P.G.SEMESTER-III

CC-XII

Environmental Chemistry and Green Chemistry

Unit-IV Green Chemistry : Def. & Obj.

Topic- Microwave Irradiation in Chemical Reactions

Dr. Jasmine Singh

Assistant Professor

Department of Chemistry

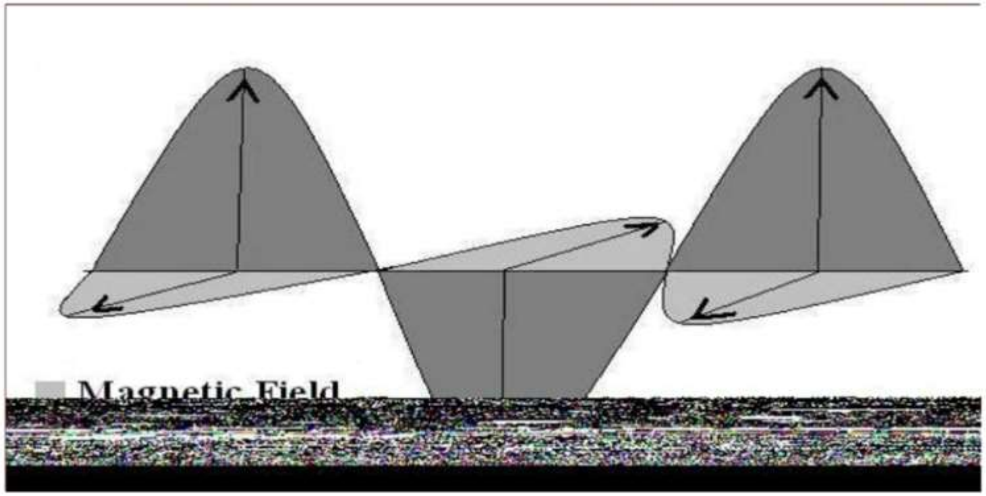
Maharaja College, Ara

Introduction

- Application of microwaves in chemical transformation was published for first time in 1986. Now the MW assisted synthesis has emerged as new green tool in synthesis of organic compounds. As the knowledge and understanding is increasing, new applications are exploring in other fields of chemical science. This presentation is focused upon the understanding of basic mechanisms of MW heating and their utility in chemistry. It also focuses on environmentally benign aspects of microwave heating including our need and responsibility.

Microwave irradiation is used in chemical reactions to provide rapid, uniform heating, which significantly accelerates reaction rates, improves product yield and purity, and supports greener synthesis methods. This technique is applicable across many fields, including organic synthesis, polymer chemistry, catalysis, and the preparation of nanomaterials

The microwaves



- *Microwaves are electromagnetic waves range from 1 cm to 1 m i.e. 30 GHz to 0.3 GHz.*

Energy Comparison

- Ionic bond ~ 7.6 eV
- Covalent [C-H] ~ 4.28 eV
- Hydrogen bond ~ 0.04 – 0.44 eV
- Brownian motion ~ 1.7×10^{-2} eV
- Microwave 2.45 GHz ~ 1.6×10^{-3} eV

Thus microwave photons are not able to break even hydrogen bond.

How Microwave Heat the Substance?

- The molecular dipoles in entire bulk tend to align with electric field of the micro wave and rotate or oscillate to follow the changing field. This Movement of molecules result into the collision and friction between molecules. And the Kinetic energy is lost as thermal energy. This is called dielectric heating which is a collective phenomenon of the bulk.

Ionic Conduction

- Charged particles (ions) oscillate under the influence of oscillating electric field of microwaves and they collide with other molecules and atoms. The kinetic energy of ions is lost in the form of heat.

Not a Quantum Mechanical Event

- Gases cannot be heated by microwave due to larger inter-particle distance (hence no friction).
- In solids, as molecules can not move freely, no heating occurs by microwaves.
- In high frequency microwaves the molecular dipole has no enough time to realign and in low frequency microwaves the reorientation is too slow. In both the cases no heating occurs. The frequency 2.45GHz is the optimum frequency, which lies between these two extremes, is usually used.
- Microwave heating effect is not a property of an individual molecule but a collective phenomenon of bulk.

Super Heating Effect

- *Using microwaves solvents can be heated well above their Boiling points for extended time.*

- *Super heating is probably due to*

  (1) Microwaves interact directly with molecules of entire volume of solvent leading to sudden and quick rise of temperature.
  (2) Nucleation points on wall of container are likely the coolest part of system hence vaporization (release of energy) is limited to top surface of liquid even on or above the b.p.

- *This effect helps Water to act as an Organic solvent.*

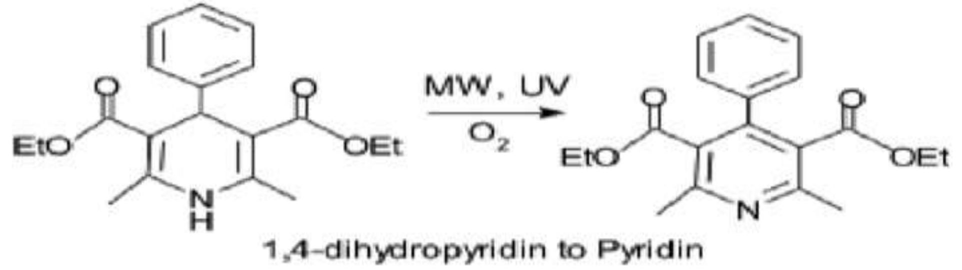
Reaction Rate Acceleration Effect

- Reaction time is reduced from hours to minutes when assisted by microwaves.
- Under microwave irradiations, high and intense temperature can be achieved very quickly and liquids are super heated.
- According to Arrhenius equation, $K=A \exp(-\Delta G°/RT)$, a simple rule is that higher is the temperature, higher is the reaction rate.

Selective Heating Effect

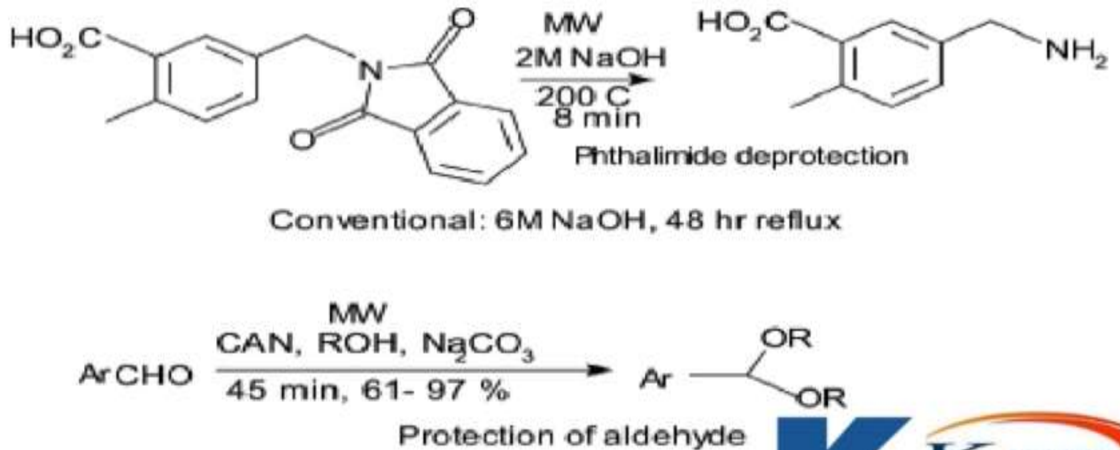
- If a solution contains more than one component only that component which can interact with microwave energy is selectively heated.
- By using poorly absorbing solvent, bulk temperature can be kept low despite the reaction proceeds at higher rate at heated heterogeneous catalyst.

Dramatic Faster Rate



Protection & Deprotection

- *Faster & milder*



Microwave Synthesis

- *Atom economy: Greater yield, lesser wastage.*
- *Clean reactions: Less byproducts, lesser purification burden.*
- *Green solvents: H_2O, EtOH and reusable IL.*
- *Less or no solvent: 0.5 - 5 ml per reaction & neat condition.*
- *Low energy input: 50W, max 300W and easy to start or stop input of energy into the reacting substance only by a switch.*
- *Reduced derivatives: Use of blocking agents, protection/deprotection require additional reagents . But in MW methods either there is no need of such temporary modifications or milder conditions can be used.*
- *Rapid reactions: Rapid method development*

Applications in Chemical Reactions

- Organic Synthesis (MAOS)
- Polymer Chemistry
- Nanomaterials Synthesis
- Catalysis

1. Organic Synthesis (MAOS)

Microwave-assisted organic synthesis (MAOS) has become a primary method for the rapid and efficient creation of organic molecules.

- **Heterocyclic compounds:** The synthesis of important nitrogen and oxygen heterocycles for drug discovery is often accelerated by microwave irradiation.
- **Cross-coupling reactions:** Palladium-catalyzed reactions, such as the Suzuki–Miyaura and Sonogashira couplings, are performed efficiently with microwave heating, even in aqueous media.
- **Diels–Alder reactions:** Microwave irradiation is highly effective for Diels–Alder cycloadditions, shortening reaction times and improving product stereoselectivity.
- **Multi-component reactions (MCRs):** The one-pot synthesis of complex molecules from three or more starting materials can be performed in minutes with microwave heating, such as in the Biginelli reaction.
- **Solvent-free reactions:** Microwave chemistry can be performed on solid mineral supports like alumina or silica, enabling cleaner reactions by eliminating toxic organic solvents.

2. Polymer Chemistry

Microwave irradiation is used to produce and modify polymers more efficiently than conventional heating methods.

- **Controlled radical polymerization (CRP):** Techniques such as Atom Transfer Radical Polymerization (ATRP) and Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization are accelerated, yielding polymers with predictable molecular weights.
- **Ring-opening polymerization (ROP):** Microwaves can dramatically decrease the time needed for ROP, for instance, reducing the synthesis of polylactide from several hours to a few minutes.
- **Polymer nanocomposites:** The technique is used for rapid, *in-situ* synthesis of nanocomposites, including graphene-based polymer and metal nanoparticle-infused materials.

3. Nanomaterials Synthesis

Microwaves enable the rapid, controlled synthesis of diverse nanomaterials by promoting uniform nucleation and growth.

- **Metallic nanoparticles:** Gold, silver, and platinum nanoparticles with controlled size and morphology can be synthesized quickly.
- **Carbon-based nanomaterials:** Microwaves assist in the preparation of graphene, carbon nanotubes (CNTs), and carbon quantum dots (CQDs) from sustainable precursors like biomass.
- **Semiconductor quantum dots (QDs):** The size of semiconductor QDs can be precisely controlled by adjusting microwave irradiation parameters

4. Catalysis

Microwave irradiation offers significant advantages for both the preparation of catalysts and the enhancement of catalytic reactions.

- **Heterogeneous catalysis:** In reactions involving solid catalysts, microwaves can cause localized heating at the active sites, leading to faster reaction rates and higher selectivity. This is due to enhanced dielectric heating of the catalyst particles, particularly at contact points.
- **Synthesis of catalysts:** The preparation of supported metal and metal oxide catalysts is often faster and more controlled under microwave conditions, leading to smaller, more uniform particles.
- **Ammonia synthesis:** Microwave irradiation enhances catalytic ammonia synthesis, providing a more energy-efficient alternative to the traditional Haber-Bosch process for certain applications.

Advantages and Underlying Principles

Key Advantages

- **Faster reactions:** By applying energy volumetrically, microwaves can reduce reaction times from hours or days to minutes, allowing for higher throughput.
- **Higher yields and purity:** The rapid, uniform heating minimizes side reactions and decomposition, leading to cleaner products and higher isolated yields.
- **Green chemistry:** The technology reduces energy consumption and supports reactions in greener solvents like water or under solvent-free conditions.
- **Rapid optimization:** The fast heating rates enable chemists to rapidly screen and optimize reaction conditions

Underlying Principles

Heating Mechanisms

Two main mechanisms explain how microwave energy is converted into heat at the molecular level:

- **Dipolar polarization:** Molecules with a permanent dipole moment attempt to align with the oscillating electric field of the microwaves. This constant reorientation causes molecular friction, converting electromagnetic energy into heat.
- **Ionic conduction:** Dissolved charged particles, such as ions, move back and forth under the influence of the electric field. This movement results in collisions with neighboring molecules, generating heat.

Thermal vs. Non-thermal Effects

- While microwave heating is primarily a thermal effect, the debate continues whether specific "non-thermal" effects contribute to enhanced reaction rates and selectivity. These potential non-thermal effects might arise from the direct interaction of the electromagnetic field with reactants or intermediates.

Conclusion

- *Microwave heating technique offers Simple, One-pot, Clean, Faster, Efficient and Economic methods for chemical transformation. It is the technology of future. We can say that it is a HAMMER in our toolkit and all the problems appear like nails.*

The students are requested to keep studying and stay tuned till further updates regarding the content .

THANK YOU !

You can mail your subject related queries on…

jasminechem1@gmail.com