



Microwave irradiation: An asset in synthetic chemistry

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Abstract: Synthesis has always been at the forefront of research and in the development of materials and compounds. A search for a novel molecule leads to the exploitation of several raw materials and techniques so as to provide a sustainable and efficient strategy for the synthesis. An ideal synthetic process must be short, clean, and high yielding. A rising concern for the environment requires the strategy to follow the Green Chemistry principles. Overcoming all these challenges, microwave-assisted synthesis has risen to the heights where it is crowned as a better synthetic method than a conventional synthetic methodology. Here, we have presented a brief overview of how this technique has affected various synthetic methodologies.

Keywords: Microwave irradiation; Synthesis; Nanoparticles; Polymers; Metal-complex

1. Introduction

Transformations in chemical compounds have been advanced by the micro-wave strategies by which a little molecules are built up into exclusive products in a division of time as compared to conventional strategies guaranteeing the acceptance of microwave irradiation as a profitable means for increasing the speed of a wide range of the chemical reaction (1,2). Microwave-assisted synthesis in chemistry improved the speed, energy and cost spent, making it as a sustainable process that is broadly welcomed as the “Green Chemistry” (2,3). It has a number of advantages, such as accelerating reactions in bulk conditions and reducing reaction times (4). By selecting the appropriate microwave parameters, It is possible to accelerate organic reactions and achieve selectivity in the products that result. This provides a number of advantages over standard heating, including rapid heating (deep inside heating), high temperature homogeneity, specific heating and instantaneous (5–7). Rapid heating belongs to microwave technology and it has many useful applications. All the possible applications for this form of heating have been identified and scientists from different fields have utilized the quick heating linked with micro-wave in applied science for a variety of beneficial activities. This includes the introduction of a compound for several analyses like polymer technology, drug discovery, alkane decomposition and ceramics. Protein and peptide hydrolysis were also known to utilize microwave irradiation among other degradation processes. It has many significant advantages in the field of inorganic and solid-state synthesis (8).

1.1. Domestic Microwave Ovens

The advance modern domestic ovens are the best option available for industrial chemists and research academicians. However, very few reports of work has been published using domestic microwaves. One drawback is that variable power levels are created with basically turning the magnetron on and off. This might be a drawback as the reaction mixture cool down rapidly. Despite of these limitations, the domestic microwave can be used for a variety of beneficial reaction.

1.2. Non-Solid State Reactions

The reactions can be carried out under conventional condition where an organic solvent is used to dissolve the reagents. One can use a very simple and basic procedure in which the reaction can be completed on an open Erlenmeyer flasks experiencing irradiation for a short period of time. Proper care should be taken that neither the solvent or starting material is inflammable or else there is a serious risk of blast or fire. The reactions are also carried out in sealed tube which has less number of limitations.

1.3. Solid State Reactions

Several chemical transformations may benefit from these kinds of reactions. Although the benefit of microwave radiation appears to have broadened the scope of such systems, there are a numbers of solid-state chemical reactions that have studied for some time. The two main types of dry reactions aided by microwaves are: one in which the reagents are 'held' on a microwave-inactive material like silicon or alumina (9). If the reaction is to many advantage from microwave irradiation, at least one of the reagents in this type of reaction should be polar. The second type of dry reactions uses a solid support that is microwave active; consequently, the reactants do not need to be microwave active (8). From a practical standpoint, solid state reactions are clearly very efficient and yield a lot. These procedures are extremely helpful for synthesis because they do not require the use of a solvent, have the high yields, and only take a short amount of time to complete the reaction, both of which are typically associated with reactions of this kind.

2. Advances in Microwave Methodology

Unlike conventional methods the microwave irradiation is found to be more effective and faster technique. It also employs both the combinatorial chemistry applications and microwave heating technology (10). The microwaves consist of electromagnetic radiation in the microwave region and most of the instruments are limited with the limits under 0.3 to 300GHz. In order to prevent the interference with radar and telecommunications, microwaves in the frequency range between 2 and 8 GHz are specifically used for domestic and synthetic purposes. The most common example is house hold ovens having MWs frequency range of 2.45 GHz. They are having negligible harmful side effect so it can be easily used on large scale. As the techniques works under high pressure it limits the formation of side products. The drug discovery and combinatorial chemistry are the fields of study that rely on building large libraries of compounds. This has the synthetic chemist to take the benefit of microwave heating process in reducing the reaction time.

The reactions are carried out very quickly and it has been reported that the final product are usually pure which itself enhance the yield of the target product. Some reactions have a liquid phase reactant which excludes the need of a solvent providing a solvent-free procedure. A number of hypothesis have been proposed by the researchers on how the microwaves are affecting the rate of reaction and enhancing the yield in conjunction with reduction in reaction time. However, it is very difficult to explain the mechanism of heating. Recently, a concept of enhanced microwave synthesis (EMS) have been put forward which is slightly different from the conventional microwave heating method (11). In EMS, an external cooling is applied by compressed air during the irradiation process. This results in the increase of the bulk temperature and the reaction mixture would get more heating during the whole process. In conventional method, when the desired temperature is achieved the machine automatically cut off the

irradiation which results the cooling of reaction mixture as the result of non-continuous irradiation. EMS helps in the homogenous irradiation of microwave so as to provide a constant heating.

3. Synthesis

3.1. Microwaves in Organic Synthesis

EMS was used to create a variety of α -keto amides. This may at last lead to further developed medicines for stroke, Alzheimer's disease, and solid dystrophy. Following a prior convention from the 1960s, the researchers coupled ketoimidoyl chloride intermediates, which were transformed into keto amides upon hydrolysis when acyl chloride were combined with various iso-nitriles (Scheme 1). This took the pathway from two to six hours under typical heating conditions. In contrast, the two steps were completed in 2 minutes and yielded 21–74% under optimal EMS conditions(12).

Scheme1: Using Enhanced Microwave Synthesis (EMS) Improved Synthesis of α -Keto amides.

The reaction with sodium phenoxide and 1,3,5-trichlorotriazine, aromatic nucleophilic substitutions are carried out under microwave irradiation (Scheme 2). The reaction rate was observed to be greatly increased during microwave irradiation as compared to conventional heating method in conjunction with the reduction of reaction time. The authors described that the modification of synthesis is significantly influenced by microwave heating (13,14).

Scheme2: Formation of substituted triazines.

The remarkable quick synthesis of N-alkylphthalimides by alkylation of phthalimide in the dry conditions under MW irradiation was reported (Scheme 3). The synthesis was carried out by simply mixing phthalimide with a catalytic amount of tetrabutylammonium bromide (TBAB) and a 25% excess of an alkyl halide. In a household microwave oven for four to ten minutes, the mixtures were irradiated in an Erlenmeyer flask and adsorbed on potassium carbonate (15). The authors used the superheating method in the domestic oven as the monitoring of temperature was a bit difficult so they keep the temperature below the boiling point of the substrate used in the chemical reaction.

Scheme 3: By using phthalimide, potassium carbonate, alkyl halide and TBAB synthesis of N-alkyl phthalimides

There are various reports available for the application of microwave-assisted synthesis using solid catalyst (16). Reaction between piperidine and chloro-alkane in presence of solid catalyst (silica) provided up to 90% yield under microwave irradiation (Scheme 4). The reaction takes place within minutes as compared to hours in conventional heating method. This suggests that the microwave-assisted technology can be coupled with a range of reaction conditions including solid supported catalyst and heterogeneous catalyst to provide the desired product.

Scheme4: Under microwave irradiation, piperidines and chloroalkanes react with silica as the solid support (6-10 min).

Microwave-assisted reaction were also applicable for Paal-Knorr reaction (17) and aza-Michael reaction (18). In Paal-Knorr reaction glutathione coated material was used as nano organocatalyst (Scheme 5). This one-step synthesis of pyrrole from amine is widely used in the field of drug discovery. Because of the efficiency with which microwaves interact with the polar nano-catalyst, MW-assisted chemistry was used because they enable a precise control over the reaction mixture rapidly reaching the required temperatures. The aza-Michael reaction synthesis also examined this catalyst (Scheme 6) and further to investigate its adaptability. In the aza-Michael reaction, the product was extracted using ethyl acetate due

to its high solubility in water due to the presence of the free –NH group. The reactions proceeded quickly, yielding excellent products within 20 minutes.

Scheme5: Microwave assisted Paal-Knor reaction

Scheme 6: Microwave-assisted aza-Michael Reaction

Guo *et al.* (19) reported Suzuki-Miyaura coupling reaction in water using 6-chloropurines and sodium tetraarylborate irradiated with microwaves. In this reaction, the isolated 6-chloro-9H-purine is reacted with sodium tetraphenylborate (0.0938mmol) in the presence of a base as catalyst 5 mol%. The isolated yields based on 9-benzyl-6-chloro-9H-purine obtained within few minutes of irradiation coupled with cleaner conversions.

Scheme7: Microwave-assisted Suzuki Miyaura coupling reaction.

3.2. Polymer Synthesis

A rising interest in bio-pharmaceutical research includes design and synthesis of biomaterial (20) as they not exclusively are significant as drug transporters yet additionally go about as more intricate frameworks who can communicate with numbers of biological system *in vivo* (21). Technology change for biomaterial synthesis has been more challenging because of failure to replicate conditions during large scale applications in industrial processes (22) However, organic biopolymers or microwave-aided technology have made this possible. Microwave heating can accelerate and be more efficient by employing large-scale reactors and controlled, solvent-free synthesis and more improvement of polymer materials (23).

The analysts have conducted extensive research on the biomedical applications of polyester and polylactic acid. Using toluene as a solvent, the first microwave assisted in the organic synthesis of d,l-Lactic Acid, which was completed using SnOct as a catalyst (24). The final products were found to have an atomic weight of 39-67 kDa and a low polydispersity list of 1.3-1.7. They were produced in a reaction time of 15 and 60 minutes, under low power (85-170W), and at 130°C. After that, the reaction was normalized to produce Poly DL-Lactic Acid with an atomic mass of 100 kDa. This was done under microwave

irradiation (255 W) to get higher yields (90 percent). However, these conditions were different to improve the degradation of polymers, which meant that the microwave-assisted organic synthesis needed to be changed again. Focus was placed on the role of excessive radiation in the development of the destructive effects on biopolymer production in terms of power and time(25)In the event that the reaction is completed in conditions that are not isothermal, rapid monomer degradation could be observed within six minutes (23).

Because it is biocompatible, poly (ϵ -caprolactone) (PCL) is a hydrophobic, semicrystalline polymer (ester) used in a variety of biomedical devices(13).When conventional and microwave methods were compared, it was found that conversion, as measured by viscosity buildup, and the number-average molecular weight of poly (ϵ -caprolactone) were the same for both processes and that microwave irradiation had no advantages (26). Since 1994, researchers have studied initiators like carboxylic acids and catalysts like lanthanide halides, lipase and Zn powder. The initiator (carboxylic corrosive) was added to the polymer chain alongside a 25/1 molar proportion of CL and benzoic acid, which was then illuminated at 680 W for four hours. Monomers in the polar functional group successfully polymerized (27).Under normal conditions, MW-assisted reactions can be carried out quickly to produce high yields (90 percent) and a high molecular weight of 200 kDa (III) (27) thereby resolving various issues that had arisen due to a homegrown microwave. The reaction temperature has increased at a faster rate since then. Microwaves can also be used to speed up polymer/biomaterial reactions and increase yields. However, thorough research is required into the fundamental aspects of the microwave assisted irradiation process. Nakamura made the observation that the reaction mix's dielectric properties would deteriorate over time, which drew the attention of more and more researchers to these parameters (28,29).

3.3. Microwave Synthesis of nano-materials

The nano-materials having novel chemical and physical properties and potential applications in various fields have received a lot of attention. The morphology, crystallography and size of the nanomaterial have a significant impact on its magnetic, electronic, and optical properties. The self-assembly of nano-scale building blocks into complex structures under morphology-controlled fabrication has recently been the focus of significant interest in device and material fabrications (30).The microwave method has recently garnered a lot of interest in material science because it helps to speed up nucleation, speed up synthesis, and produce small particles and high purity. As a result, it has a lot of potential and is simple to use in industrial processes. Results from the microwave-assisted preparation of various NiO nanostructures shows a great development on the concerned field (31).Among different nanoparticles which have applied in industrial applications, the silver nanoparticles track down a core point. Utilizing silver nanoparticles for HIV deactivation at concentrations with little or no cytotoxicity, photonics, medicine, plasmonics, optics and catalysis among other applications, has sparked significant interest. Silver nanoparticles are used as a spectrally selective coating for solar energy in the coatings industry. Silver nanoparticles have better properties than the bulk material because of their extremely small size. This includes those with an increased antibacterial efficacy, a large surface area for their volume, and the capacity to easily interact with other particles (32).

An easy-to-follow method for the synthesis of palladium(Pd) nanosheets, nanobelt and nanoplates has been developed utilizing Vitamin B₁. The synthesis of Pd nanoparticles with an variety of morphologies does not required any capping agents and water serves as the solvent. Under MW irradiation, these are highly structured Pd materials with various morphologies were utilized for Heck, Suzuki, and Sonogashira C-C coupling reactions (Scheme 8) (33).

Scheme8: Synthetic application of Pd nanoparticles.

Glycerol, a plentiful and safe byproduct of the production of biodiesel, due to its distinct chemical and physical properties, such as its low toxicity, high polarity, biodegradability, and high boiling point, has attracted attention as an alternative sustainable solvent for the synthesis of nanomaterials and catalytic reactions (34). Under non-stirred MW irradiation conditions, glycerol, a cheap and biodegradable solvent that functions as both a solvent and a reductant, was used to create diameter-controlled Ag nanowires (35). Ag nanowire bundles were produced when less sodium dodecyl sulfate (SDS) was used, while unbundled Ag nanowires were produced when more SDS was used. Changing the overall measurements of glycerol and AgNO₃ can limit the thickness of the acquired Ag nanowires. Surfactants such as cetyltriethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) are used to synthesize noble metal nanoparticles of various morphologies. It has been demonstrated that this greener method that makes use of glycerol is effective for the production of Pt, Pd and Au nanoparticles. The glycerol content and MW irradiation time can be used to adjust the size of nanosheet, and the formation of Au nanosheets in the presence of CTAB took only two minutes. The expansion of different surfactants can change the resulting molecule shapes (36).

Kijima *et al.* reported a microwave-assisted synthesis of α -Fe₂O₃ nanoparticle also be used as an electrode material that can be recharged. Between 4 V and 1.5 V, the charge-discharge test revealed a good rechargeable capacity of approximately 150 mAh/g (37). The solution changed color from bright yellow to wine red in both the conventional heating method and the microwave-assisted method, indicating the formation of a colloidal dispersion, when the solution was continuously irradiated with microwaves. Within 80 seconds, the solution's temperature rises to 100°C as a result. Despite the absence of a stabilizer in the solution, the colloidal scattering remained remarkably constant. On the other side, a magnetic hot stirrer gradually raised the temperature of the solution as it heated. After 30 minutes, a reddish-brown suspension was obtained. Although a well-crystallized α -Fe₂O₃ was produced in the solution after 60 minutes of microwave exposure, no α -FeOOH was produced. On the other hand, conventional 60-minute heating yielded both α -Fe₂O₃ and α -FeOOH. It is known that nucleation of α -FeOOH and α -Fe₂O₃ competed with one another at temperatures below 80°C. Because the solution can be rapidly heated to

100°C, microwave heating can prevent the formation of undesirable α -FeOOH. α -Fe₂O₃ nanoparticle showed altogether high electrochemical performance in view of their size and consistency. This enhancement exemplifies the advantages of microwave heating. Selenium nanoparticles were also efficiently synthesized under microwave irradiation nanoparticles from SeCl₄ in aqueous solution in order to extend the microwave method to the production of inorganic nanoparticles. In addition, the product's particle size was examined in relation to reaction time, radiation power, and surfactant type. Organic surfactants like PEG 600, SDS and PEG were also injected into molecular precursors to produce samples with uniform and controlled size distributions. All of the chemicals that were used in this method were of analytical grade and they were used as without being purified further. In the beginning, 15 mL of distilled water was used to dissolve 0.05g of SeCl₄ as a selenium precursor. After that, at room temperature, 0.05 g of SDS was added to the solution as a surfactant while stirring. 2 milliliters of hydrazine were then added to the solution. Then, the reagents were stacked into a microwave Teflon holder (100 mL), which was loaded up with 20 mL of refined water. The obtained transparent solution was placed in the center of a microwave and subjected to 750 W of radiation. When the reaction time was increased to one minute, the solution's color changed to a dark red, indicating the presence of Se₂⁺. The solution took on a dark color when the reaction time was increased to four minutes. The system was allowed to naturally cool to room temperature after irradiation, and the precipitate that was obtained was collected through filtration and washed multiple times with absolute ethanol and distilled water. At long last, the item was dried in vacuum at 70°C for 4 hr. A few boundaries including the response time, light power, and kind of surfactant were changed to make the upgraded condition (38).

3.4. Microwave Synthesis of metal complexes

The fundamental benefits of microwave synthesis is significant acceleration of reaction rates. A first-row transition metal elements complexation reaction is typically relatively quick. For the complexation reaction to produce the desired metal complex when this metal is substituted with an element of the second row, more vigorous conditions are required. Similarly, if a metal for the second row is replaced, more rigorous conditions are required with third row elements. Due to time constraints and the requirement of an inert atmosphere (often due to the air sensitivity of intermediate products) metal carbonyl chemistry is rarely investigation at this stage. Consequently in 1990, they originally arranged the significant synthesis of cis-[Mo(CO)₄(pip)₂] in 80 to 90% yield more than 30-40 min and this was effectively turned into an undergrad experiment (39).

Scheme9: Mo(CO)₆ reactions accelerated by the microwave.

In this reaction, without the need for an inert gas or a decarbonylation reagent, microwave heating makes it possible to efficiently and quickly synthesize Os₃(CO)₁₁(NCMe) from Os₃(CO)₁₂ with less than 5% of acetonitrile that was needed in the methods that were published before. It is not necessary to purify the

residue or isolate it in order to produce other high yields of mono-substituted trismium carbonyl cluster complexes $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ after the excess acetonitrile has been removed (40).

Scheme10: Microwave-assisted synthesis of Os complex.

Both conventional and microwave heating were used to quickly produce clean, high-purity, and high-yielding *cis*- $[\text{Rh}(\text{bpy})_2\text{X}_2][\text{PF}_6]$ (Scheme11) reactions in ethylene glycol. The yields from the two methods were comparable. While controlling the temperature was more difficult, the microwave reaction required a very short reaction time. The microwave method makes use of standard laboratory glassware and an unmodified domestic microwave oven. Before heating the reaction mixture, completely dissolving the $(\text{RhX}_3)_n\text{H}_2\text{O}$ is essential to obtain only the desired bis-product. For each complex, this necessitates the addition of a small amount of water to the reaction mixture and for the iodo complex, the solution must also be preheated to dissolve the reactants (41).

Scheme11: Microwave-assisted synthesis of Rh complex.

$[\text{Pd}(2,4'\text{-bypMe})\text{Cl}_3] \cdot 2\text{H}_2\text{O}$ cyclometallates in the solid phase upon heating for approximately one hour in an oven at 140°C (Scheme12) $[\text{Pd}(2,4'\text{-bypMe})\text{Cl}_3] \cdot 2\text{H}_2\text{O}$ only loses the crystalline water at the same temperature and heating upto 200°C for an hour is required for cyclometallation. The complex $[\text{Pd}(2,4'\text{-bypMe})\text{Br}_3]$ is still less reactive and 200°C , there is no reaction (42).

Scheme12: Synthesis of Pd complex by using Microwave.

As building blocks, metal polypyridine complexes are frequently utilized. The coordination sphere of Ir(III), the third row transition metal is extremely inert, and harsh reaction condition to replace the chlorine ligands of $(\text{NH}_4)[\text{IrCl}_6]\text{H}_2\text{O}$. However, in the design of supramolecular systems, a major issue is whether or not the synthetic assembly of mononuclear building blocks results in the formation of isomers. In 1964, Chiswell *et al.* reported a process of heating K_3IrCl_6 at 493K for 12 hours to make the $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$ complex (43).

Scheme13: Microwave-assisted synthesis of Ir complex.

4. Conclusions and Future Perspective

A thirst for novel compounds in medicinal, material and polymer chemistry leads to the discovery of new technologies and methods. The competing world never let anything to stay at peak and always putting a challenge to the leading candidate. Microwave-assisted synthetic technologies, no doubt have provided a successful alternative to conventional heating method with diverse advantages ranging from, reaction time, yield, efficiency and many more. It has been known to solve several bottle necks in the synthetic chemistry. The present paper is a small effort in highlighting the usage of microwave irradiation in the synthesis of different compounds and its applicability to provide better results. However, this journey also shed a light that there are still so many scope for the development in the field. For example, it is very important to decide what exactly the reason behind acceleration of reaction is and how it is effecting the mechanism of reaction. We hope that present paper will help the research community to move forward in the same direction achieving new heights.

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