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A brief review: Microwave assisted organic reaction

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ABSTRACT

This review presents a summary of reactions performed using microwave irradiation. This green processes have resulted through use of less or no catalyst, readily recyclable solvents and yield that are often higher than conventional method. It also focus on the principle of microwave activation, various types of Microwave Reactor and its characteristics.

Keywords: Microwave irradiation, radarange, magnetron,

INTRODUCTION

In early days, it was recognized that microwaves could heat water in a dramatic fashion. Domestic and commercial appliances for heating and cooking of foods began to appear in the 1950s. In 1947, the appliances called “Radarange” appeared on the market, it was intended for food processing. Cooking food with microwaves was discovered accidentally in the 1940s. Percy Spencer, a self-taught engineer, was building magnetrons for radar sets with the company Raytheon. He was working on an active radar set when he noticed that a peanut chocolate bar he had in his pocket started to melt. The radar had melted his chocolate bar with microwaves. The first food to be deliberately cooked with Spencer's microwave was popcorn, and the second was an egg, which exploded in the face of one of the experimenters. The first microwave oven was introduced by Tappan in 1955 but the widespread use of domestic microwave ovens occurred during the 1970s and 1980s. The first application of microwaves irradiation in chemical synthesis was published in 1986.

The organic synthesis is one of the major role of research in chemistry, from plastics to medication it participates in the improvements of everyone life. Over the past few decades, many significant advances in practical aspects of organic chemistry have included novel synthetic strategies and methods as well as advent of a vast array of analytical techniques. In these environmentally conscious days, the developments in the technology are directed towards environmentally sound and cleaner procedures. Hence, the present day chemists are no longer confined to using only thermal energy for driving chemical reactions. With increasing complexity of the problems and the availability of newer methods of activation of chemical reactions, chemist have restored to using wide variety of techniques such as photochemical, electrochemical, sonochemical, microwave and enzymatic methods. The first methods are as old as chemistry itself, their use by synthetic chemist has gained importance only in the past decade. With easy availability of ultrasound and microwave sources, their use in chemistry has gained momentum recently.[1]

Microwave irradiation has gained popularity in the past decade as a powerful tool for rapid and efficient synthesis of a variety of compounds because of selective absorption of microwave energy by polar molecules.[2] The application of Microwave irradiation to provide enhanced reaction rate and improved product field in chemical synthesis and it is providing quite successful in the formation of a variety of carbon-heteroatom bonds.

1.02.0 Microwave in organic Synthesis

Microwave have been used to speed up chemical reactions in the laboratories [3] which led scientists to investigate the mechanism of microwave dielectric heating and to identify the advantages of the technique for chemical synthesis.[4]

During recent years, microwaves have been extensively used for carrying out chemical reactions and have become a useful non-conventional energy source for performing organic synthesis.[5] This is supported by a great number of publications in recent years, particularly in 2003, related to the application of microwaves as a consequence of a great availability of dedicated and reliable microwave instrumentation.[6-9]

The first recorded application of microwave energy in organic synthesis is the aqueous emulsion polymerization of butyl acrylate, acrylic acid and methacrylic acid using pulsed electromagnetic radiation. The start of the rapid growth of microwave assisted procedures in organic synthesis was ignited in 1986 by pioneering papers by Gedye and co-workers[9] and Giguere and co-workers.[10] During the last two decades, the activity in this new technique has experienced exponential growth and has been extensively reviewed.[11–15] Kappe and Dallinger have reported the impact of microwaves on drug discovery.[12] Even microwave-assisted reactions under solvent-free conditions promoted the synthesis of Zincke’s salt and its conversion to chiral pyridinium salts in water[13] and microwave- assisted organic transformations using benign reaction media have also been reported.[14,16] Moreover, Varma and co-workers have reported the drug discovery by using aqueous microwave chemistry.[13,14]

1.03.0 Principles of Microwave Activation

In the electromagnetic spectrum the microwave radiation region is located between infrared radiation and radio-waves.[15] Telecommunication and microwave radar equipment occupy many of the band frequencies in this region. In order to avoid interference with these systems, the household and industrial microwave ovens operate at a fixed frequency of 2.45 GHz.[17–19] The energy of the quantum involved can be calculated by the Planck’s law $E = h\nu$ and is found to be 0.3 cal mol–1.

Presently, organic transformations take place by either of the two ways.

Conventional heating: In this method of heating, reactants are slowly activated by a conventional external heat source. Heat is driven into the substance, passing first through the walls of the vessel in order to reach the solvent and the reactants. This is a slow and inefficient method for transferring energy into the reacting system.

Microwave heating: Here, microwaves couple directly with the molecules of the entire reaction mixture, leading to a rapid rise in the temperature. Since the process is not limited by the thermal conductivity of the vessel, the result is an instantaneous localized superheating of any substance that will respond to either dipole rotation or ionic conductivity. Only the reaction vessel contents are heated and not the vessel itself; better homogeneity and selective heating of polar molecules might be achieved.

The acceleration of chemical reactions by microwave exposure results from the interactions between the material and electromagnetic field leading to the thermal and specific (non-thermal) effects. For microwave heating, the substance must possess a dipole moment. A dipole is sensitive to external electric field and tries to align itself with the field by rotation. If submitted to an alternating current, the electric field is inversed at each alterance and therefore dipoles tend to move together to follow the inversed electric field. Such a characteristic induces rotation and friction of the molecules, which dissipates as internal homogeneous heating. The electric field of commonly used irradiation frequency (2450 MHz) oscillates 4.9 × 109 times per second. Thus, microwave heating is directly dependent on dielectric properties of a substance, dielectric constant (ε') and dielectric loss (ε"). The ability of a material to convert electromagnetic energy into heat energy at a given frequency and temperature, is calculated using

$$\varepsilon'' / \varepsilon' = \tan \delta \quad (1)$$

where δ is the dissipation factor of the sample, ε" is the dielectric loss, which measures the efficiency with which heat is generated from the electromagnetic radiation and ε' is the dielectric constant which gives the ability of a molecule to be polarized by an electric field. The high value of dissipation factor δ indicates large susceptibility to microwave energy.[20]

The conduction mechanism leads, due to the much stronger interaction of ions with electric field, to the generation of heat. The ions will move under the influence of an electric field, resulting in expenditure of energy due to an increased collision rate, converting kinetic energy into heat. The heat generated by both mechanisms adds up resulting in a higher final temperature.

Since the ability of a molecule to couple with the microwave radiation is a function of its molecular polarisability (i.e. a function of its dipole moment), only polar molecules interact with microwave energy. As a guide, compounds with high dielectric constants such as water, ethanol, acetonitrile, *N*,*N*-dimethylformamide (DMF), acetic acid, chloroform. dichloromethane, acetone, ethylene glycol etc., tend to heat rapidly under microwave irradiation, while less polar substances, such as aromatic and aliphatic hydrocarbons or compounds with no net dipole moment, such as carbon dioxide, carbon tetrachloride, diethyl ether etc. as well as highly ordered crystalline substances, are poorly absorbing. Thus, polar molecules in a non-polar solvent would absorb energy, but not the solvent or the reaction vessel, if it is made of teflon ($\mu = 2.1$ at 22 °C) or ceramic or even pyrex ($\mu = 4.5–6.0$). Sometimes it is possible to use mixtures comprising microwave active reactants and microwave inactive solvents. It has also been suggested that if microwave energy is absorbed by the solvent and not by the substrate, only modest rate increase will result relative to those observed with conventional energy. If, on the other hand, the microwave energy is absorbed selectively by a reactant, by a complex or by an intermediate during the rate determining step, then large rate increase will result.

1.04.0 Instrument of Microwave Reactor

Two types of microwave reactors can be used in the Laboratory. Multimode Microwave Reactors and Monomode Microwave Reactors.

1.04.01 Multimode Microwave Reactors

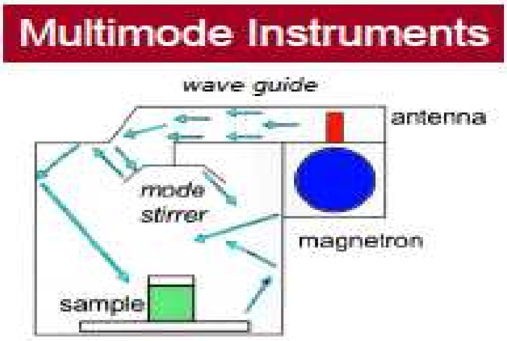

Figure:1 Multimode Microwave Reactor

Even though the microwave reactors have been introduced on the market as household devices for cooking, heating and thawing of food, they have found use in organic laboratory for carrying out organic synthesis on the laboratory scale. Most of the publications in the area of microwave chemistry from Asian countries involve use of domestic microwave ovens. These ovens (with limited power 800–1000 W) are characterized by a non-homogeneous distribution of electric field due to several reflections off the metallic walls of the oven. Since the field is heterogeneous, so their use in synthetic purposes requires mapping of the field, involving determination of hot spots of high energy using a filter paper sheet impregnated with a solution of cobalt chloride.[21] Some modifications of domestic microwave ovens have been suggested by various workers[22] such as introduction of condensers[23] by boring through the top of the oven or reaction flasks being fitted with condensers[24] and charged with pre-cooled, microwave-inactive coolants, like xylene, carbon tetrachloride etc. In addition to these, there are many dedicated large multimode versions with rotors (8 or more reactions simultaneous), but claimed to have (quasi) in-phase microwave irradiation achieved by special design of their equipment.

The use of multimode reactors has however, following limitations:
a) the distribution of electric field inside the cavity results from multiple reflections off the walls and reaction vessel and is consequently heterogeneous;
b) the temperature cannot be simply and accurately measured;
c) the power is not tunable.

There are a few examples in the literature which indicate that microwave heating was used in stirred tank reactors, for example for the esterification of benzoic acid with ethanol by conventional and microwave heating,[25] for the hydrolysis of sucrose by conventional and microwave heating[26] and for the esterification of benzoic acid and with 2 ethylhexanol.[27]

1.04.02 Monomode Microwave Reactors

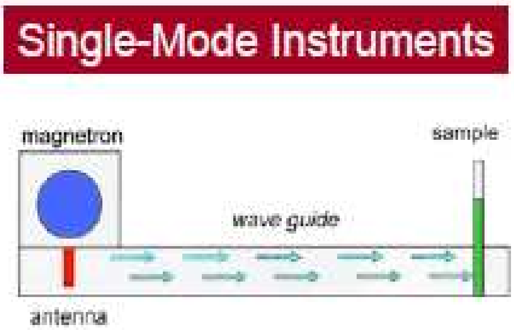

Figure :2 Monomode Microwave Reactor

In the monomode microwave oven the dimensions of wave belt (wave guide) and excitations are specially calculated so to allow only one mode of propagation or resonance. They are able to obtain a homogeneous distribution of the electric field in the wave belt (focalized fasciculus) and hence in the heated reaction mixtures. They are used with less power emitted with a high return of energy, and thus, the utilization of monomode reactor is energy efficient and leads to better yields in organic synthesis, while preserving the thermally unstable products.

Figure:3Rotative Solid Phase Microwave Reactor (RSPMR)

Figure:4Microwave Batch Reactor (MBR)

Microwave-assisted organic chemistry is reviewed[28] in the context of the methods employed. A range of technical difficulties indicated that specifically designed microwave reactors are required. Hence, Rotative Solid Phase Microwave Reactor (RSPMR), continuous microwave reactor (CMR) and microwave batch reactor (MBR) were developed for organic synthesis. On the laboratory scale, they operate at temperatures (pressures) up to 200 °C (1400 kPa) and 260 °C (10 MPa), respectively.

1.05.0 Working of the Microwave Oven

In a microwave oven, microwaves are generated by a magnetron. A magnetron is a thermo-ionic diode having an anode and a directly heated cathode. As the cathode is heated, electrons are released and are attracted towards the anode. The anode is made up of an even number of small cavities, each of which acts as a tuned circuit. The anode is, therefore, a series of circuits, which are tuned to oscillate at a specific frequency or at its overtones.

A very strong magnetic field is induced axially through the anode assembly and has the effect of bending the path of electrons as they travel from the cathode to the anode. As the deflected electrons pass through the cavity gaps, they induce a small charge into the tuned circuit, resulting in the oscillation of the cavity. Alternate cavities are linked by two small wire straps, which ensure the correct phase relationship. This process of oscillation continues until the oscillation has achieved a sufficiently high amplitude. It is then taken off by the anode via an antenna. The variable power available in domestic ovens is produced by switching the magnetron on and off according to the duty cycle.

Microwave dielectric heating is effective when the matrix has a sufficiently large dielectric loss tangent (i.e. contains molecules possessing a dipole moment). The use of a solvent is not always mandatory for the transport of heat.[29] Therefore, reactions performed under solvent-free conditions present an alternative in the microwave chemistry and constitute an environmentally benign technique, which avoids the generation of toxic residues, like organic solvents and mineral acids, and thus allows the attainment of high yields of products at reduced environmental costs. This emerging environmentally benign technique belongs to the upcoming area of green chemistry.

1.06.0 Microwave effect vs. thermal effect

Although the first publications concerned with the possibilities of use of microwave irradiation in organic synthesis appeared in 1980’s[30,31] and in polymer chemistry even earlier at the end of 1960’s[32], the sudden growth of interest in the application of microwave irradiation in almost all fields of chemistry took place at the end of 1980;s. Nowadays, there is hardly find any reaction that has not been attempted under microwave conditions. The application of microwaves in chemistry is therefore so attractive that form the very beginning it was realized that a number of chemical process can be carried out with a substantial reduction in the reaction time in comparison to conventional process. Reactions that usually take many hours or days, under influence of microwave irradiation can be run in considerably shorter time of several minutes or even seconds[33] .These phenomena are not fully understood yet; however, there are two groups of theories that are proposed to explain the reduction of the reaction time under microwave conditions in comparison with process under conventional conditions.

According to the first group of theories in spite of the fact that the course of chemical process under microwave conditions is considerably shorter than under conventional conditions, the kinetics and mechanism of the reactions are still the same. The reduction of the reaction time is the result of sudden and, sometimes, uncontrollable temperature growth of the reaction mixture under microwave irradiation, which in turn leads to the increase of reaction rates following common kinetic laws.

The second group of theories supposes that during microwave irradiation of the reaction mixture there is a specific effect of microwave activation that cause an increase of the reaction rates for which bulk temperature of the reaction mixture is an inadequate to explain. Such an effect has been accepted tot be called the non thermal microwave effect or the specific microwave, effect. Recent critical reviews concerned with both group of theories have been published by Loupy et al.[34]. Nuehter et al. [35], and de la HOz et al[36], respectively.

It is worth stressing that microwaves, in contrast to conventional heating methods, are means of volumetric heating of materials(Figure:5), which causes more extensive heating inside the material in comparison with outer layers of the material, which in turn makes hard a proper measurements of the reaction temperature. Temperature measurement under microwaves conditions, particularly for the reactions in dense and solvent less media, is difficult. Therefore, it source of inappropriate interpretation of experimental results and divergence in descriptions of the same experiments.

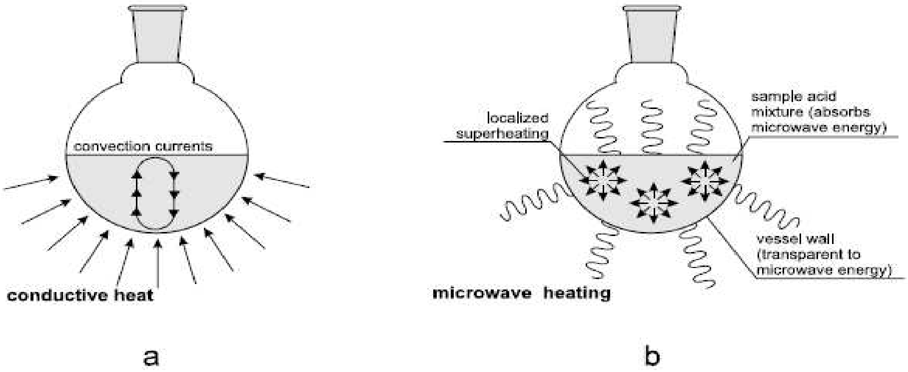

Figure:5 Different heating mechanisms for conventional and microwave heating.

1.07.0 Interaction of microwaves with different materials

Microwaves are electromagnetic radiation placed between infrared radiation and radio frequencies, with wavelengths of 1 mm to 1m, which corresponds to the frequencies of 300GHz to MHz, respectively. The extensive application of microwaves in the field of telecommunications means that only specially assigned frequencies are allowed to be allocated for industrial, scientific or medical applications(e.g. most of wavelength of the range between 1 and 25 cm is used for mobile phones, radar and radio-line transmission).Currently, in order not to cause interference with telecommunication devices, household and industrial microwave ovens are operated at either 12.2 cm(2.45 GHz) or 32.7 cm(915MHz). However, some other frequencies are also available for heating 1. Most common domestic microwave ovens utilize the frequency of 2.45 GHz, and this may be a reason that all commercially available microwave reactors for chemical use operate at the same frequency.

Heating in microwave cavities is based upon the ability of some liquid and solids to absorb and transform electromagnetic energy into heat. In general, during the interaction of microwaves with materials three different behaviors of a material can be observed depending whether the material is counted among.

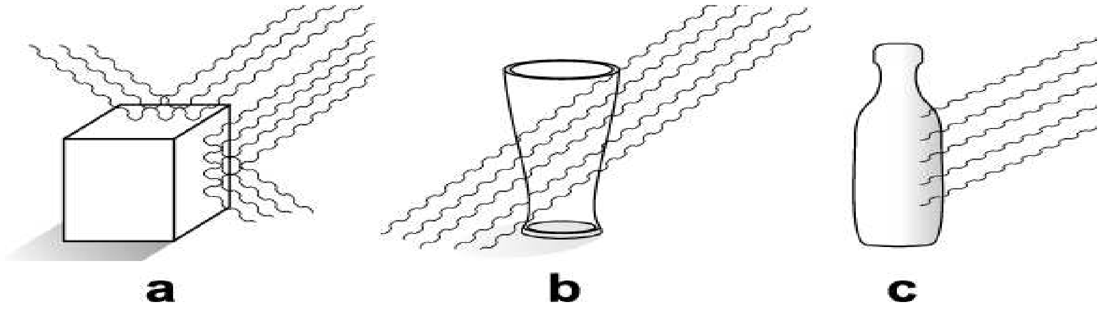

Figure:6. Interaction of microwaves with different materials
(a) electrical conductor, b) insulator, (c) Lossy dielectric.

(1) electrical conductors (e.g. metals, graphite- fig 6a)

(2) Insulators, which are considered as materials with good dielectric properties ex-tremly poor conductors) (e.g. quartz glass, porcelain, ceramics, Teflon-fig 6b)

(3) Lossy dielectrics, which are materials that exhibit so called dielectric losses, which in turn results in heat generation in an oscillating electromagnetic field (e.g. water fig 6c).

When a strongly conducting material (e.g. a metal) is exposed to microwave irradiation, Microwaves are largely reflected from its surface (fig.6a). However, the material is not effectively heated by microwaves, in response to the electric field of microwave radiation, electrons move freely on the surface of the material, and the flow of electrons can heat the material through a resistive heating mechanism. In opposite, in the case of insulators (e.g. porcelain), microwaves can penetrate through the material without any absorption, losses or heat generation. They are transparent to microwave (fig.6b). Passage of microwave radiation which is electromagnetic in nature can give rise to absorption of microwave energy and heat generation due to the so called dielectric heating mechanism(fig.6c)[37]

1.08.0 Various Types of Microwave assisted Organic Reactions

The microwave-assisted organic reactions have been broadly classified into two categories: microwave-assisted reactions using solvents; microwave-assisted reactions using solvent-free conditions.

1.08.01 Microwave Assisted Reactions using Solvents

In the case of the microwave-assisted reactions using (organic) solvents, the reactants are usually dissolved in the solvent, which often couples effectively with microwaves and thus acts as the energy transfer medium.

The use of aqueous media for organic reactions[38-42] is also under active investigation and temperatures of up to 100 °C and above have been employed for the syntheses[43,44,46] often intended to exploit the hydrophobic effect.[45] Water has a dielectric constant 78 at 25 °C which decreases to 20 at 300 °C; the latter value being comparable with that of the solvents, such as acetone, at ambient temperature.[46] Thus, water at elevated temperature can behave as a pseudo-organic solvent[51] and is a possible environmentally benign replacement for organic solvents. In addition to the environmental advantages[47,48] of using water instead of the organic solvents, isolation of the products is often facilitated by the decrease of the solubility of the organic material upon post-reaction cooling.[50]

An alternative method for performing microwave assisted organic reactions, termed enhanced microwave synthesis (EMS),[49] has also been examined. By externally cooling the reaction vessel with compressed air, while simultaneously administering microwave irradiation, more energy can be directly applied to the reaction mixture. In the conventional microwave synthesis (CMS), the initial microwave power is high, increasing the bulk temperature (TB) to the desired value very quickly. However, upon reaching this temperature, microwave power decreases or shuts off completely in order to maintain the desired bulk temperature without exceeding it. When microwave irradiation is off, classical thermal chemistry takes over, losing the full advantage of microwave irradiation, which is used to reach TB faster. Microwave enhancement of chemical reactions will only take place during the application of the microwave energy. This source of energy will directly activate the molecules in a chemical reaction, and therefore it is not desirable to suppress its application. EMS ensures that a high, constant level of microwave energy is applied, resulting in the significantly greater yields and cleaner chemistries.

Recently, the combination of two prominent green chemistry principles, namely microwaves and water has become very popular and received substantial interest.

A plethora of very recent synthetic applications describes a variety of new chemistries that can be performed with microwave irradiation but a wide range of microwave- assisted applications is still waiting.[52] Many organic transformations proceed via radical chemistry. As chemists

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wonder if microwave irradiation can promote radical transformations, microwave-assisted free-radical chemistry is increasingly being explored.[53] Microwave irradiation is applicable not only to the solvent phase chemistry, but also to the solid-phase organic synthesis. Following are the example of microwave assisted reaction using solvents.

(1) Hydrolysis[51]

Hydrolysis of benzyl chloride with water in microwave oven gives 97 % yield of benzyl alcohol in 3 min. The usual hydrolysis in normal way takes about 35 min.

$$C_6H_5CH_2Cl + H_2O \xrightarrow{\text{MW, 3 min}} C_6H_5CH_2OH$$

Benzyl Chloride Benzyl alcohol 97 %

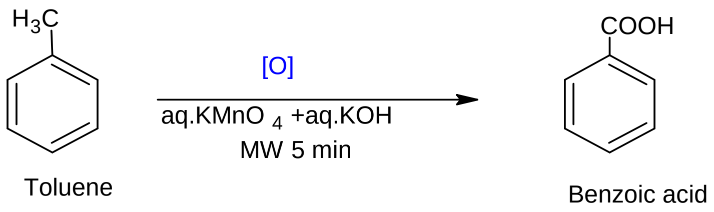
The usual hydrolysis of benzamide takes 1 hr. However, under microwave conditions, the hydrolysis is completed in 7 min giving[52] 99 % yield of benzoic acid.

$$C_6H_5CONH_2 \xrightarrow[\text{MW 7 min}]{20\%H_2SO_4} C_6H_5COOH$$

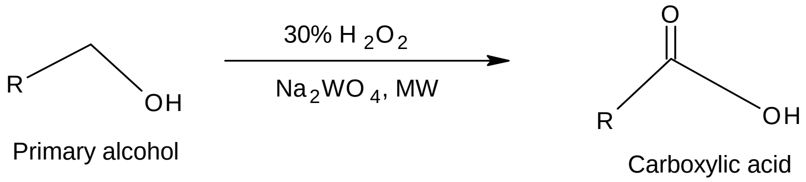
Benzamide Benzoic acid 99%

(2) Oxidation

Oxidation[52] of toluene with KMnO4 under normal conditions of refluxing takes 10-12 hr compared to reaction in microwave conditions, which takes only 5 min and the yield is 40 %.



A Number of primary alcohols can be oxidized to the corresponding carboxylic acid using sodium tungstate as catalyst in 30 % aqueous hydrogen peroxide.



(3) Esterification[53]

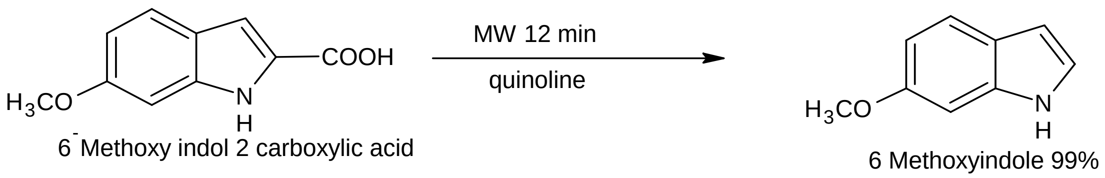
A mixture of benzoic acid and n- propanol on heating in a microwave oven for 6 min in presence of catalytic amount of conc. Sulfuric acid gives propylbenzoate.

$$C_6H_5COOH + nC_3H_7OH \xrightarrow[\text{MW 6 min}]{\text{Conc } H_2So_4} C_6H_5COOC_3H_7$$

Benzoic acid Propylbenzoate

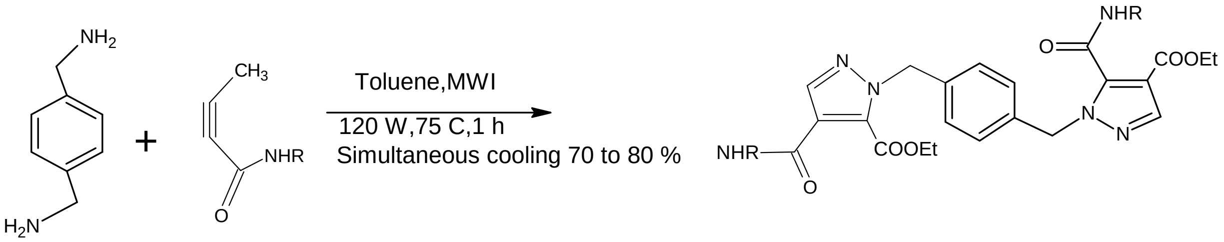
(4) Decarboxylation[54]

Conventional decarboxylation of carboxylic acids involve refluxing in quinoline in presence of copper chromate and the yields are low. However, in the presence of microwaves decarboxylation takes place in much shorter time.



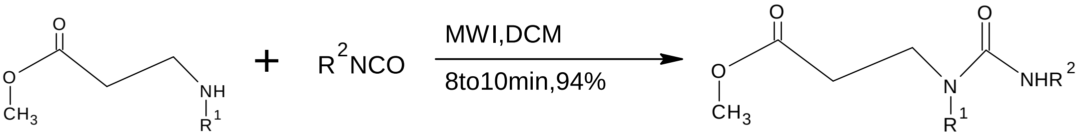
(5) Cycloaddition

1,3-Dipolar cycloadditions[55] are important reactions in organic synthesis. Cycloaducts were prepared by carrying out the reaction between an azide and a substituted amide in toluene. This reaction was carried out under microwave irradiation at 120 W at 75 °C for 1 h. The product was isolated in 70–80 % yield**.**



(6) N-Acylations [56]

N-Acylations were carried out using secondary amines and isocyanate in dichloromethane under microwave irradiation (8–10 min), yielding the product in 94% yield.



1.08.02 Microwave assisted Reactions under Solvent-Free Conditions

Due to the environmental concerns, there has currently been an increasing demand for efficient synthetic processes and solvent-free reactions. Some old and new methodologies are being used to diminish and prevent pollution caused by chemical activities. In this context, the microwaves have become an important source of energy in many laboratory procedures.[57]

Furthermore, microwave-assisted solvent-free organic synthesis (MASFOS) has been developed as an environmentally friendly process as it combines the selectivity associated with most reactions carried out under microwaves with solvent and waste-free procedures in which organic solvents are avoided throughout all stages.[58] In these environmentally conscious days, the research and development are directed towards devising cleaner processes. Environmental hazards and the subsequent degradations are instrumental for the rapid evolution of green chemistry concept involving benign reagents and conditions. The MASFOS reactions are of three types:

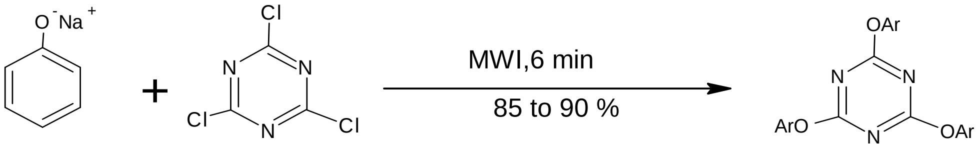
- reactions using neat reactants;
- reactions using solid-liquid phase transfer catalysis (PTC);
- reactions using solid mineral supports.

For carrying out reactions with neat reactants i.e without the use of a solvent or a support (heterogeneous reactions), at least one of the reactants at the reaction temperature should normally be liquid. In such a set-up, either the solid is partially soluble in the liquid phase or the liquid is adsorbed onto the surface of solid with the reaction occurring at the interface. There is also another possibility, namely that both the reactants are solid. Usually, they melt during the reaction course and then undergo reaction as described above.[59]

Following are the Examples of Microwaves assisted Reactions with neat reactants.

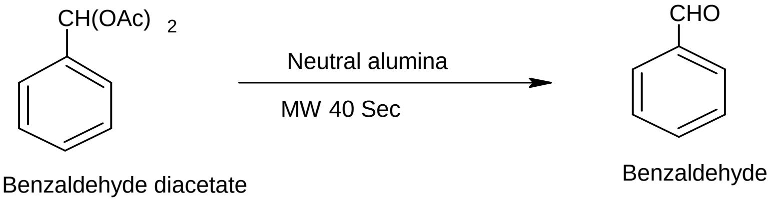
(1) Aromatic Nucleophilic Substitutions

Formation of Substituted Triazines[60,61] Aromatic nucleophilic substitutions are carried out using sodium phenoxide and 1,3,5-trichlorotriazine under microwave irradiation (6 min). The products, 1,3,5-triarlyoxytriazines are obtained in 85–90% yields.



(2) Deacetylation [62]

Aldehydes, phenol and alcohols are protected by acetylation. After the reaction, the deacetylation of the product is carried out usually under acidic or basic conditions the process takes long time and the yields are low. Use of microwave irradiation reduces the time of deacetylation and the yields are good.



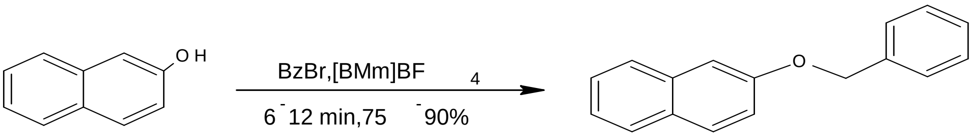
1.08.03 Microwave assisted Reactions using Solid Liquid Phase

Solid liquid phase transfer catalysis (PTC) has been described as an effective method in organic synthesis and is under active investigation. This methods is specific for anionic reactions as it involves anionic activation. A catalytic amount of a tetralkylammonium salt or a cat ion complexing agent is added to the mixture (in equimolar amounts) of both pure reactants. Reactions occur in the liquid organic phase, which consists here only of the electrophilic R-X. The presence of an additional liquid component is disadvantageous as it induces a dilution of reactants and consequently a decrease in reactivity. The electrophile R-X is therefore both the reactant and the organic phase for the reaction.

Following are the Example of Microwave assisted Reaction using Solid Liquid Phase

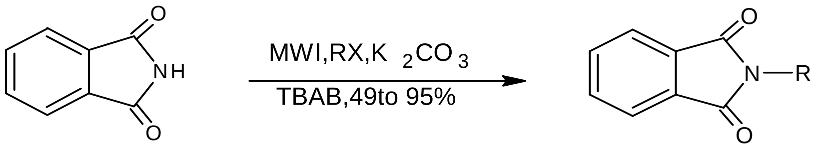
(1) O-Alkylation

Preparations of ethers were carried out from β-naphthol using benzyl bromide and 1-butyl-3-methyl-imidazolium tetrafluoroborate under microwave irradiation (6-12 min) the products were isolated in 75-90% yields.



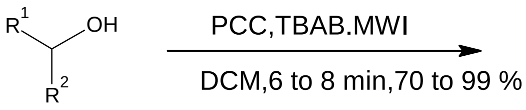
(2) N-Alkylations[63]

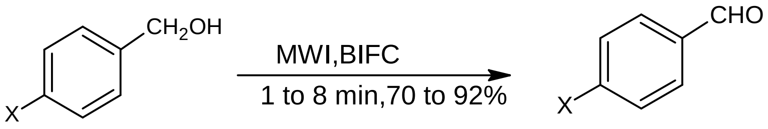
N-Alkylations under microwave irradiation using phase transfer catalysts occupy a unique place in organic chemistry. Bogdal and co-workers reported the synthesis of *N*-alkyl phthalimides using phthalimide, alkyl halides, potassium carbonate and TBAB; giving products in 45–98% yields.



(3) Oxidations[64]

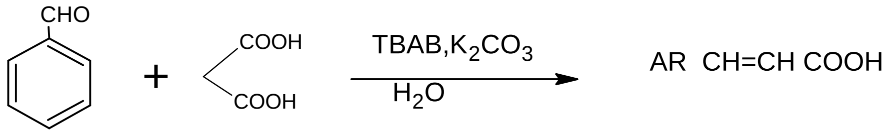
Chakraborty reported the oxidation of secondary alcohol and benzyl alcohols using phase transfer catalysts. Oxidation of secondary alcohols to acetone derivatives was carried out using PCC, tetrabutylammonium bromide and dichloromethane under microwave irradiation (6–8min), products were isolated in 70–99% yields. Oxidation of benzyl alcohols was conducted using BIFC under microwave irradiation (1–8 min) yielding benzaldehyde derivatives in 70–92% yields.





(4) Knoevenagel Condensation[65]

Knoevenagel condensation is a well known organic reaction, other applied in the synthesis of unsaturated acids, which are used as precursors for perfumes, flavonoids and as building blocks of many heterocycles. Gupta and Wakhloo studied knoevenagel condensation between carbonyl compounds and active methylene compounds, such as malonic acid, using tetrabutylammonium bromide, potassium carbonate in water forming unsaturated acids in excellent yield and purity under microwave irradiation.



Reactants $\xrightarrow{\text{Supported reagents}}$ Reactant on Supported reagents

MWI $\longrightarrow$ Products (After washing and filtration with suitable solvents)

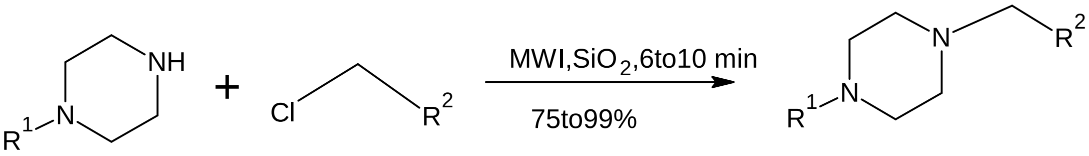
1.08.04 Microwave assisted Reactions on Mineral Supports in Dry Media

Solid supports are often very poor conductor of heat but behave as very efficient microwave absorbents. This, in turn results in very rapid and homogeneous heating. Consequently, they display very strong specific microwave effect with significant important in temperature homogeneity and heating rates enabling faster reactions and less degradation of final products as compared to the classical heating.

Following are the Example of the Microwave Activation with Supported Reagents

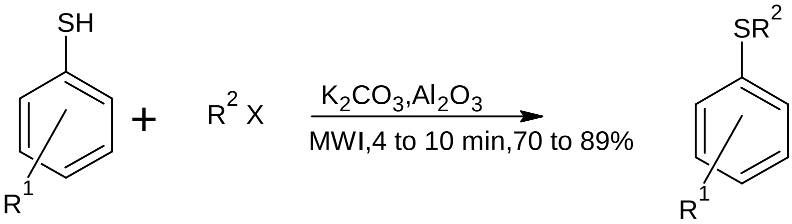
(1) N-Alkylation[66]

N-Alkylation were carried out between piperidines and chloroalkanes in the presence of silica as the solid support under microwave irradiation (6-10 min). N- Alkyl products were isolated in 79-99% yields.



(2) S Alkylation[67]

S-Alkylation was studied and accomplished by carrying out the reaction between mercaptobenzene and alkyl halides using potassium carbonate and alumina under microwave irradiation (4-10 min). Products were isolated in 70-89 % yields.



1.09.0 Application of Microwave

(1) Application of Microwave in material Chemistry

The use of microwave for synthesis of inorganic solid is very efficient and useful technique in material chemistry. Microwave has been used in preparation of ceramics and theoretical modeling of microwave interaction with ceramic material have been studied by Ayappa[68] and groups of kenkre et al[69]. And Lee et al[70].Rao et al[71]. reported that when Si and C (Charcoal) in their powder form is taken in silica crucible and is exposed to microwave for 4 to 10 min in domestic microwave oven operating at 2.45 GHz, SiC is obtained. SiC is a large volume ceramic and is extensively used for industrial application such as for grinding wheels and in manufacture of abrasion tools.

(2) Preparation of catalyst under microwave irradiation

Synthesis of a high permeance NaA zeolite $YBa_2Cu_3O_{7-X}$ membrance[72] was prepared from an aluminate and silicate sodium with molar ratio of 5 SiO_2 : Al_2O_3: $50Na_2O$:$1000H_2O$ in a modified domestic microwave oven operating at 2450 MHz in 15 min. It was observed that the permeance of the zeolite membrane synthesized by the microwave heating is 4 times higher than that of the zeolite membrane synthesized by conventional heating.

(3) Application of Microwave Technology for Nanotechnology

Today nanotechnology[73,74] is being applied in the fields of synthesis of single-site catalyst, antimicrobial nanocomposites, fire retardant materials, novel electro-optical devices, sensors, ultra soft magnets and also in the area of drug delivery systems.

(4) Application of Microwave in polymer synthesis

The synthesis of polyacrylamide(PAM)[75] was studied under microwave irradiation. PAM is used as a flocculating agent in waste water treatment. Effects of microwave radiation power on acrylamide molecular transformation ratio, with respect to PAM molecular weight, initiation and dissolve time were discussed.

(5) Analytical Chemistry

The application of microwave irradiation is immense in the field of analytical chemistry. Microwave irradiations are routinely used for sample digestion and solvent extraction techniques. They have also been put to use for gravimetric, moisture determination and to find out enthalpy of vaporization of solvents.

(6) Digestion

Development of high pressure Asher focused microwave(HPAFM) a novel approach to microwave digestion is described by H. Matusiewics. [76] The system uses focused MW operating at 2.45 GHz at 650 W power. The pressure vessels are made up of quartz discover pressure and temperature can be conducted up to 130 bar and 320□ C respectively. Using this apparatus the methodology was developed for digestion of biological reference material such as bovine liver.

(7) Microwave irradiation in waste management

Microwave heating is plying an important role in treatment of domestic and hazardous industrial and nuclear waste. Microwave heating can be advantageously used for waste management in areas where human exposure can cause health problems. The MW and high frequency technology needed for handling such type of hazardous waste is ready to use.

A process for carbonization of organic waste for manufacturing of activated carbon using MW heating has been patented by Kasai et al.[77] Activated carbon can be manufactured form organic wastes such as used paper, wood, waste plastic etc. in high carbonization efficiency using MW heating. The method and apparatus for continuous and batch process is developed for waste treatment by Roszel.[78] In this process waste such as automobile shedder waste, medical wastes, ores, sludge etc are treated by MW energy in anaerobic atmosphere.

1.10.0 Advantage and Disadvantage of Microwaves

Advantages

Rapid reactions
High purity of products
Less side-products
Improved yields
Simplified and improved synthetic procedure
Wider usable range of temperature
Higher energy efficiency
Sophisticated measurement and safety technology
Modular systems enable changing from mg to kg scale.

Disadvantages

Heat force control is difficult
Water evaporation
Closed container is dangerous because it could be burst

CONCLUSION

Microwave is a convenient way toward the goal of green/sustainable chemistry, and is strongly recommended to use in organic preparations.

The examples cited above are impressive and provide a good insight into the field of microwave-assisted organic synthesis. The benefits of microwave-assisted organic synthesis are increasingly making the technique more established worldwide. In order to achieve further development in this field, novel instruments, which give rise to reproducible performances and that constitute a minimal hazard should be used instead of the domestic microwave ovens.

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