

Review Article

AN OVER-VIEW OF MICROWAVE OVEN IN THE FIELD OF SYNTHETIC CHEMISTRY

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ABSTRACT

In the recent years Microwave-induced Organic Reaction Enhancement (MORE) chemistry has now found an important utility values for carrying out chemical reactions in organic synthesis of compounds. This technique as an alternative to conventional energy sources for introduction of energy into reactions has become a very well-known and practical method in various fields of chemistry. Microwave-assisted organic synthesis is known for the spectacular accelerations produced in many reactions as a consequence of the heating rate, a phenomenon that cannot be easily reproduced by classical heating methods. Its specific heating method attracts extensive interest because of rapid volumetric heating, suppressed side reactions, energy saving, direct heating, decreased environmental pollutions, and safe operations. Another area of interest which has been under focus recently is to avoid the use of organic solvent, which leads to wastage and is detrimental to the environment.

Keywords: Microwave, reaction, organic solvent, heating rate.

INTRODUCTION

Microwave energy is a natural phenomenon that occurs when electric current flows through a conductor. Microwaves are a form of electromagnetic radiation that is very similar to sunlight and radio waves. The Microwave region of the electromagnetic spectrum lies between infrared radiation and radio frequencies and corresponding to wavelength of 1cm to 1m, as shown in the table 1⁴

A BRIEF HISTORY OF THE MICROWAVE OVEN

Like many of today's great inventions, the microwave oven was a by-product of 20th century technology. It was during a radar-related research project around 1946 that Dr. Percy Spencer, a self-taught engineer with the Raytheon Corporation, noticed something very unusual. He was testing a

new vacuum tube called a magnetron, when he discovered that the candy bar in his pocket had melted. This intrigued Dr.

Table 1

Electromagnetic spectrum	λ / m	ν / Hz
Cosmic rays	10^{-14}	10^{22}
Gamma rays	10^{-11}	10^{19}
X-rays	10^{-9}	10^{17}
Far ultra violet	10^{-7}	10^{15}
Ultra violet	10^{-7}	10^{15}
Visible	10^{-6}	10^{14}
Infra red	10^{-4}	10^{12}
Microwave	10^{-2}	10^{11}
Radar	10^{-2}	10^{10}
Television	10^0	10^8
N.M.R.	10	10^7
Radio	10^2	10^6

Spencer, so he tried another experiment. This time he placed some popcorn kernels near the tube and, perhaps standing a

little farther away, he watched with an inventive sparkle in his eye as the popcorn sputtered, cracked and popped all over his lab.

The next morning, Dr. Spencer decided to put the magnetron tube near an egg. Dr. Spencer was joined by a curious colleague, and they both watched as the egg began to tremor and quake. The rapid temperature rise within the egg was causing tremendous internal pressure. Evidently the curious colleague moved in for a closer look just as the egg exploded and splattered hot yoke all over his amazed face. The face of Spencer lit up with a logical scientific conclusion: the melted candy bar, the popcorn, and now the exploding egg were all attributable to exposure to low-density microwave energy. Thus, if an egg could be cooked quickly, why not other foods? Experimentation began and Dr. Spencer fashioned a metal box with an opening into which he fed microwave power. The energy entering the box was unable to escape, thereby creating a higher density electromagnetic field. When food was placed in the box and microwave energy fed in, the temperature of the food rose very rapidly. Dr. Spencer had invented what was to revolutionize cooking, and form the basis of a multimillion-dollar industry- the Microwave oven.

In 1947, Raytheon demonstrated the world's first microwave oven and called it a "Radarange," the winning name in an employee contest. Housed in refrigerator-sized cabinets, the first microwave ovens cost between \$2,000 and \$3,000. Tappan introduced the first home model priced at \$1295. In 1965 Raytheon acquired Amana Refrigeration. Two years later, the first countertop, domestic oven was introduced. It was a 100-volt microwave oven, which cost just under \$500 and was smaller, safer and more reliable than previous models.

Microwave heating is routinely used for rapid cooking of foodstuffs. There are also other potential applications for the method of heating in a number of disciplines in science. It is having a great impact in the field of chemical analysis. Biologists began using microwaves in the 1970's as a quick way of decomposing samples of tissue in concentrated acids. The best containers for chemical analysis of trace elements such as copper, zinc and nickel are sealed in teflon bottles. Geological specimens have also been

analyzed by microwaves. Apart from chemical analysis the microwave heating finds applications in polymer technology, drug release/targeting, ceramics and alkane decomposition. It has also found use in a range of decomposition processes including hydrolysis of protein and peptides. Applications to inorganic and solid state synthesis have also been shown to have significant advantages. In the 1970s there was an upsurge of microwave ovens elsewhere in the world. Up to the middle of 1980's microwave oven was used only for defrosting frozen food and cooking. Since 1986 the microwave has become a source for accelerating chemical reactions, extraction etc. In inorganic chemistry microwave technique has been used since the late 1970's, while it has only been implemented in organic chemistry since the mid 1980's. Commercial microwave oven has found its way into India only recently.

CONSTRUCTION

The source is generally a magnetron in which the microwaves are generated. A magnetron is a thermionic diode having an anode and a directly heated cathode. As the cathode is heated, electrons are released and are attracted toward the anode. The anode is made up of even number of small cavities, each of which acts as a tuned circuit. The gap across the end of each cavity behaves as a capacitance.

A very strong magnetic field is induced axially through the anode assembly, and has the effect of bending the path of the electrons as they travel from the cathode to the anode. As the deflected electrons pass through the cavity gaps, they induce a small charge in 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 sufficiently high amplitude. It is then taken off the anode via an antenna. Of the 1200W of electric line power used by the magnetron, around 600w is converted into electromagnetic energy. The remainder is converted into heat that must be dissipated through air or water-cooling. Switching the magnetron on-and-off according to duty cycle produces the variable power available in domestic oven. For example, a typical 600W oven with a 30 sec duty cycle can be made to deliver an average of 300 by switching the magnetron on and off every 15 sec. When working with small

quantities of material, poorly absorbing material or at high power, a beaker of water should always be placed in the cavity along with the sample to absorb the excess energy. A wave-guide is a rectangular channel made of sheet metal. Its reflective walls allow the transmission of microwaves from the magnetron to the microwave cavity. The reflective walls of the microwave cavity are necessary to prevent leakage of radiation and to increase the efficiency of the oven. In the absence of any smoothing mechanism, the electric field pattern produced by the standing waves set up in the cavity may be extremely complex. Some areas may receive large amount of energy while others may be almost neglected. For smoothing the incoming energy in the cavity, a mode stirrer (a reflective, fan-shaped paddle) is sometimes used. Most microwave ovens are also having a turntable, which ensures that the average field energy experienced by the sample is approximately the same in all directions.[1,2]

MECHANISM

Microwave radiation can be divided into an electric field component and magnetic field component. Both conduction and dielectric polarization are sources of microwave heating.[3]

Dipolar polarization mechanism

One of the interactions of the field component with the matrix is called the dipolar polarization mechanism. For a substance to generate heat when irradiated with microwaves it should possess an element with a dipole moment- e.g. H₂O molecules. A dipole element is sensitive to external electric fields and will attempt to align with the field by rotation. The applied field provides the energy for this rotation.

In gases, molecules are spaced far apart and their alignment with the applied field is therefore rapid, while in liquids instantaneous alignment is prohibited by the presence of adjacent molecules.

The ability of molecules in a liquid to align with the applied electric field will vary with different frequencies with viscosity of the liquid. Under low frequency irradiation, the molecules will rotate in phase with the oscillating electric field. The molecules gain some energy by this behavior but the overall heating effect by this full alignment is small. Alternatively under the influence of a high frequency electric field the

dipoles do not have sufficient time to respond to the oscillating field and do not rotate. Since no motion is induced in the molecules, no energy transfer takes place and therefore no heating occurs.

If the applied field is in the microwave radiation region, however, a phenomenon occurs between two extremes. In the microwave radiation region the frequency of the applied irradiation is low enough so that the dipoles have time to respond to the alternating electric field and therefore rotate. The frequency is, however not high enough for the rotation to precisely follow the field. Therefore, as the dipole reorients to align with the electric field, the field is already changing and generates a phase difference between the orientation of the field and that of the dipole. This phase difference causes energy to be lost from the dipole by molecular friction and collisions, giving rise to dielectric heating.

Conduction mechanism

A solution containing ions or even a single isolated ion with hydrogen bonded cluster in the sample, the ions will move through the solution under the influence of an electric field resulting in expenditure in energy due to an increased collision rate, converting the kinetic energy to heat.

For example- if two samples containing distilled water and tap water respectively, are heated in a single mode microwave cavity at a fixed radiation power and for a fixed time the final temperature will be higher in the tap water sample. The conductivity mechanism is much stronger interaction than the dipolar mechanism with regard to the heat generating capacity [2, 3].

Loss of Angle

It is defined as the ability of a material to convert electromagnetic energy to heat energy at a given frequency and time.

$$\tan\delta = \frac{\Sigma''}{\Sigma'}$$

Where Σ' = Dielectric constant.

$$\Sigma'' = \text{Dielectric loss}$$

The dielectric constant of acetone and ethanol are indeed in the same range but ethanol possesses a much higher loss tangent. For these reason ethyl alcohol couples better with microwave irradiation resulting in a more rapid temperature rise.

Microwave assisted synthesis

Some of the reactions successfully carried out by microwave irradiation technique are;

1. N-Acylation.
2. Alkylation.
3. Aromatic and nucleophilic substitution.
4. Cycloaddition.
5. Condensation.
6. Deprotection and protection.
7. Esterification and transesterification.
8. Organometallic reactions.
9. Oxidation.
10. Rearrangement.
11. Reduction.

Techniques of microwave assisted synthesis

Domestic microwave oven

The relatively low cost of modern domestic microwave ovens makes them reasonably readily available to the academic and industrial chemists. There are a number of useful reactions that can be carried out in a domestic microwave oven by using different procedures. e.g -

i. Non solid state reaction

Reactions can be carried out under traditional conditions in which the reagents are dissolved in an organic solvent. This procedure can be carried out if neither the solvent nor the reactants nor the products are flammable; otherwise there is a serious risk of fire or explosion due to sparking.

ii. Solid-state—reaction

There are generally two types of microwave assisted dry reactions:

1. The reagents are supported on a microwave inactive (or poorly active) material such as alumina/ silica. In this type of reaction at least one of the reagents must be polar if the reaction is to benefit from microwave irradiation.

2. It will utilize a microwave active solid support, thus the reactants do not have to be microwave active.

Solid state reactions are of course very convenient from a practical viewpoint. In general, the reagents and solid support are efficiently mixed in an appropriate solvent, which is then evaporated. The adsorbed reagents are then placed in a vessel and subjected to microwave irradiation after which

the organic products are simply extracted from the support by washing and filtration. The absence of solvent coupled with the high yields and short reaction times and often simplicity associated with reactions of this type makes these procedures very attractive for synthesis.

Modification of domestic microwave ovens

The safety of modified microwave ovens improvised is particularly attractive. The advantage of modifying an oven is that the reaction vessel is neither sealed nor directly open to the microwave. The reaction can be carried out using a flask attached to a reflux condenser.

There are two advantages of using this system (i) A wide variety of solvents can be used because the fire hazard is significantly reduced compared to an open vessel system (ii) Reactions can be carried out under inert conditions. Recent reports have also detailed the use of continuous microwave reactors for organic transformations.

The modifications usually found in the domestic microwave ovens are:

i. Reflux system

A number of reflux systems have been developed in an effort to use solvents in microwave assisted organic synthesis without the risk of explosion. Some systems are modified domestic ovens, while others have been designed with single mode cavities. There is little risk of explosions with reflux system, since the systems are at atmospheric pressure and flammable vapor can not be released into the microwave cavity. The temperature however can not be increased by more than 13-26 °C above the normal boiling points of the solvent and only for a limited time. Although this particular superheating effect will, of course, speed up the reactions to some extent, it will not result in the same effects as at much higher temperatures.[3]

ii. Pressurized systems

Reactions performed under pressure in a microwave cavity also benefit from the rapid heating rates and remote heating of microwave dielectric heating. These types of experiments led to one of the very early development-using microwave assisted organic synthesis. The lack of control however could make these reactions very unpredictable, often resulting in explosions. Nowadays,

modern apparatus for running organic synthesis under pressure has overcome this difficulty with good temperature control and pressure measurement, which avoids a great deal of the failures due to thermal runaway reactions and poor heating. The technique offers a simple method of performing rapid synthesis and is the most versatile of the approaches presented above, but has so far not been extensively explored [3].

iii. Continuous flow systems

If the outcome of a reaction is strongly dependent on the heating profile of the reaction mixture, it is crucial to maintain that heating profile, when scaling up the reaction. If, for example, 3ml of a solvent is heated to 150 °C in 20 sec using microwave irradiation at 300W, it will be necessary to use at least 15kW power to heat 150ml of the same solvent, in order to maintain the same heating profile. High power microwave equipment is widely used for non-synthetic process purposes, but is large and not easy to accommodate, often requiring water cooling when working with volumes more than 500ml. Single mode cavity microwaves are no longer the best choice and multi-mode cavity microwave have to be used. An alternative approach is to use continuous flow system in which the reagents are pumped through the microwave cavity, allowing only a portion of the sample to be irradiated at a time. It is thus possible to maintain exactly the same heat profile even for large-scale synthesis. The main drawback is that, for some reactions, not all substances will be in solution prior to or after, microwave irradiation and this can cause the flow to stop, due to pipes becoming blocked [3].

iv. Commercial systems

The commercial system is a more expensive way of carrying out microwave assisted organic reaction. A number of systems are currently available although these have mostly been developed for analytical applications.

This type of system operates with a rotating carousel, so that a number of reaction vessels can be irradiated and agitated at the same time. The vessels are made of poly (etherimide) with teflon inserts and it is possible to monitor both the internal temperature and pressure of the reaction. Additional advantages of this type of system are the incorporation of a “microwave active” dummy load to protect the magnetron and the more reliable, accurately controlled and continuous source

of microwave radiation produced. The monitoring of temperature is a significant issue if one is attempting to compare microwave and conventionally heated reactions. A number of approaches have been used including the use of a fiber optic probe; a gas thermometer; thermochromic paints and infrared pyrometry.

Vessels

Microwave assisted reactions can, under the appropriate conditions, be carried out using conventional vessels Pyrex, PTFE etc. However, if reactions are to be carried out under pressure in sealed systems the major concern is the ability of the vessels to withstand the changes in pressure and temperature associated with the particular transformation. The rapid increases in temperature and pressure associated with microwave promoted superheating of organic materials makes it very difficult to ensure the safety of this type of procedure. It is essential that great precautions are taken when carrying out reactions in sealed vessels. The technology of vessel design is improving and ranges of vessels are now available for carrying out reactions under pressure, many incorporate pressures releasing systems as an additional safety measure. An alternative simple procedure suitable for small-scale experiments is to seal the reagents in Pyrex vials, surround them in vermiculite and irradiate with microwaves. However great care must be taken when using this type of protocol.

Reaction Medium

In microwave-induced organic reaction enhancement (MORE) chemistry the reaction are carried out in solvent medium or on solid support in which no solvent is used. For reaction in solvent medium the choice of solvent used should have a dipole moment so as to absorb microwave and a boiling point atleast 20-30°C higher than the desired reaction temperature. Microwave irradiation superheats certain solvents rapidly depending upon the dielectric constant of the solvents.

Dielectric Constant: - The magnitude of the force acting between two given electric charges placed at a definite distance apart in a uniform medium, is determined by property of the medium and is known as dielectric constant.

If 'e₁' and 'e₂' are the values of the two electric charges placed at a distance 'r' apart in a uniform medium, then the force 'F' acting between them is given by Coulombs Law as $F = e_1 e_2 / \Sigma r^2$, where $\Sigma =$ Dielectric constant of the medium.

The larger the dielectric constant the greater the coupling with microwaves and thus faster the rate of heating [4].

List of the solvents and their physical properties:

The following table gives the relative physical constants.

Solvents	Dielectric Constant	Boiling Point (°C)
Water	80.00	100
Formic acid	51.10	100-101
DMF	38.25	160
Ethylene Glycol	37.70	196
Acetonitrile	36.64	80-81
Methanol	33.00	65
Ethanol	25.30	78
Acetone	21.01	55-56
Dichloromethane	8.93	39-40
Tetrahydrofuran	7.52	65-67
Chlorobenzene	5.69	116-118
Chloroform	4.80	60-62
Xylene	20.50	137-144
Toluene	2.38	110-111

Although the dielectric constant is the guiding factor behind absorption of energy, there are several other factors, which are involved in microwave heating. Even if a solvent has a much lower dielectric constant, the solvent can get heated up rapidly due to its lower heat capacity. For example 1-propanol ($\epsilon = 20.1$) having a lower dielectric constant than water ($\epsilon = 78.54$) heats up 1.7 times faster than water mainly because of propanol has lower heat capacity (2.45 J/gK) compared with water (4.18 J/gK). Similarly porcelain has a higher dielectric constant (6.0 – 8.0) than acetic acid (6.15 at 20° C) but the latter heats up rapidly since ceramic

molecules cannot rotate in the alternating microwave field.

Water has a dielectric constant, which decreases from 78 at 25°C to 20 at 300°C. Water can therefore behave as a pseudo- organic solvent at elevated temperature; hence it is not an ideal solvent system in microwave oven.

ADVANTAGES

The short reaction times and expanded reaction range that is offered by microwave assisted synthesis are suited to the increased demands in industry. In particular, there is a requirement in the pharmaceutical industry for a higher

number of novel chemical entities to be produced, which require chemists to employ a method to reduce the time for the production of compounds. Chemistry data bases, software for diversity selection, on-line chemical ordering system, open access and high throughput system for analysis and high speed parallel and combinatorial synthesis equipment have all contributed in increasing the throughput. The common factor for these technical resources is automation and computerized control. They do not however speed up the chemistry itself. Development in the chemistry has generally been concerned with novel high reactive reagents in solution or on solid support.

In general most organic reactions have been heated using traditional heat transfer equipment such as oil bath, sand bath and heating jacket. These heatings are however rather slow and temperature gradients can develop within the sample. In addition local overheating can lead to product, reagent and substrate decomposition.

In contrast, in microwave dielectric heating, the microwave energy is introduced into the chemical reaction remotely and direct access by the energy sources to the reaction vessels is obtained. The microwave radiation passes through the walls of the vessels and heats only reactants and solvents and not the reaction vessel itself. If the apparatus is properly designed, the temperature increase will be uniform throughout the sample, which can lead to less by-products and decomposition products. In pressurized systems, it is possible to rapidly increase the temperature far above the conventional boiling point of the solvents used.

PRECAUTIONS

Long heating times and reaction using a large volume of reactants should be avoided because these conditions generate very high pressure in the vessels in some reactions. If the volume of reaction is kept between 10 and 15% of the volume of the containers, the pressure will not exceed safe limits. To ensure safe experiments heating time of more than 5 min at a power of 500 watts should be avoided. Higher power levels should be avoided regardless of the heating times or the volume of the container.

Metallic containers should not be used in the microwave oven because sparking may occur and may damage the oven. Microwave oven should not be operated when it is empty because the oven wall may be damaged.

CONCLUSION

Since its inception in 1986, microwave-assisted organic chemistry has become an exciting and vibrant field for research and development. In this review, we have presented an overview on microwave-assisted technique for performing successful chemical reactions. Microwave assisted organic synthesis is a technique which can be used to rapidly explore chemistry space and increase the diversity of the compounds produced. In this method reaction times are reduced from days/hours to minutes/seconds. Thus, there can be significant time saving in polymerization reactions, in contrast to the conventional heating which needs very longer reaction times. Besides, we have shown that it is possible to conduct very clean reactions with the use of less toxic reagents than conventional heating. The overall process in which direct "in-core" heating of the medium takes place is more energy efficient than classical oil-bath heating. Nowadays, it could be considered that all of the previously conventionally heated reactions could be performed using this technique.

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