized copolymers comprising segments that are CO_2-phobic and CO_2-philic, effectively combining both characteristics within the polymer structure. This innovative approach allowed these copolymers to interact favorably with liquid or supercritical CO_2, demonstrating their solubility and utility in various applications.



- **Micelle Structure for a CO_2 Surfactant**:



- Historically, the dry cleaning industry has relied on perchloroethylene (PERC) as its primary solvent for cleaning garments and fabrics.



In 1998, approximately 344 million pounds of perchloroethylene (PERC) were produced in the United States. The dry cleaning industry alone consumed about 172 million pounds annually, which accounts for roughly 50% of the total PERC production each year.

However, PERC has been classified by the EPA as a groundwater contaminant and poses potential human health hazards. It is considered a suspected human carcinogen and has been proven to be carcinogenic in rodents. Short-term exposure to PERC through inhalation can adversely affect the central nervous system.

While environmental levels of PERC typically do not reach concentrations high enough to cause immediate harm, individuals working in the dry cleaning industry face the greatest risk of exposure.

- **Current use of CO_2 surfactants**

Founded in 1995, Micell Technologies has brought CO_2 surfactant technology into commercial use. Their Micareô system, a commercial washing machine, utilizes CO_2 along with CO_2 surfactants as alternatives to perchloroethylene (PERC), effectively eliminating the dependency on PERC in cleaning processes.

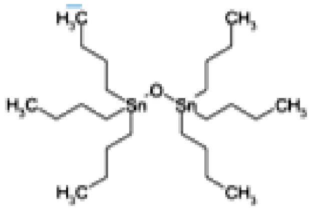
3.3 Designing of Environmentally safe marine antifoulant:

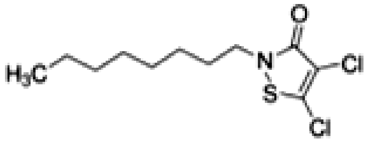
Designing environmentally safe marine antifoulants involves creating coatings or treatments that prevent the attachment of marine organisms to ship hulls and marine structures without causing harm to the marine environment. Traditional antifoulants often contain toxic biocides that can leach into the water, posing risks to marine life and ecosystems. Here are key considerations and strategies for designing environmentally safe marine antifoulants:

The fouling of ships' underwater areas by algae, micro-organisms, and small invertebrates significantly increases operational costs in the shipping industry due to higher fuel consumption. This unwanted growth results in approximately $3 billion in annual expenses, primarily due to increased hydrodynamic drag. The escalated fuel consumption also contributes to environmental issues such as pollution, global warming, and acid rain.

Traditionally, organotin antifoulants like tributyltin oxide (TBTO) have been widely used globally to control fouling. Despite their effectiveness, these compounds persist in the environment and pose serious ecological risks, including acute toxicity, bioaccumulation, reduced reproductive viability, and shell thickening in shellfish. In response, efforts have been made to find environmentally safer alternatives to organotin compounds. One promising category explored was the 3-isothiazolone class, with over 140 compounds screened for their antifouling properties.

Among these, 4,5-dichloro-2-N-octylisothiazol-3-one (commercially known as Sea-Nine™ antifoulant by Rohm and Haas Company) emerged as a leading candidate for commercial development due to its effectiveness and reduced environmental impact compared to organotin compounds.





3.4 Rightfit pigment:

Developing "Rightfit Pigment," which are synthetic azo pigments aimed at replacing toxic organic and inorganic pigments, involves creating colorants that are safe, environmentally friendly, and perform comparably or better than traditional pigments. Here’s how the development and characteristics of such pigments can be approached:

3.4.1 Characteristics of Rightfit Pigment:

1. **Non-Toxicity**:
    - Rightfit Pigments should be free from heavy metals such as lead, cadmium, and chromium, which are common in many inorganic pigments and pose environmental and health risks.

2. **Environmental Safety**:
    - These pigments should not contribute to pollution or harmful effects on ecosystems during production, use, or disposal.

3. **Color Stability**:
    - They should exhibit good color stability, resistance to fading, and compatibility with various applications such as paints, coatings, plastics, and textiles.

4. **Performance**:
    - Rightfit Pigments should offer comparable or superior performance characteristics to the pigments they are intended to replace, including color strength, opacity, dispersion properties, and durability.

5. **Regulatory Compliance**:
    - Adherence to regulatory standards and certifications (such as REACH in Europe or EPA guidelines in the US) for safety and environmental impact is crucial.

3.4.2 Strategies for Developing Rightfit Pigment:

1. **Synthesis of Azo Pigments**:
    - Azo pigments are synthesized from diazonium salts and coupling components. Focus on developing azo dyes that are structurally stable, economically viable, and environmentally benign.

2. **Substitution of Toxic Components**:
    - Replace toxic metal components (like lead and chromium) with safer alternatives without compromising color intensity or performance.
3. **Biodegradability**:
    - Design pigments that are biodegradable under natural environmental conditions, reducing persistence in the environment.
4. **Surface Modification**:
    - Incorporate surface modifications or coatings to enhance pigment dispersion, stability, and compatibility with different media.
5. **Testing and Validation**:
    - Conduct thorough testing for color fastness, chemical stability, lightfastness, and toxicity to ensure the pigments meet industry standards and customer expectations.

3.4.3 Benefits of Rightfit Pigment:

- **Environmental Sustainability**: By eliminating toxic elements, Rightfit Pigments contribute to reducing environmental impact and improving eco-friendliness in various industries.
- **Health Safety**: Workers and consumers are protected from exposure to harmful substances, enhancing safety in production, application, and use.
- **Market Acceptance**: Increasing demand for eco-friendly and sustainable products drives market acceptance and adoption of Rightfit Pigments.

3.4.4 An Efficient, Green Synthesis of a Compostable and Widely Applicable Plastic (Poly Lactic Acid) Made from Corn:

What is polylactic acid; Polylactic acid, or polylactide (PLA), is a thermoplastic aliphatic polyester derived from renewable resources. By 2010, PLA had become one of the most extensively used bioplastics globally, though it has yet to achieve the status of a commodity polymer. Its broader adoption has been impeded by several physical and processing limitations. The term "polylactic acid" does not adhere to IUPAC standard nomenclature and may be misleading since PLA is not a polyacid (polyelectrolyte) but rather a polyester.

- **An efficient Synthesis of PLA**

Poly lactic acid (PLA) is a biodegradable and compostable plastic derived from renewable resources such as corn starch or sugarcane. Developing an efficient and green synthesis of PLA involves several key steps and considerations to ensure sustainability and environmental friendliness throughout the manufacturing process:

A sustainable and efficient method for synthesizing polylactic acid (PLA), a compostable and versatile plastic derived from corn, involves several key steps that minimize environmental impact and maximize resource efficiency.

1. **Feedstock Selection**: Start with corn starch, a renewable and abundant feedstock that serves as the precursor for PLA production.

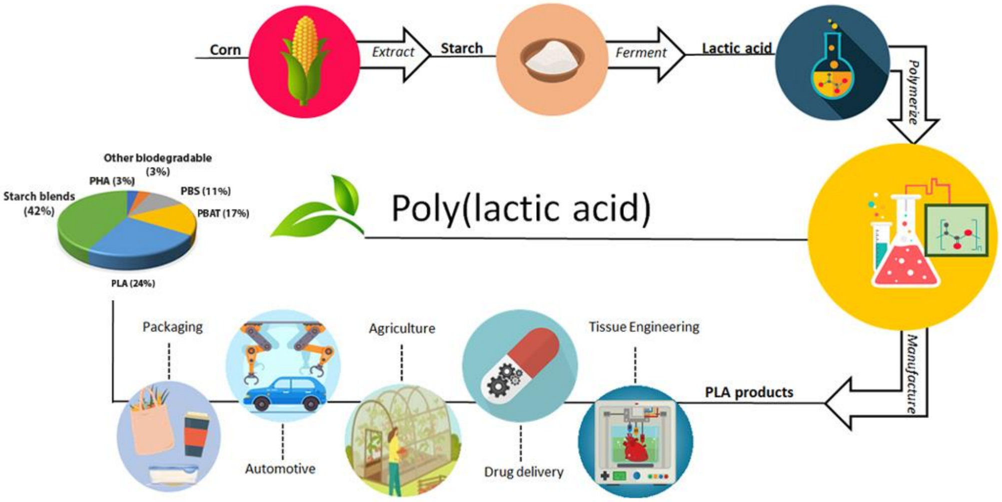
2. **Fermentation**: Ferment the corn starch to produce lactic acid, the monomer required for PLA synthesis. This step can be achieved through microbial fermentation processes that convert sugars in corn starch into lactic acid.

3. **Polymerization**: Polymerize lactic acid into PLA polymer chains. This can be done through either condensation polymerization or ring-opening polymerization methods, depending on the desired properties of the PLA.

4. **Purification**: Purify the PLA polymer to remove any residual impurities and to achieve the desired molecular weight and polymer characteristics.

5. **Processing**: Shape and form the purified PLA into various plastic products using techniques such as extrusion, injection molding, or thermoforming. This allows PLA to be used in a wide range of applications including packaging, consumer goods, biomedical devices, and more.

6. **End-of-Life Options**: Ensure that the PLA products are compostable by design, meaning they can biodegrade under controlled conditions into carbon dioxide and water, leaving behind no toxic residues. This promotes circularity in the product lifecycle and reduces environmental impact compared to traditional petroleum-based plastics.



PLA plastic is utilized in various forms across different applications:

Rigid Thermoforms:

- Meat trays and opaque dairy containers (e.g., yogurt)
- Bakery, fresh herb, and candy containers
- Disposable articles for consumables and cold drink cups
- Consumer displays and electronics packaging
- Clear clamshells for fresh fruits and vegetables

Biaxially Oriented Films:

- Envelopes and display carton windows
- Candy twist wraps and floral wraps
- Lamination films
- Tapes, stand-up pouches, and die-cut labels
- Bags for cake mix, cereal, and bread
- Lids for containers

Bottles:

- Short-shelf life milk bottles
- Bottles for edible oils
- Bottled water

Summary:

This chapter replaces conventional solvents with CO_2-based surfactants for precision cleaning and dry cleaning, reducing smog and ozone-depleting emissions, and promoting environmental and worker safety. Develops coatings using green chemistry principles to prevent marine organism attachment without harmful environmental impacts, maintaining marine ecosystem health. Synthetic azopigments replace toxic organic and inorganic pigments, ensuring minimal environmental impact throughout their lifecycle, from production to disposal. Uses corn-based feedstocks and green catalysts to produce PLA, a compostable plastic, reducing reliance on fossil fuels and promoting biodegradability.

Keywords:

Green Synthesis: Green synthesis refers to the development of chemical processes and methods that prioritize sustainability, efficiency, and environmental stewardship.

PLA; Polylactic acid or polylactide, is a biodegradable and compostable thermoplastic polyester derived from renewable resources such as corn starch or sugarcane

Safe marine antifoulant: Marine antifoulants are coatings or treatments applied to the hulls of ships and marine structures to prevent the attachment and growth of organisms

MCQ

Q.1 Which of the following statements about CO_2 surfactants is true?

A) CO_2 surfactants are only effective in polar solvents.

B) CO_2 surfactants have hydrophilic and hydrophobic regions.

C) CO_2 surfactants are primarily used in oil extraction.

D) CO_2 surfactants are derived exclusively from fossil fuels.

Answer: B

Q.2 Azo pigments are synthesized through a reaction between:

A. An amine and an alcohol

B. An amine and a carboxylic acid

C.A diazonium salt and a phenol

D. A diazonium salt and an aromatic amine

Answer: D

Q.3 Which step in the green synthesis of polylactic acid (PLA) from corn is crucial for achieving compostability?

A) Purification of lactic acid.

B) Fermentation of corn starch.

C) Polymerization of lactic acid.

D) Processing into PLA products.

Answer: C

Q.4 What is a key consideration in the designing of environmentally safe marine antifoulants?

A) High persistence in marine ecosystems.

B) Ability to enhance marine biodiversity.

C) Effective inhibition of marine growth without toxicity.

D) Promotion of bioaccumulation in marine organisms.

Answer: C.

Q.5 What is Rightfit Pigment known for in the industry?

A) Biodegradability in marine environments.

B) High heat resistance in automotive coatings.

C) Resistance to UV degradation in outdoor applications.

D) Compatibility with water-based paints.

Answer:C

Short Answer Questions:

1. How do surfactants used with carbon dioxide (CO_2) contribute to green chemistry practices in precision cleaning and dry cleaning of garments?
2. Discuss the environmental and health benefits of using synthetic azopigments like Rightfit to replace toxic organic and inorganic pigments in various industries.
3. Discuss the environmental advantages and challenges associated with the efficient, green synthesis of poly lactic acid (PLA) made from corn.
4. What are Micelles
5. Write a note onenvironmentally safe marine antifoulant

Chapter 4

Future Trends in Green Chemistry

Objectives:

- Develop efficient, sustainable oxidizing agents and catalysts to reduce environmental impact and improve reaction selectivity.
- Mimic biological processes to create versatile reagents that enhance efficiency and specificity in chemical reactions.
- Advance methods for rapid synthesis and screening of diverse compounds under environmentally friendly conditions, accelerating discoveries in various fields.
- Expand solvent-free techniques to minimize environmental footprint, lower costs, and simplify reaction procedures.

4.1 Introduction

Green chemistry continues to evolve with advancements in technology and increasing awareness of environmental sustainability. Here are some future trends that are expected to shape the field:

a) **Bio-based Feedstocks**: There is a growing emphasis on using renewable, bio-based feedstocks as alternatives to fossil fuels. This trend aims to reduce dependency on non-renewable resources and decrease the environmental footprint of chemical production.

b) **Catalysis and Greener Reaction Conditions**: Development of efficient catalytic processes and milder reaction conditions is a key focus. This includes the use of enzymes, organocatalysts, and other innovative catalytic systems that enhance reaction selectivity and reduce energy consumption.

c) **Circular Economy Principles**: Integration of circular economy principles into chemical manufacturing involves designing products and processes that minimize waste generation, maximize resource efficiency, and promote recycling and reuse of materials.

d) **Safer Chemicals and Materials**: There is a shift towards designing chemicals and materials that are inherently safer, reducing hazards to human health and the environment throughout their lifecycle. This includes the reduction or elimination of toxic substances.

e) **Energy Efficiency and Sustainable Energy Sources**: Continued efforts to improve energy efficiency in chemical processes, as well as increasing the use of sustainable energy sources such as solar and wind power to power chemical manufacturing.

f) **Digitalization and Data-driven Approaches**: Adoption of digital tools, machine learning, and computational modeling to optimize chemical processes, predict environmental impacts, and design greener chemicals and materials.

g) **Green Chemistry Metrics and Standards**: Development of standardized metrics and criteria to assess the environmental impact of chemical processes and products, facilitating comparisons and driving continuous improvement in sustainability.

h) **Public Policy and Regulatory Drivers**: Increasing regulatory pressures and consumer demand for sustainable products are likely to drive companies towards adopting greener chemistry practices and technologies.

i) **Collaboration and Interdisciplinary Approaches**: Collaboration across disciplines (chemistry, biology, engineering, etc.) and sectors (academia, industry, government) to foster innovation and develop holistic solutions to environmental challenges.

j) **Education and Awareness**: Enhanced education and awareness among scientists, engineers, policymakers, and the public about the principles and benefits of green chemistry, promoting its widespread adoption and implementation.

4.2 Oxidizing Reagent and Catalysts

Numerous oxidizing agents have historically been employed in organic chemistry to selectively oxidize various functional groups. While transition metals are effective in this role, they often necessitate stoichiometric quantities and can generate substantial amounts of hazardous metallic waste. Moreover, some metals are costly or toxic. Thus, there is a growing demand for alternative, cost-effective oxidizing reagents. Non-metallic catalysts have garnered attention recently as potential solutions. However, many traditional non-metallic oxidants suffer from issues such as excessive consumption (beyond stoichiometry), hazardous properties, and difficulties in recovery or regeneration, often requiring external additives.

a) **Metal oxidant:** Metal-based oxidants offer significant potential to enhance oxidation reactions in a cleaner and more efficient manner. They provide benefits such as easier product isolation and purification, as well as increased reaction selectivity. In many instances, these reagents or catalysts can be recovered and recycled, further improving their economic and environmental impact.

b) **Potassium permanganate** is a widely recognized oxidizing agent in organic chemistry, extensively employed for converting alcohols into carbonyl compounds and alkylbenzenes into benzoic acids. Its oxidation activity is notably slow under neutral conditions but accelerates in acidic or basic environments. In alkaline conditions, potassium permanganate is renowned for its ability to synthesize cis-diols from alkenes and convert tertiary amines into nitro compounds.

c) **Jones reagent;** The oxidation of alcohols using chromium trioxide in acetic acid with sulfuric acid is commonly referred to as the Jones oxidation. This reagent is highly selective as it specifically targets alcohols in the presence of alkenes, alkynes, benzylic, and allylic functional groups.

d) **Collins reagent**, also known as pyridiniumchlorochromate (PCC), is a popular and versatile oxidizing agent used in organic chemistry. It is particularly valued for its ability to selectively oxidize primary alcohols to aldehydes without further oxidizing them to carboxylic acids. This makes it a valuable tool in synthetic organic chemistry where the preservation of aldehyde functionality is desired. Compared to other oxidizing agents like chromium-based reagents (e.g., chromium trioxide), Collins reagent offers several advantages. It operates under mild conditions, typically at room temperature, which helps to avoid over-oxidation and degradation of sensitive functional groups. Additionally, it produces less hazardous waste and is relatively easy to handle in the laboratory.

e) **Non-metal oxidants** are compounds or reagents that are used in organic chemistry to facilitate oxidation reactions without relying on transition metals. These oxidants are valuable alternatives to metal-based oxidants due to various reasons such as cost-effectiveness, lower toxicity, and reduced environmental impact. They are particularly useful in cases where metal-based oxidants might introduce unwanted metal contaminants or hazardous waste.

- **Dess-Martin Periodinane**: This reagent is commonly used for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively. It operates under mild conditions and avoids the use of transition metals.
- **IBX (o-Iodoxybenzoic acid)**: IBX is a versatile oxidizing agent that can selectively oxidize primary alcohols to aldehydes and secondary alcohols to ketones. It is stable and effective under various reaction conditions.
- **TEMPO (2,2,6,6-Tetramethylpiperidine-1-oxyl)**: TEMPO is a stable nitroxyl radical that is often used as a catalyst in combination with co-oxidants such as sodium hypochlorite (NaClO) for selective oxidation of primary alcohols to aldehydes.
- **PyridiniumChlorochromate (PCC)**: While containing chromium, PCC is classified as a non-metal oxidant due to its unique properties and selective oxidation capabilities. It is used for converting primary alcohols to aldehydes without further oxidation.
- **Swern Oxidation Reagent**: A combination of oxalyl chloride, dimethyl sulfoxide (DMSO), and a base, this reagent is used for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively.

4.3 GreenOxidants

Green oxidants refer to environmentally benign oxidizing agents used in organic chemistry that minimize or eliminate the generation of hazardous wastes and reduce environmental impact compared to traditional oxidants. These oxidants play a significant role in promoting sustainable chemistry practices. Here are some examples and characteristics of green oxidants:

a) **Hydrogen Peroxide (H_2O_2)**: Hydrogen peroxide is a versatile and environmentally friendly oxidant that can be used in various oxidation reactions. It decomposes into water and oxygen, leaving no harmful residues. It is often used in combination with catalysts such as transition metals or enzymes to enhance its efficacy.

b) **Ozone (O_3)**: Ozone is a powerful oxidizing agent that can be used in organic synthesis for selective oxidations. It decomposes into oxygen, making it environmentally benign. Ozone reactions often require careful control of conditions to prevent over-oxidation.

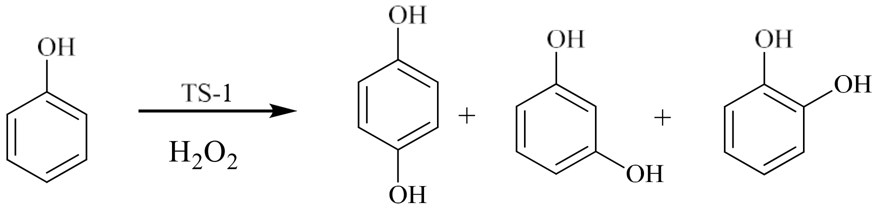
c) **Organic Peroxides**: Certain organic peroxides, such as tert-butyl hydroperoxide (TBHP), can serve as green oxidants. They are relatively stable and can selectively oxidize alcohols to carbonyl compounds under mild conditions.

d) **Sodium Hypochlorite (NaClO)**: Sodium hypochlorite, commonly known as bleach, is used as a mild oxidant in some organic transformations. It can be effective for oxidizing alcohols to carbonyl compounds and is generally less toxic compared to other chlorinated oxidants.

e) **Hydrogen Peroxide-Based Oxidants**: Modified forms of hydrogen peroxide, such as peroxy acids (e.g., performic acid, peracetic acid), can offer selective oxidation capabilities while degrading into harmless by-products.

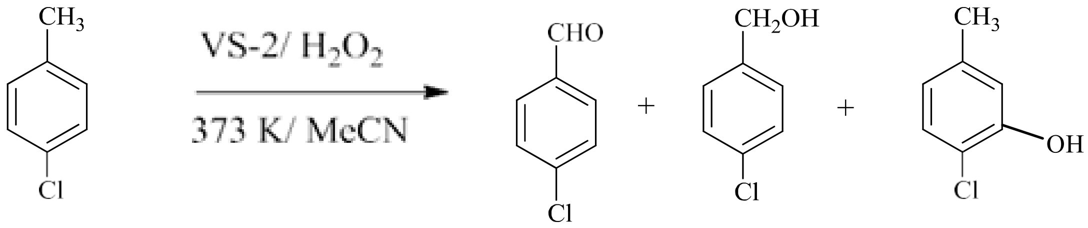
f) **Enzymes**: Certain enzymes, such as laccases or peroxidases, can catalyze oxidation reactions under mild conditions and with high selectivity. They are biodegradable and can be regenerated, making them environmentally friendly options for oxidation reactions.

4.4 Oxidation catalysts play a crucial role in the liquid-phase partial oxidation of organic substrates. Supported reagents, particularly molecular sieves containing titanium and vanadium, have demonstrated significant success in industrial applications. Titanium silicates (TS-I) are notably employed in the hydroxylation of phenol, yielding mixtures of hydroquinone and catechol, highlighting their pivotal role in these processes.



The process is environmentally friendly, achieving high product conversion with minimal waste generation.

Vanadium silicate molecular sieves selectively oxidize 4-chlorotoluene to 4-chlorobenzaldehyde using hydrogen peroxide as the oxygen source in acetonitrile solvent.



4.5 Biomimetic, Multifunctional Reagents

Scientists are working to understand the underlying mechanisms behind the various reactions that keep life in the human body. The goal of chemists is to simulate these processes in the lab. Biological processes use the same reagent to execute various manipulations, unlike synthetic chemistry, which frequently uses catalysts for transformations including oxidation, reduction, and methylation. These procedures consist of various transformations, conformational shifts, and activation. Enzyme-catalyzed hydrolysis, biological oxidations, and reductions are now possible in laboratories. Many different kinds of proteins, including ligases, transferases, oxidoreductases, hydrolases, lyases, isomerases, and ligases, are essential to these activities.

Biocatalytic conversions offer several advantages in the context of green chemistry:

a) **High Selectivity**: Enzymes are highly selective catalysts, often producing desired products without generating undesired by-products. This reduces the need for purification steps and minimizes waste.

b) **Mild Reaction Conditions**: Enzymes operate under mild conditions of temperature and pH, reducing energy consumption and potentially hazardous conditions compared to traditional chemical catalysts.

c) **Renewable and Sustainable**: Biocatalysts are derived from renewable resources (microorganisms, enzymes from plants or animals), making them environmentally sustainable.

d) **Reduced Chemical Waste**: The selectivity of biocatalysts means fewer side reactions and less chemical waste generated during the process, contributing to cleaner production methods.

e) **Biodegradability**: Enzymes are typically biodegradable and pose minimal risk to the environment after use, aligning with principles of sustainability and environmental safety.

f) **Versatility**: Enzymes can catalyze a wide range of reactions, including complex transformations, offering versatility in synthetic applications.

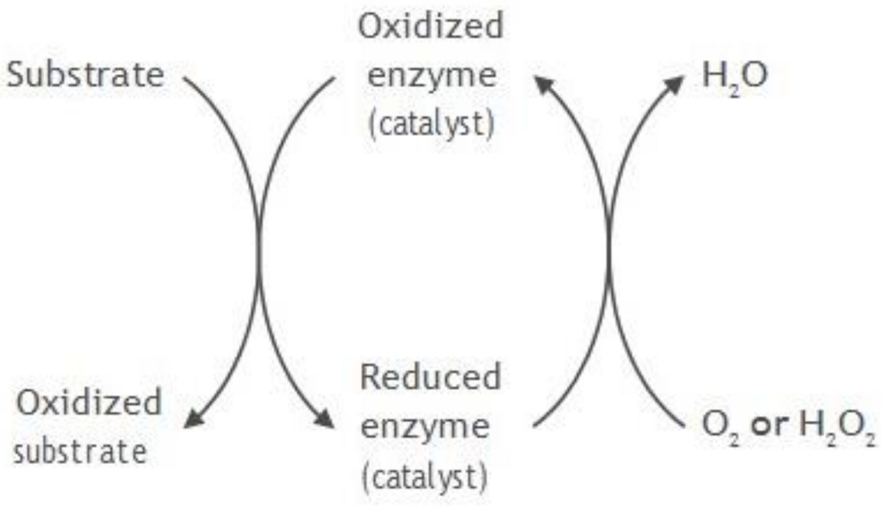
g) **Lower Energy Requirements**: Enzymes often require lower activation energies compared to traditional chemical catalysts, resulting in energy-efficient processes.

h) **Facilitates Use of Renewable Feedstocks**: Biocatalysts enable the use of renewable feedstocks and bio-based materials, further reducing reliance on fossil fuels and petrochemicals.

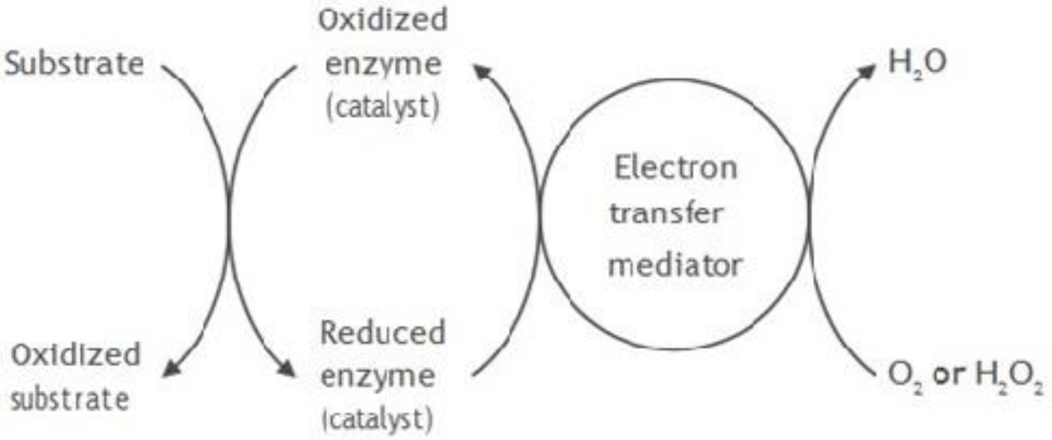
i) **Potential for Process Integration**: Biocatalytic processes can be integrated into existing industrial processes or combined with other green chemistry principles, such as solvent-free or aqueous reactions, to enhance sustainability.

j) **Regio- and Stereo-selectivity**: Enzymes can often control regio- and stereochemistry in complex molecules, enabling precise synthesis of chiral compounds, which is challenging with traditional chemical methods

A biomimetic catalyst operates in a manner similar to natural enzymes, mimicking their mode of action.



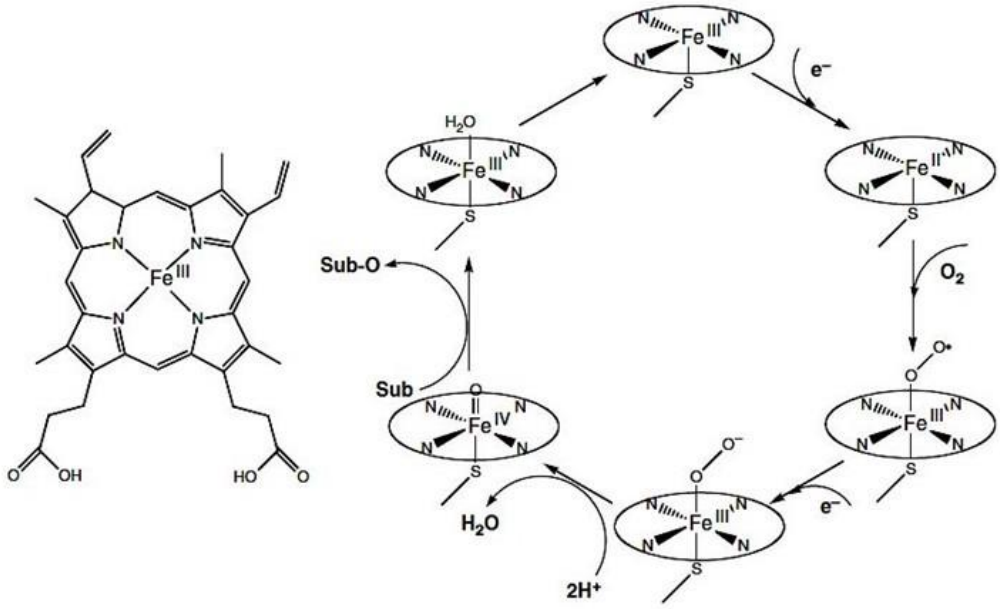
Biomimetic catalysis based on direct reocidation of enzyme(catalyst) by O_2 or H_2O_2



Biomometic catalysis based on electron-transfer mediator reoxidation of the enzyme

Biomimetic oxidation reactions, particularly those catalyzed by transition metal complexes, have significantly advanced scientific knowledge across various domains including structure, function, thermodynamics, kinetics, mechanism, synthesis, and improved analytical and spectroscopic techniques. Biomimetic chemists benefit from designing environmentally friendly catalysts, inspired by nature's preference for using non-toxic and abundantly available metals from the Earth's crust. Metals like manganese, iron, and copper are prominently involved in biological oxidation processes, with additional roles played by metals such as vanadium. These metals facilitate efficient electron transfer cycles essential for oxidation processes.

In natural oxidations, transition metals are typically coordinated by organic ligands. However, the challenge of ligand oxidation has often impeded the widespread adoption of highly effective commercial biomimetic oxidation catalysts. Nonetheless, even these imperfect catalysts can be classified as green catalysts due to their use of natural elements. They remain valuable in specific applications and contexts.



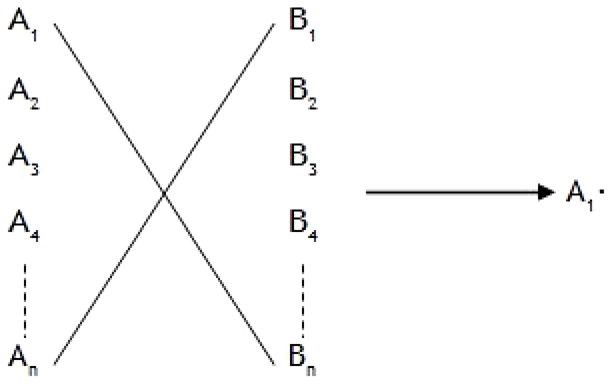
4.6 Combinatorial Chemistry

Combinatorial chemistry is a powerful approach in modern chemistry that revolutionizes the way new compounds are discovered and developed. It involves systematically creating large libraries of diverse compounds and rapidly screening them to identify those with specific desired properties. This method accelerates the process of drug discovery, materials science, catalysis, and other areas of chemical research.

Traditionally, chemists produced compounds one at a time. For instance, they would react compound A with compound B to obtain product AB. This product would then be isolated following reaction workup and purified using methods such as crystallization, distillation, or chromatography.

A+B→AB

In contrast to this traditional approach, combinatorial chemistry enables the synthesis of every possible combination of compound A_1 to An with compound B_1 to Bn.



Combinatorial Synthesis

Combinatorial techniques encompass a broad range, allowing for the synthesis of products either individually in parallel or as mixtures, utilizing both solution and solid-phase methods. Regardless of the technique employed, the key factor is the significant increase in productivity compared to traditional methods used over the past century.

4.6.1 Key Concepts and Techniques:

a) **Parallel Synthesis**: Combinatorial chemistry allows for the simultaneous synthesis of numerous compounds in a single experiment. This is achieved through automated systems or by utilizing solid-phase synthesis techniques where reactions occur on a solid support.

b) **Diversity-Oriented Synthesis**: The goal is to generate libraries of compounds that cover a wide range of chemical structures and properties. This diversity increases the likelihood of finding compounds with novel and useful characteristics.

c) **High-Throughput Screening (HTS)**: Once a library of compounds is synthesized, high-throughput screening methods are employed to quickly test each compound for specific activities or properties. This screening can involve biological assays, spectroscopic techniques, or other analytical methods.

d) **Rapid Optimization:** Combinatorial chemistry facilitates the optimization of lead compounds by systematically varying chemical structures and analyzing their effects on activity or properties. This iterative process accelerates the development of improved compounds.

e) **Computational Tools**: Computational methods play a crucial role in designing combinatorial libraries, predicting properties of compounds, and analyzing screening data. This integration of experimental and computational approaches enhances efficiency and effectiveness.

f) **Green Chemistry**: There is increasing emphasis on applying combinatorial chemistry principles to promote sustainability and reduce environmental impact. This includes using greener solvents, minimizing waste, and optimizing synthetic routes.

4.6.2 Applications:

- **Drug Discovery**: Combinatorial chemistry has significantly impacted pharmaceutical research by enabling the discovery of potential drug candidates with enhanced efficacy and reduced side effects.
- **Materials Science**: It has contributed to the development of new materials with tailored properties such as polymers, catalysts, and sensors.
- **Catalysis**: Rapid screening of catalyst libraries has led to the discovery of more efficient catalysts for various chemical transformations.

4.7 Proliferation of solvent-less reactions

Solvent-free reactions have gained widespread adoption in recent years due to their numerous advantages and contributions to green chemistry principles. Traditionally, chemical reactions have relied heavily on solvents to facilitate the mixing of reactants, control reaction conditions, and aid in product isolation. However, the use of solvents poses environmental and safety concerns, including waste generation, toxicity, and energy-intensive solvent recovery processes.

Solvent-free reactions have garnered significant attention among synthetic organic chemists. Many reactions have been discovered to proceed cleanly and efficiently in the solid state or without the use of solvents. Reduced chemical pollution, lower costs, and simplified procedures are key factors driving the recent surge in popularity of solvent-free reactions.

From the perspective of Green Chemistry, an ideal reaction should be conducted under solvent-free conditions, minimizing or eliminating side-product formation and maximizing atom economy. Solvent-free techniques are strategically important because solvents are often toxic, expensive, and pose challenges in terms of usage and disposal. This necessity has driven the development of modern technologies in this area.

Furthermore, these approaches facilitate experiments without the need for strong mineral acids (e.g., HCl, H_2SO_4), which can contribute to corrosion, safety hazards, handling difficulties, and environmental pollution through waste generation. Solid and recyclable acids such as clays offer advantageous replacements for these mineral acids.

4.7.1 Advantages of Solvent-Free Reactions:

a) **Environmental Sustainability**: Solvent-free reactions significantly reduce or eliminate the need for organic solvents, leading to reduced environmental impact and lower carbon footprint. This aligns with the goals of sustainable chemistry and resource conservation.

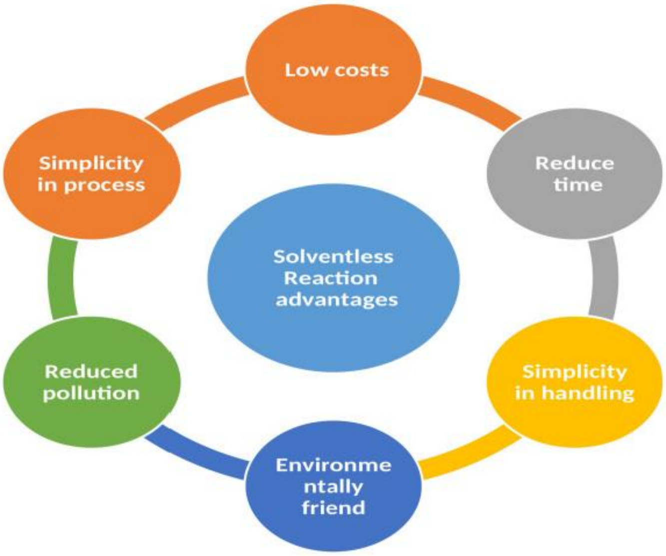
b) **Improved Safety**: Solvent-free conditions reduce the risk of solvent-related hazards such as flammability, toxicity, and exposure risks to workers. This enhances laboratory safety and minimizes health risks associated with chemical handling.

c) **Energy Efficiency**: Without the need for solvent evaporation or recovery, solvent-free reactions often require less energy input compared to traditional solvent-based processes. This contributes to overall energy efficiency and cost savings.

d) **Increased Reaction Concentration**: Solvent-free conditions allow for higher reactant concentrations, which can promote reaction efficiency and yield. This is particularly advantageous for reactions that are equilibrium-limited or require high concentrations of reactants.

e) **Simplified Product Isolation**: Products of solvent-free reactions are often easier to isolate and purify. They may require fewer purification steps, such as simple filtration or extraction, compared to solvent-based reactions involving solvent removal and recovery.

f) **Compatibility with Green Chemistry Principles**: Solvent-free reactions support several principles of green chemistry, including waste prevention, atom economy, and the use of safer chemicals and processes.



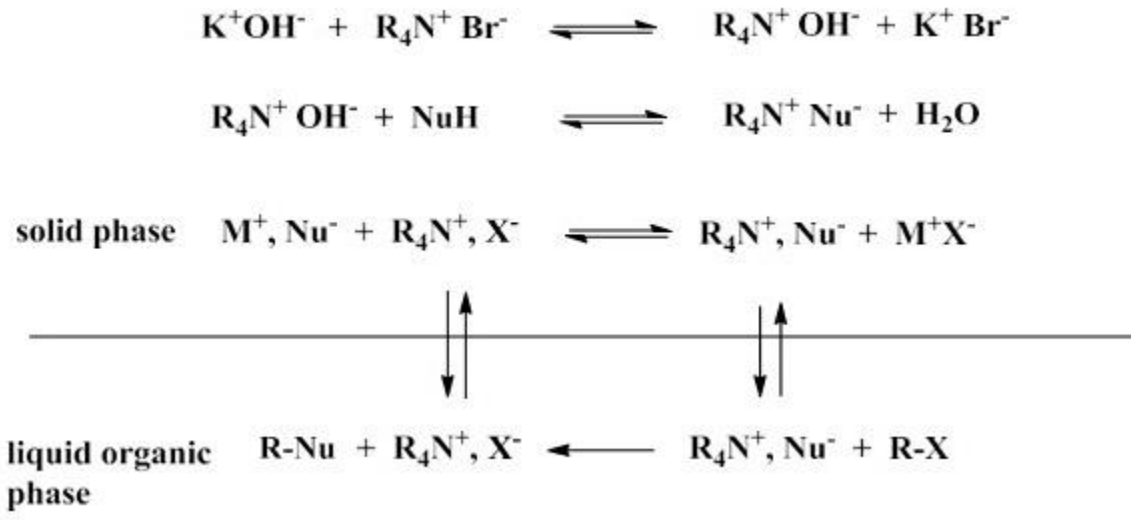
Some common advantages of solvent-free reactions

4.8 Solvent-freeTechniques

Reactants are initially applied either as neat liquids onto solid supports like aluminas, silicas, and clays, or via solutions in suitable organic solvents, with subsequent solvent removal in the case of solid supports. Reactions in "dry media" proceed with individually impregnated reactants, often followed by heating. Upon completion of the reaction, organic products are easily extracted by elution with diethyl ether or dichloromethane.

Solvent-free and catalyst-free reactions: These heterogeneous reactions occur between neat reactants in approximately equivalent amounts without any additional substances. In solid-liquid mixtures, the reaction involves either dissolution of solids into the liquid phase or adsorption of liquids onto the solid surface, facilitating interfacial reactions.

Solid-liquid phase transfer catalysis (PTC) involves reactions where neat reactants are used in approximately equivalent amounts, facilitated by a catalytic quantity of tetraalkylammonium salts or cation-complexing agents. When conducted without solvents, the liquid organic phase contains the electrophilic reagent and potentially the reaction product.



Nucleophilic anionic species can be generated in situ by reacting their conjugate acids with strong solid bases, facilitated by ion-pair exchange involving $R_4N^+X^-$.

7.9 co crystal controlled solid state synthesis

Cocrystals are crystalline solids composed of two or more different molecular or ionic compounds in a specific stoichiometric ratio. They are distinct from solvates and simple salts. A broader definition describes cocrystals as having a unique crystalline structure and unique properties due to their composition of multiple components. Cocrystals can include hydrates, solvates, and clathrates, exemplifying the principles of host-guest chemistry. Numerous instances of cocrystallization are reported annually, demonstrating their versatility and wide-ranging applications.

Cocrystal-controlled solid-state synthesis utilizes cocrystals to align reactive components, enhancing reaction speed and yield compared to traditional solution methods. Cocrystallization of drug substances presents a significant opportunity for developing new drugs with improved physical and pharmacological properties, including solubility, stability, hygroscopicity, dissolution rates, and bioavailability.

Advancements in green chemistry have enabled the engineering and development of cocrystals through environmentally friendly approaches such as solvent-free solid-state synthesis. Moreover, there has been considerable focus on computational screening, continuous manufacturing of cocrystals, and real-time quality monitoring using various analytical tools.

4.9.1 Application of Cocrystals

- Cocrystals have demonstrated diverse applications, including altering electrical properties and serving as organic semiconductors.
- In another notable application, hydroquinones were synthesized with diaminecoformers and utilized in instant photograph development.
- Cocrystal reagents present intriguing opportunities as well. By forming cocrystals from olefins, solid-state reactions were conducted with high yields.
- Diarylethene exhibited unique photochemical reactions facilitated by the conformation induced by cocrystals.
- Furthermore, co-crystals have been employed to influence chiral resolution. For instance, co crystals prepared from the racemic mixture DL-arginine demonstrated differential solubility, leading to enantiomeric separation of D- and L-based co-crystals.

4.10 Green chemistry in sustainable development

Green chemistry is poised to become one of the most crucial fields in the future. Despite rapid advancements over the past two decades, it remains in its nascent stages. Promoting green chemistry is a long-term endeavor, requiring resolution of numerous challenging scientific and technological issues spanning chemistry, materials science, engineering, environmental science, physics, and biology. Collaboration among scientists, engineers, and industrialists is essential to advance this field. The development and adoption of green chemistry undoubtedly promise significant contributions to achieving sustainable societal development.

In the future, the expansion of green chemistry must accelerate significantly to meet the sustainability challenges posed by molecular science. Collaboration among relevant scientific, engineering, educational, and other communities is essential for fostering a sustainable future through green chemistry. Indeed, the principles of green chemistry are closely intertwined with a new ethical approach, suggesting that revolutionary practices today will become tomorrow's norms. Once the twelve principles of green chemistry are fully integrated into everyday chemical practices, the need to emphasize and rename green chemistry will diminish. At that point, chemistry will face unimaginable new challenges.

Moreover, the success of green chemistry hinges on educating and training a new generation of chemists. Students at all educational levels must be introduced to the philosophy and practical application of green chemistry. Education plays a pivotal role in overcoming the challenges of implementing green chemistry principles into practice. As Albert Einstein famously remarked, "The significant problems we face today cannot be solved at the same level of thinking we were at when we created them." This underscores the need for innovative approaches and transformative thinking in advancing green chemistry towards a sustainable future.

Summary: The chapter explores several innovative approaches within green chemistry, beginning with oxidation reagents and catalysts that aim to minimize environmental impact while enhancing efficiency in chemical reactions. Biomimetic and multifunctional reagents draw inspiration from natural systems to develop synthetic methods that mimic biological processes. Combinatorial green chemistry methodologies focus on optimizing chemical processes through systematic exploration of reaction conditions and parameters. Green chemistry's role in sustainable development is underscored throughout these advancements, emphasizing the integration of environmentally friendly practices with economic viability

Keywords

Biomimetic, multifunctional reagents: Synthetic substances that mimic biological processes and perform multiple functions in chemical reactions.

Combinatorialchemistry: Methodologies for optimizing chemical processes by exploring various reaction conditions simultaneously.

Solvent-less reactions: Increasing use of techniques that eliminate the need for solvents in chemical reactions, reducing environmental footprint.

FAQ

1.Which type of chemistry focuses on minimizing environmental impact in oxidation processes?

A) Reductive chemistry
B) Green chemistry
C) Biochemistry
D) Inorganic chemistry

Answer: B)

2.**What is a primary objective of biomimetic, multifunctional reagents in green chemistry?**

A) Enhancing toxicity
B) Mimicking biological processes
C) Increasing waste generation
D) Using traditional reagents

Answer: B)

3.**Combinatorial green chemistry aims to optimize processes by:**

A) Increasing waste
B) Using toxic chemicals
C) Systematically exploring conditions
D) Minimizing resource use

Answer: C)

4. Advancements in solventless reactions contribute to:

A) Increased pollution
B) Lower safety standards
C) Enhanced production efficiency
D) Greater solvent use

Answer: C)

5. **Co-crystal controlled solid-state synthesis focuses on:**

A) Maximizing solvent use
B) Minimizing purity
C) Using hazardous chemicals
D) Minimizing solvent use

Answer: D)

6. Green chemistry in sustainable development integrates practices such as:

A) Increasing waste production
B) Avoiding renewable resources
C) Energy efficiency and waste reduction
D) Toxic material use

Answer: C)

Short Answer Questions

1. What are biomimetic, multifunctional reagents in green chemistry? How do they differ from traditional reagents?
2. Describe the concept of combinatorial green chemistry.
3. Explain the co-crystal controlled solid state synthesis (C2S3)
4. How does green chemistry contribute to sustainable development

References

1) Green Chemistry: Theory and Practice. P.T. Anastas and J.C. Warner.Oxford University Press, 2000.

2) Green Chemistry: Introductory Text. M. Lancaster,Royal Society of Chemistry (London), 2010.

3) Introduction to Green Chemistry. M.A. Ryan and M.Tinnesand, American Chemical Society (Washington), 2002.

4) Real World Cases in Green Chemistry. M.C. Cann and M.E. Connelly.American Chemical Society,2008.

5)A Textbook of Green Chemistry,Dey, Sankarand Sepay, Nayim., 2021.