A Platinum Open Access Journal
for Organic Chemistry

Review

Free to Authors and Readers

DOAJ Seal

Arkivoc **2025** (2) 202412288

Microwave thermal effects in chemistry

Angel Díaz-Ortiz and Antonio de la Hoz*

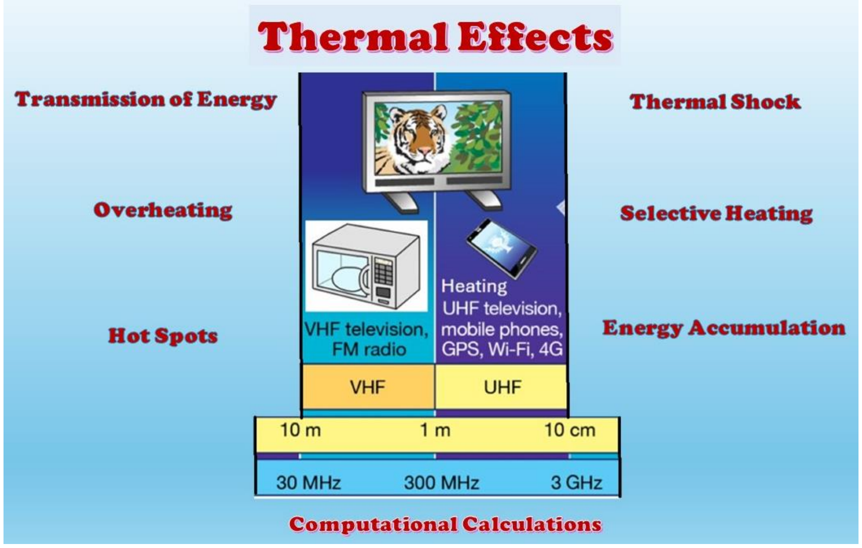
Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, E-13071 Ciudad Real, Spain
Email: Antonio.Hoz@uclm.es

Dedicated to Prof. Rajender Varma

Received 09-14-2024 **Accepted** 11-16-2024 **Published on line** 11-20-2024

Abstract

Microwave radiation has been successfully applied in chemistry, with a notable increase in publications, especially since the introduction of equipment specifically designed for chemical synthesis. The most striking effects are the extraordinary reduction in reaction times, leading to better yields and the possibility of minimizing the decomposition of sensitive reagents and products. However, the differences in energy transmission compared to conventional heating can also be exploited to carry out impossible reactions and modify selectivity. This is the aim of this review, which shows the thermal effects of radiation, its practical aspects, and how they can be efficiently utilized.



Keywords: Microwave, thermal effects, computational calculations

Cite as *Arkivoc* **2025** (2) 202412288
DOI: https://doi.org/10.24820/ark.5550190.p012.288

Table of Contents

1. Introduction

Microwave radiation is an electromagnetic radiation, composed of orthogonal electric and magnetic fields, encompassing frequencies between 300 MHz and 300 GHz, corresponding to wavelengths between 1 cm and 1 m (Figure 1).

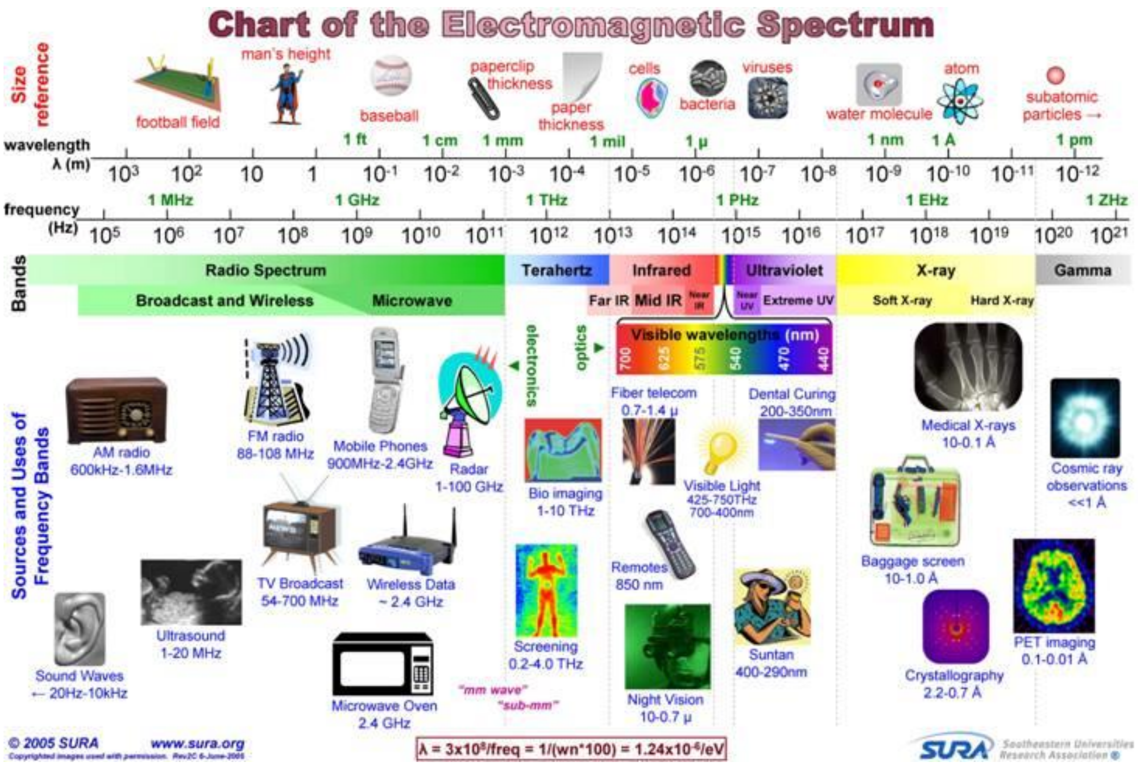


Figure 1. Chart of the Electromagnetic Spectrum. Reproduced from https://www.yardimcikaynaklar.com/mikrodalga-radyo-dalgalari-ve-gama-isinlarinin-bilim-ve-teknolojideki-kullanim-alanlari/.[1]

Due to its impact on RADAR and telecommunications, this part of the electromagnetic spectrum is highly regulated. Therefore, the ISM (Industrial, Scientific, Medical) frequencies allowed for applications are very limited, with the most commonly used being 2.45 GHz, which corresponds to a wavelength of 12.2 cm.

With microwaves, energy transfer does not occur through convection or conduction as in conventional heating, but through dielectric losses. The propensity of a sample to heat with microwaves is highly dependent on its dielectric properties. The dielectric loss factor (ε”) and the dielectric constant (ε’) of a material are two determinants of the efficiency of heat transfer to the sample. ε’ is the real part of the complex permittivity, reflecting dipole polarization and representing the material's ability to store microwave energy. ε” is the imaginary part of the complex permittivity, indicating the material's ability to dissipate microwave energy (as heat). Their ratio (ε”/ε’) is the dissipation factor (tan δ); high values of tan δ indicate easy susceptibility to microwave energy and are required for rapid microwave heating to occur.

As a guideline, compounds with high dielectric constants tend to heat rapidly with microwaves, while less polar substances, compounds without a dipole moment, and highly ordered crystalline compounds absorb poorly.[2]

The transformation of radiation into heat occurs through polarization mechanisms. Generally, it is considered that the electric component is responsible for heating, although some materials heat more efficiently through the magnetic component.

Materials dissipate energy from the electric component through two mechanisms: dipole rotation and ionic conduction (Figure 2). Dipole rotation refers to the alignment of molecules with permanent or induced dipoles to the electric field component of the radiation. At 2450 MHz, the field oscillates 4.9 x 10^9 times per second, and the sympathetic agitation of the molecules generates heat. The efficiency of heat production through dipole rotation depends on the characteristic dielectric relaxation time of the sample, which varies with temperature and viscosity.

The second dissipation mechanism, ionic conduction, involves the migration of dissolved ions in the oscillating electric field. Heat generation in this case results from frictional losses that depend on the size, charge, and conductivity of the ions as well as their interactions with the solvent.

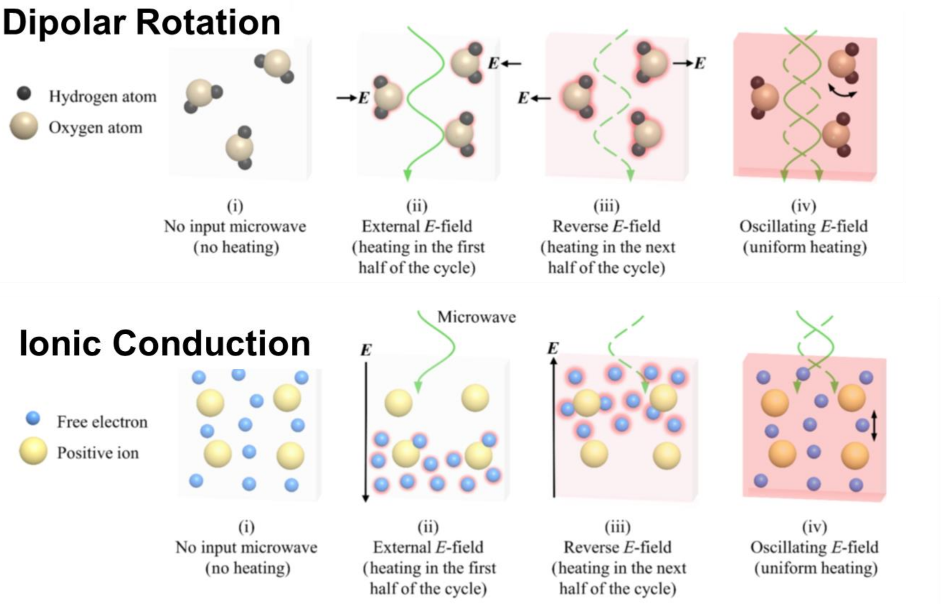


Figure 2. Polarization mechanisms in the presence of the E field. Reproduced from Ref. 2 with permission.

In the presence of a magnetic field, eddy currents can occur in magnetic media near the surface of a conductor, creating an induced field that opposes the inductor. The resulting field produces heating through the Joule effect when the direction of the induced current changes.

In ferromagnetic materials, which have magnetic domains, hysteresis can also occur in the presence of a magnetic field, undergo rapid flipping, resulting in friction and considerable heating (Figure 3, Table 1).[3,4]

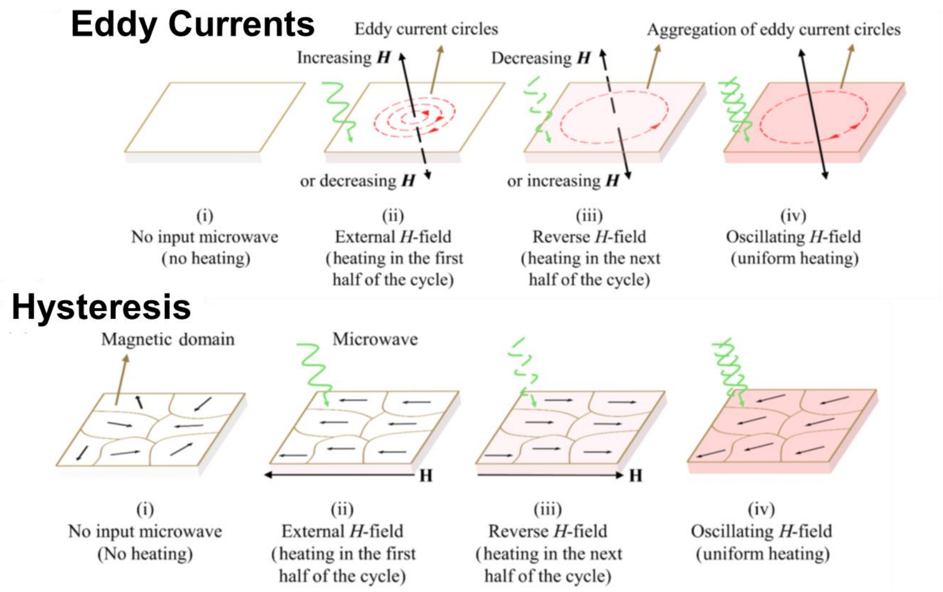


Figure 3. Polarization mechanisms in the presence if the H field. Reproduced from Ref. 2 with permission.

Table 1 shows the predominant polarization mechanisms based on the material.

Table 1. Predominant polarization mechanisms based on the material

Material		Example	Mechanism
Insulator	Low loss factor	Teflon y Quartz	Negligible losses
	High loss factor	H_2O, Zirconite Organic Compounds	Dipolar rotation
Semiconductor		SiC y MgO	Ionic conduction
		Graphite, graphene	Ionic conduction Eddy currents Interfacial losses
Conductor	No magnetic	KCl (melted)	Ionic conduction
		Cu, Zn, Al y W	Eddy currents
	Magnetic	Fe, Co, Ni y Fe_3O_4	Magnetic losses

Finally, another important factor is the penetration depth. The microwave field decreases as it penetrates into the material. Penetration depth is described as the distance at which the microwave field decreases to 37% of its initial value. It depends on the wavelength of the radiation and the dielectric properties of the material.

$$PD = \frac{\lambda}{2\pi} * \sqrt{\varepsilon'}/\varepsilon''$$

Equation 1. Penetration Depth.

Thus, substances like Teflon have a high penetration depth factor, radiation crosses the sample but does not heat up. Metals, on the other hand, have a very low penetration depth factor and reflect the radiation, whereas organic compounds, which are diamagnetic, absorb radiation throughout the volume of the sample and heat up efficiently (Figure 4).[5]

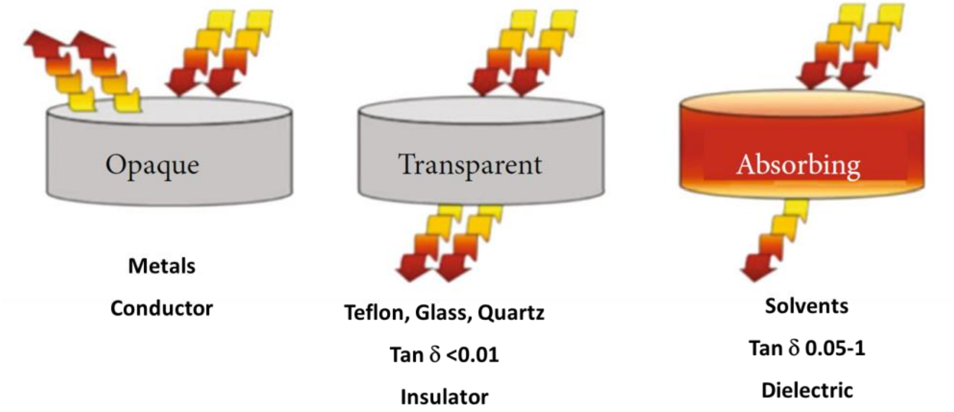


Figure 4. Macroscopic behaviors of a material under microwave radiation. Reproduced from ref. 5 with permission.

All of this makes microwave heating fundamentally different from conventional heating, which can be leveraged to achieve different results by exploiting the characteristics of dielectric heating with microwaves (Table 2).

Table 2. Comparison between microwave irradiation and conventional heating

Microwaves	Conventional heating
Energy coupling	Conduction/convection
Coupling at molecular level	Superficial heating
Volumetric	Superficial
Rapid	Slow
Selective	Non selective
Dependent on the properties of the material	Less dependent
Smart Control	Control by the superficial temperature
Emerging Technology	Established Technology

2. Thermal Effects

The achievement of positive results using microwave radiation that could not be solely explained by a rapid heating effect led several authors to propose the existence of specific effects directly related to electromagnetic radiation and not to heating. Many of these results have subsequently been refuted, attributed to errors in measurement of reaction temperature, which was one of the main problems encountered in the early years. In any case, both thermal effects and "possible" non-thermal effects stem from the interaction of the wave with the material, making it very difficult to experimentally separate them, further complicating the detection of "non-thermal" effects.

Considering the Arrhenius equation, thermal effects are related to the reaction temperature and can thus be determined with efficient and accurate temperature measurement. Non-thermal effects should be related to variations in activation energy, stabilization of the transition state, or the pre-exponential factor, which determines the probability of effective collisions, although the increase in temperature can also favor them (Figure 5).[6]

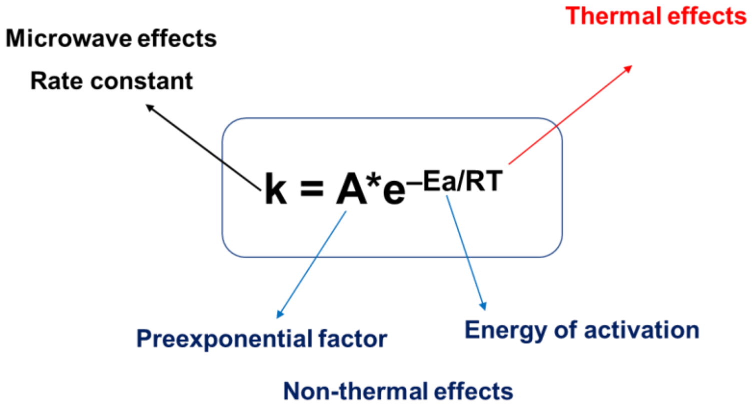


Figure 3. Thermal and non-thermal effects in reactions considering the Arrhenius equation.

2.1. Transmission of energy

The transmission of energy is fundamentally different in conventional heating and dielectric microwave heating. In the former, an external heat source is used to directly heat the sample's surface. Heat is then transferred to the interior through conduction and convection currents, making good agitation, essential for rapid and homogeneous heat distribution. Generally, the surface temperature is higher than that of the interior.

Microwave heating arises from the transformation of the absorbed radiation by the sample into heat. The radiation penetrates the material, heating the entire volume of the sample, where localized overheating can occur. It doesn't require vigorous agitation for efficient heat transmission as conventional heating requires, and contrary to it, temperature at the surface is lower than the temperature inside the sample, especially for solids with low thermal conductivity. Therefore, the temperature profile differs in both cases, potentially leading to different outcomes.

The shape and size of the sample have a significantly different and greater influence with microwaves than with classical heating. Spherical containers are the best choice with conventional heating to favor heat transfer, but they tend to accumulate radiation and thus heat in the center, this is why cylindrical containers are commonly used under microwaves. Penetration into a material is on the order of the wavelength. Even in liquids, temperature can be stratified, as convection cannot move the hot, less viscous zones to colder regions of the fluid more rapidly than power can accumulate heat (Figure 6).[7]

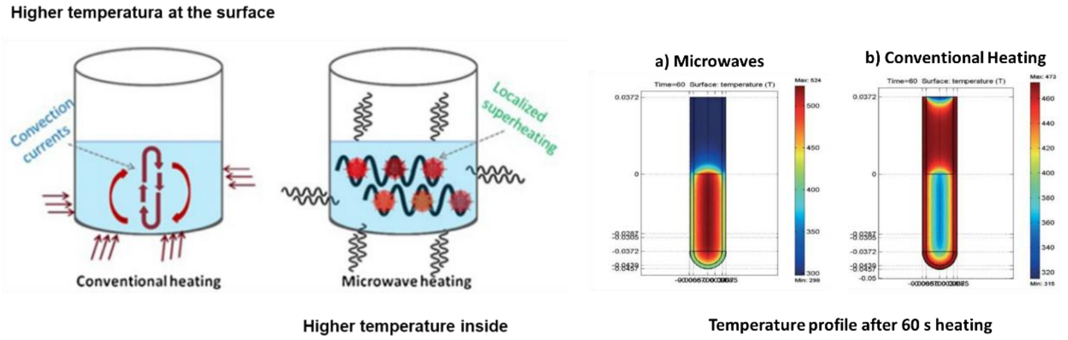


Figure 6. Transmission of energy in conventional heating and dielectric microwave heating. Reproduced form ref 7 with permission.

We have conducted a numerical and experimental study on the heating of two solvents, ethanol and water, with microwaves. The experimental results were carried out in a single-mode microwave reactor operating at 2.45 GHz and using an optical fiber sensor located at different positions of a cylinder fitted to the cavity. A numerical model based on a spectral collocation method was developed that allowed predicting the behavior. The calculated results agreed with the experimental ones. In both cases, a stratified temperature profile was observed, but differences between the two studied solvents were noted. The center of the cylinder remained hotter in water but only at the first levels in ethanol. The structure of the convective rolls was also different in both cases. For water, a main roll is observed throughout the cell with two rolls, while in ethanol, the main roll is located near the center of the cylinder (Figure 7).

The results clearly indicated the importance of dielectric parameters in heating and heat transmission with microwaves. Likewise, the interest of numerical modeling to describe the behavior of solvents under microwave irradiation was shown.[8]

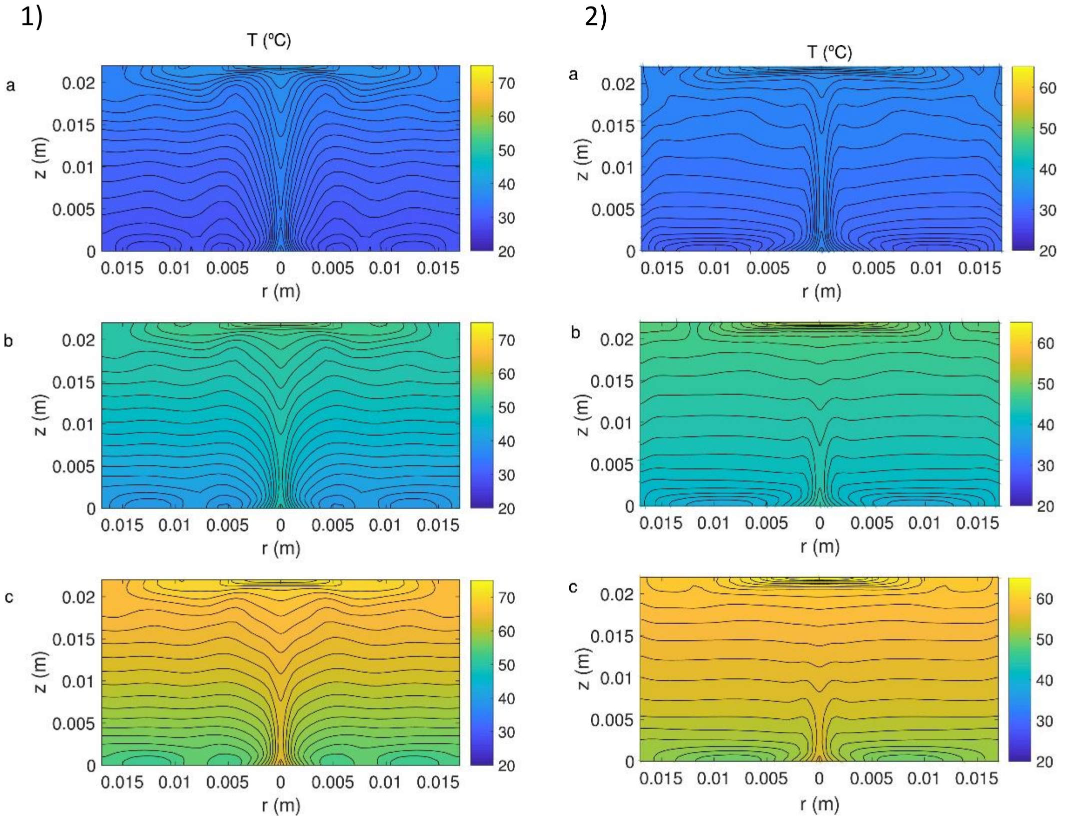


Figure 7. Contour of the predicted temperature, velocity field and streamlines 1) for water at 2.45 GHz and 30 W at time a) 40 s b) 80 s, c) 120 s. 2) for ethanol at 2.45 GHz and 20 W at time a) 30 s, b) 60 s, c) 90 s.

2.2. Overheating effects

Mingos detected an overheating effect in polar liquids under microwave radiation, which can overheat between 13-26°C above their conventional boiling point. This effect could be explained by the "inverted heat transfer" effect (from the irradiated medium to the exterior) since boiling nuclei occur on the liquid's surface in contact with glass walls, which could justify the observed increases in reaction rates in organic and organometallic chemistry (Figure 8, left).[9]

A similar effect has been described by Chemat and Esveld. If the reaction rate is plotted against temperature, it can be deduced that the heating limit, and thus the reaction rate limit, is constrained in conventional heating by the solvent's boiling temperature, whereas with microwaves, this limit can be surpassed. It is considered that an increase of 10°C in the reaction temperature results in doubling the reaction rate, allowing for shorter reaction times. For example, a reaction that takes 8 h at 80°C would occur in 2 min. if the temperature is doubled to 160°C. This overheating effect could explain many of the acceleration effects observed with microwaves and many of the improvements seen (Figure 8, right).[10]

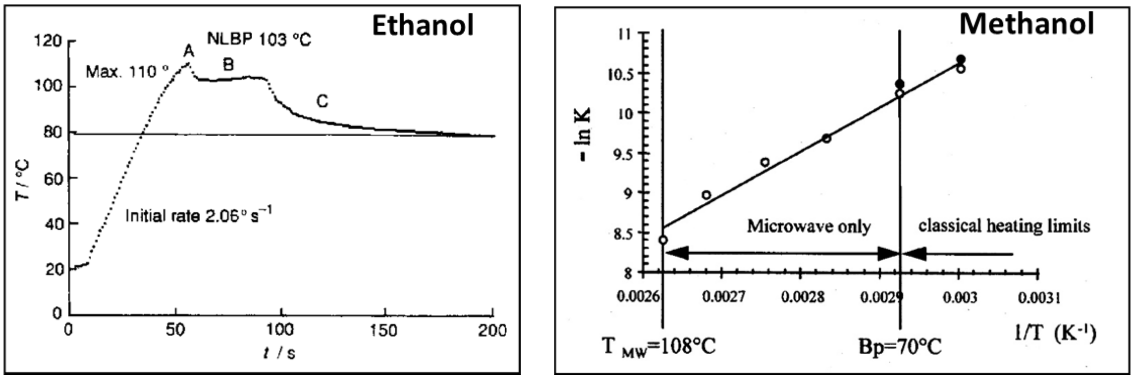


Figure 8. Overheating effects in ethanol and methanol under microwave irradiation. Reproduced from ref. 9 and 10 with permission.

As Stuerga indicated, thermal reactions occur optimally when rapidly heated to the highest tolerable temperature and maintained at that temperature for the shortest possible time, allowing for rapid quenching to minimize thermal decomposition.

Under conventional heating response time is slow: heating to high temperatures and subsequent cooling usually requires much longer times than they do with microwave systems where such operations may be completed within a few minutes.

With temperature gradients difficult to avoid, pyrolytic degradation of components on or near the inner walls is common. Under microwaves the energy can be absorbed directly by the reaction mixture instead of the container. Thus, the response time under microwaves will be shorter than under conventional heating (Figure 9).[11]

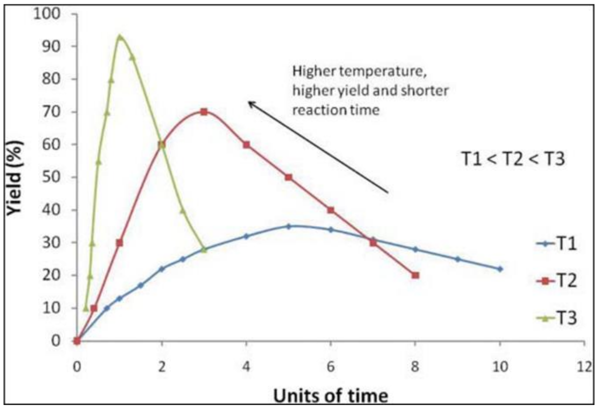


Figure 9. Influence of time and temperature upon the product yield for the same competitive thermal process performed at temperatures of T1 (lowest), T2 and T3 (highest). Reproduced from ref. 11 with permission.

2.3. Hot spots

Various authors have postulated the presence of 'hot spots' in samples irradiated by microwaves. This effect, related to that observed in ultrasound, would be caused by the inhomogeneity of the field and would imply that in certain areas of the sample, the temperature is much higher than the macroscopic temperature, meaning that the latter would not be representative of the reaction conditions. This would be a thermal effect, hence it has been called the 'false microwave effect'.

Marken and colleagues investigated the electrochemical oxidation of ferrocene under microwave irradiation. The progress of the oxidation is monitored by voltammetry. A significant acceleration is observed compared to classical conditions. They show that microwave activation of electroorganic processes on small electrodes improves both mass transport and the chemical process coupled to the interfacial proton transfer. The observed effect (in a solvent that absorbs the radiation) is thermal and is based on the formation of a "hot spot" near the electrode surface. The temperatures of these hot spots are considerably higher than those of the electrode surface and can exceed the boiling point of the liquid.

For example, in acetonitrile, the temperature can increase in the hot spot up to 40 mm from the electrode surface. The temperature of the hot spot (118ºC) is considerably higher than the electrode temperature (47ºC) and also higher than the boiling point of the solvent (81.6ºC). Under these conditions, the convection speed of acetonitrile in the hot spot region is 0.1 cm s^{-1}, and thus, the solvent passes through the high-temperature region in less than 100 ms (Figure 10). If the microwave radiation is turned off, the voltametric characteristics observed at room temperature return.[12]

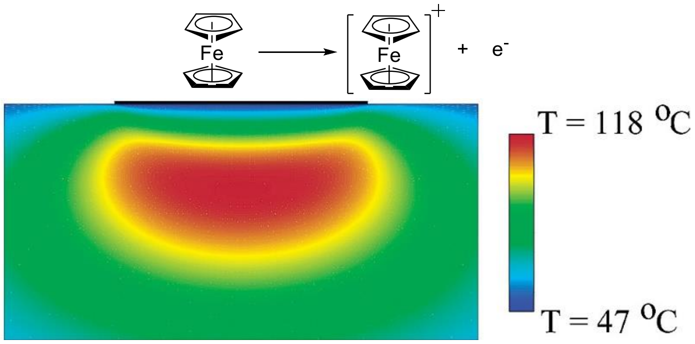
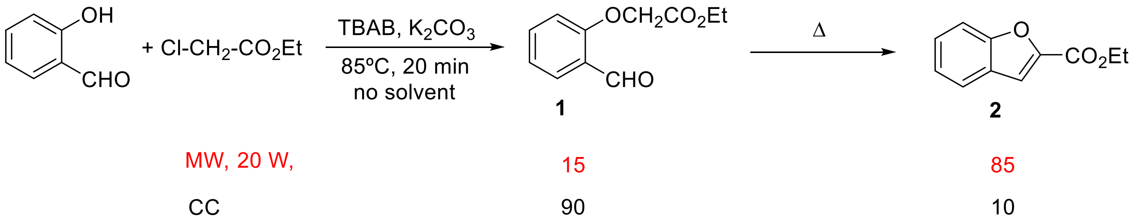


Figure 10. "Hot spot" formation near the electrode surface in the electrochemical oxidation of ferrocene under microwave irradiation. Reproduced from ref. 12 with permission.

Bogdal used a thermal camera to determine the reaction temperature and detect the presence of hot spots. The application of a pyrometer or a fiber optic thermometer does not provide accurate values when high temperature gradients develop within the reaction mixture. When the reaction shown in Scheme 1 was carried out with the same reaction temperature profiles under both conventional (oil bath) and microwave conditions, different distributions of the intermediate (**1**) and the final product (**2**) were determined. It is worth noting that the product distribution was much more affected by microwaves, and the yield of **2** was higher compared to conventional experiments when the reaction was conducted at lower temperatures; for example, 85°C *vs* 110°C. The addition of ethanol strongly shifted the product distribution towards the final product (**2**), while the addition of cyclohexane resulted in a much lower yield of **2**.[13]



Scheme 1. Formation of (2-formylphenoxy)acetic acid ethyl ester (**1**) and benzofuran-2-carboxylic acid ethyl ester (**2**).

Thermal gradients were revealed by the thermal camera, which detected a temperature increase in the central part (on the side of the microwave waveguide in the reactor) of the reaction mixture compared to the outer regions. The rotation of the reaction vessel inside the microwave cavity substantially reduces the temperature gradient; however, the regions are still characterized by different colors, indicating different concentrations of **1** and **2** in the reaction mixture. In fact, rotating the reaction vessels reduced overheating, exposing the reaction mixture to a more homogeneous microwave field and, as a consequence, the yield of **2** was lower than in experiments without rotation but much closer *(i.e.*, comparable) to the yield of the reaction under conventional conditions.

Mechanical stirring with a quartz spatula placed inside the reaction mixture improved the thermal homogeneity of the reaction mixture to a greater extent than the rotation of the reaction vessels; the results are comparable to those obtained under conventional conditions. Although it is difficult to draw additional conclusions since the conventional protocol with stirring of the reaction mixtures was not executed, it can be observed that the surface of the reaction mixture was more homogeneous compared to the experiments with vessel rotation and particularly without rotation. In the latter case, a high temperature gradient within the reaction mixture generated by microwaves leads to higher conversion rates of reactants and/or reaction rates, which in turn could be a reasonable explanation for the so-called non-thermal microwave effects, *i.e.*, an increase in reaction rates that is disproportionate to the temperature of the reaction medium (Figure 11).[13]

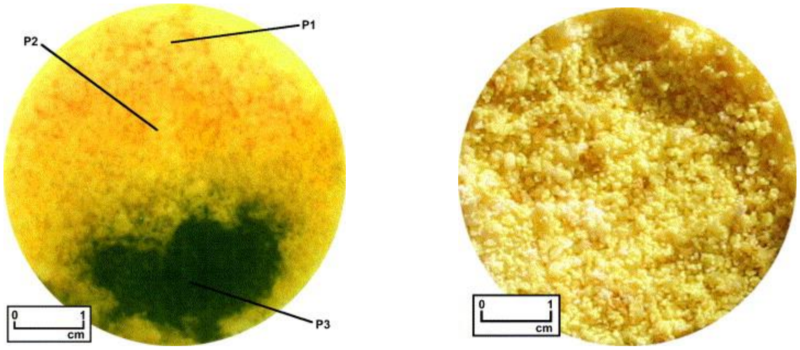


Figure 11. Photograph of the surface of the reaction mixture, without stirring (left) and with vessel rotation and stirring (right). Reproduced from ref. 13 with permission.

The presence of hot spots in liquids have been visualized with a video camera. The heating of water shows the presence of hot spots, especially at the interface with air. In a binary mixture of dichloromethane/water, the hot spots appear in the more polar phase, the aqueous phase.[14]

Horikoshi and Serpone demonstrated the formation of hot spots in Pd-catalyzed reactions. They use a monomode reactor and a TE_{103} waveguide, which allows the sample to be placed in the area where the electric field or the magnetic field is maximized. They show that the effectiveness of hot spot generation depends on the nature of the microwave generator: solid-state generator *vs* magnetron. Additionally, hot spots can have either a positive or negative effect on chemical reactions (Figure 12).[15]

It is well known that sparks are produced whenever a conductive metallic element is placed in a microwave oven. This occurs when electrons in the metal oscillate with the microwave radiation's electric field to produce a high voltage that, when exceeding the dielectric limit of the air, generates a conductive plasma visible as a spark. The sparks were generated under electric field conditions of the microwaves emitted by the semiconductor generator.

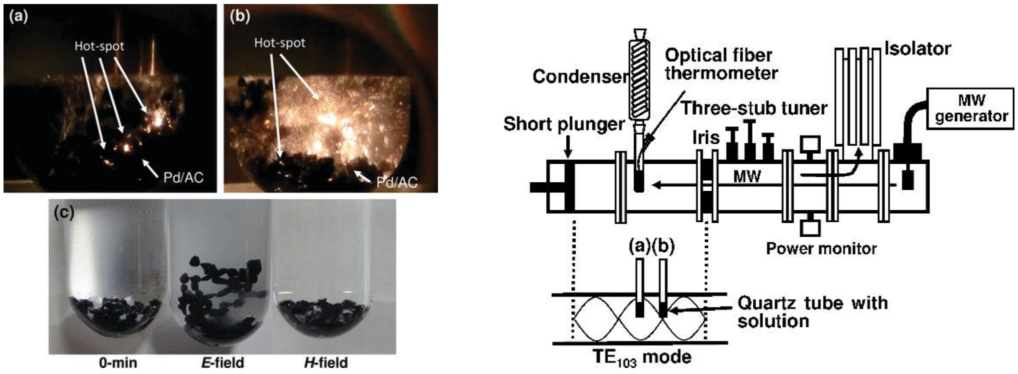


Figure 12. (Left) Photographs of the electric discharges on the Pd/AC catalyst surface under ***E***-field conditions: (a) 40 s irradiation and (b) 120 s irradiation. (c) Pd/AC catalyst appearance in solution at 0 min, and after 30 min of microwave irradiation under ***E***-field and ***H***-field conditions. (Right) Experimental Setup: (a) Maximal Position of the Electric Field (***E***-Field), and (b) Maximal Position of the Magnetic Field (***H***-Field). Reproduced from ref. 15 with permission.

The study showed that hot spots are generated on the surface of activated carbon particles when irradiated with the electric field component of microwaves, resulting in the particles being attracted to each other in the direction of the electric field due to the microwave-induced polarization of the particles. Hot spots were also formed under microwave magnetic field irradiation because of the generation of eddy currents.

In the synthesis of 4-methylbiphenyl (4-MBP) via the Suzuki-Miyaura cross-coupling reaction, the efficiency of the process decreased significantly compared to the Suzuki-Miyaura homocoupling process due to the generation of hot spots (Figure 13). The distance between particles is evidently an important parameter in the formation of hot spots. For instance, the generation of a hot spot could be suppressed in a flow reaction using a fixed-bed reactor (catalyst deposited in the reactor).[15]

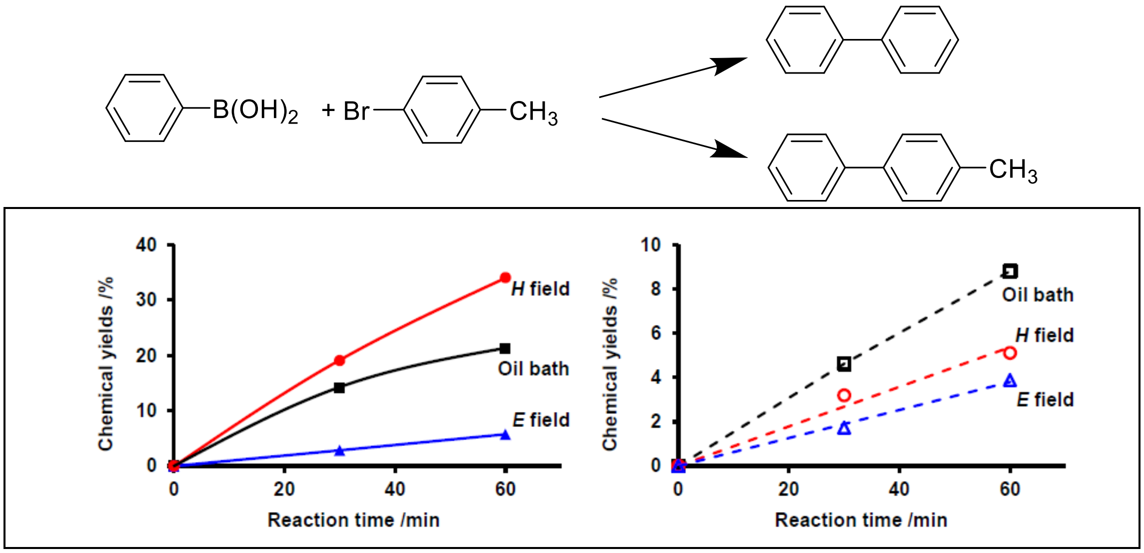


Figure 13. Product yields of 4-methylbiphenyl (4-MPB) (left), and biphenyl (BP) (right) in toluene solvent under irradiation with the microwaves' ***H***-field and ***E***-field components and oil bath heating. Reproduced from ref. 15 with permission.

Kappe and col. described the formation of organomagnesium compounds by reacting halogenated derivatives with magnesium. At the same reaction temperature determined macroscopically, this organometallic process can be accelerated (relative to the conventionally heated control experiment) in a low-density microwave field or suppressed by applying a high-density field.[16]

Using the CEM Discover system under THF reflux conditions in an open vessel as described above, a slight arcing between individual Mg chips was observed at a constant applied magnetron power of 200 W. Violent electrostatic discharges were observed using a built-in camera, particularly during the initial 25 s heating phase of the experiment where nominal magnetron output power levels of up to 150 W were reached.

The arcing was particularly intense when the reaction vial was simultaneously cooled with compressed air during microwave irradiation. In our case, when using simultaneous cooling, a maximum power level of 240 W was observed, leading to very intense arcing during the initial phase of the experiment. To our surprise, monitoring of the reaction mixture by HPLC-UV revealed that under these high-density power conditions, virtually no conversion was observed.

When a 2-minute heating ramp was programmed on the Monowave 300 instrument, gradually increasing the reaction temperature to the target value of 65°C, the applied magnetron power was drastically reduced and never exceeded 16 W. Under these conditions, the occurrence of electrostatic discharges is minimized, as clearly seen in the built-in camera, and complete conversion of the starting material 2-chloropyridine was observed within 60 minutes for all runs. Using the CEM Discover system under THF reflux conditions in an open vessel as described above, a slight arcing between individual Mg chips was observed at a constant applied magnetron power of 200 W.[16]

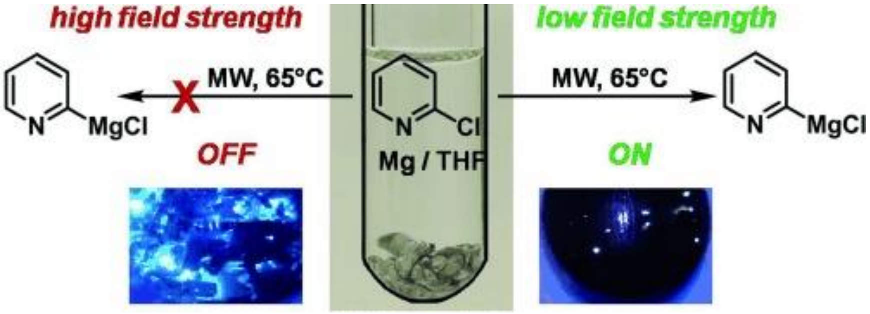


Figure 14. Activation and Deactivation in the Formation of Grignard Reagents by an Electromagnetic Field. Reproduced from ref. 16 with permission.

Kappe also provided a qualitative description of discharge phenomena in metal-solvent systems in a high-density single-mode microwave reactor. Metallic particles reflect the microwaves and concentrate the field at edges and sharp points. When the field exceeds the dielectric resistance of the solvent, breakdown processes occur. Various factors such as the quantity, size, morphology, and physical properties of the conductor or semiconductor influence the breakdown processes in a given solvent at a given magnetron output power.[17]

Discharge phenomena for diamagnetic and paramagnetic materials strongly depend on the size of the particles used. With small particles, fractions of a second discharges were observed, such as uniform bright sheets around the metal, but they did not lead to complete material breakdown. Under these conditions, the 2.45 GHz microwave period is too short for current development and propagation. However, under high power conditions or with large particles and/or many particles, complete breakdown was observed. Bright sparks and arcs were frequently accompanied by solvent decomposition and the formation of considerable amounts of graphitized material.

For ferromagnetic particles, the magnetic field component plays a critical role. In particular, small Fe and Ni powders with a particle size <40 µm heated very quickly and began to glow in the microwave field. This suggests local temperatures more than 500°C. There is considerable interest in electrical breakdown processes under microwave conditions for various reasons. Several authors have recently described liquid-phase applications of microwave-induced discharges or extreme local temperatures (i.e., hotspots), particularly in materials science and nanomaterials research. However, the influence of arcing phenomena on microwave chemistry may be more common than generally assumed. We suspect that in several published cases where metals with zero valency (or other highly electrically conductive materials) have been used under microwave conditions, electrostatic discharges could play an important role.

The authors have recently reevaluated the microwave-assisted dehalogenation of 2-chloroethylbenzene, performed in the presence of metal powders and metal oxide such as Fe, Ni, and Fe_3O_4 in decalin as the solvent. Using a monomode microwave apparatus with an integrated chamber, intense and strong arcing phenomena were observed in all these cases under the published reaction conditions. These discharges could potentially be responsible for the microwave effects observed in these dehalogenations. Therefore, arcing phenomena could also play a role in microwave-assisted formation of inorganic metal or metal oxide nanomaterials, as some of these products are typically highly electrically conductive.[17]

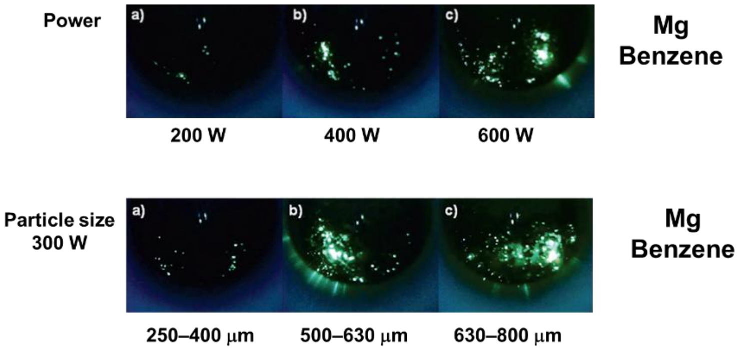


Figure 15. Effect of increasing microwave power (up), and Mg particle size (down) on electric discharges. Reproduced from ref. 17 with permission.

An interesting review of microwaves-metal discharge interactions and the application of controlled discharge to the preparation of nanomaterials have been recently published.[18]

Li and Gao used Eu/Tb metal complexes that are transparent to microwaves as microsensors to detect the presence of hot spots, functioning as nanothermometers. When the powder is excited at 265 nm, the emission spectra of the complexes (Eu-BPTC and Tb-BPTC) exhibit characteristic red and green luminescence of Eu^{3+} (590 nm, 614 nm, and 700 nm) and Tb^{3+} (484 nm, 543 nm, 587 nm, and 619 nm).

The results show that C-800 dispersed in *n*-propanol indicates that the intrinsic temperature of the C-800 particles is 12°C higher than the temperature of the liquid. The temperature gradient between the solid particles and the liquid can be increased by enhancing the dielectric loss of the solid particles, the intensity of the microwaves, and the size of the particles. Microwave-induced micro-hotspots are weakened by increasing the dielectric loss and thermal conductivity of the liquid solutions (Figure 16).[19]

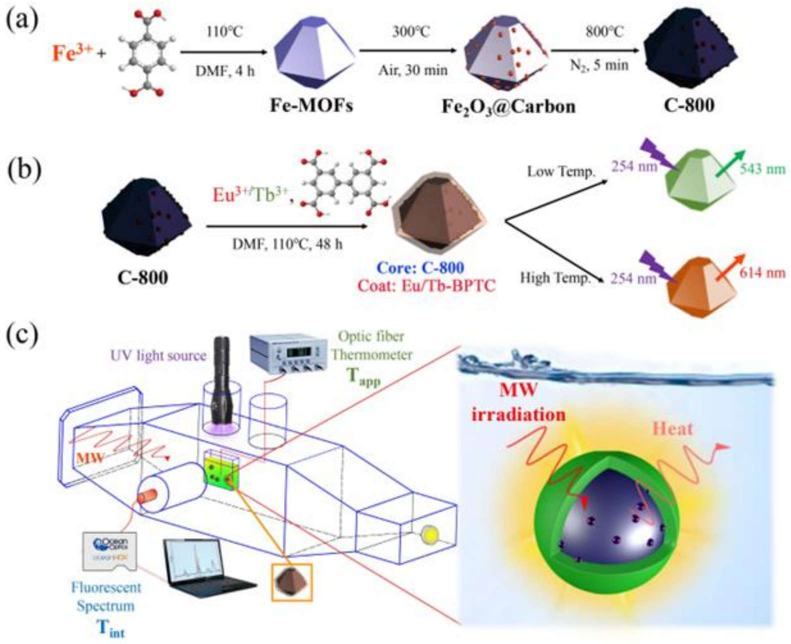


Figure 16. Preparation of MOF-derived porous carbon particles (a), MW-adsorbing particles coated by fluorescent materials (b), and equipment for probing the intrinsic temperature of MW-absorbing particles (c). Reproduced from ref. 19 with permission.

2.4. Selective heating

Microwave radiation is selectively absorbed by polar systems, whereas non-polar systems do not heat up. This fact can be utilized to selectively heat solvents, catalysts, or polar compounds in the presence of non-polar systems and achieve results different from those obtained through conventional heating, which is non-selective.

2.4.1. Solvents. Strauss et al. described the Hofmann elimination reaction as shown in Figure 17. The reaction takes place in water at 110°C. However, at this temperature, the final product polymerizes, resulting in very low yield. The authors solved this problem by using a biphasic water/chloroform system. The polar starting material is soluble in water, which is efficiently heated to 110°C by microwaves. The non-polar final product is extracted into chloroform, which is at a lower temperature, preventing decomposition and improving the results. This is a simple and ingenious system that takes advantage of selective microwave absorption and heating, which cannot be achieved with conventional heating.[20]

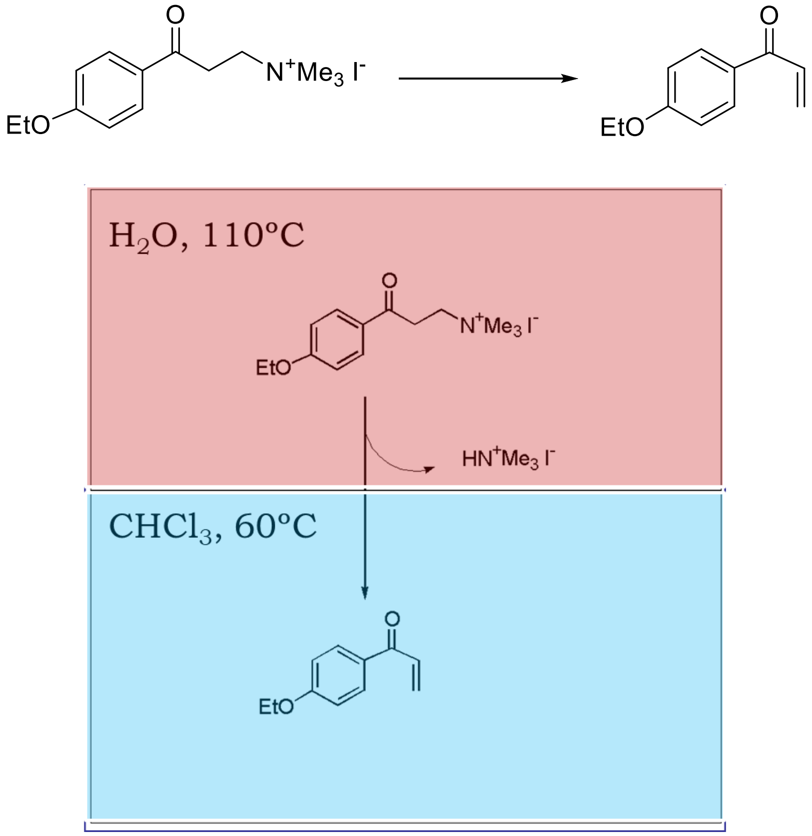


Figure 17. Schematic Hofmann elimination reaction in a biphasic water/chloroform system under microwave irradiation.

2.4.2. Catalysts. The following example described by Bogdal et al. is an interesting demonstration of applications in catalysis. It involves the use of Magtrieve^{TM} as an oxidant in a heterogeneous phase. The oxidant absorbs the radiation, heating up to around 450°C, but in a somewhat uneven manner. When the oxidant is irradiated in toluene, the temperature distribution is more homogeneous, reaching temperatures around 140°C without the toluene boiling (boiling point 110°C). This means the catalyst is selectively heated. The authors have applied this technique to the oxidation of alcohols to carbonyl compounds with excellent results.[21]

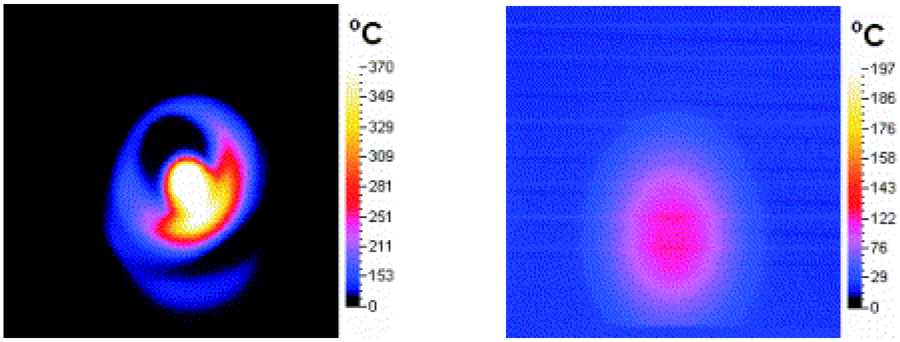
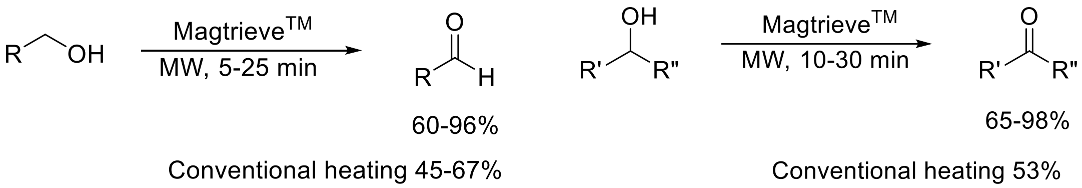


Figure 18. Temperature profile for Magtrieve^{TM} under microwaves (2 min) without solvent (left) and in a toluene solution (right). Reproduced from ref. 21 with permission.

The authors use this procedure for the oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, achieving good to excellent yields without oxidizing the aldehyde to the carboxylic acid (Scheme 2).[21]

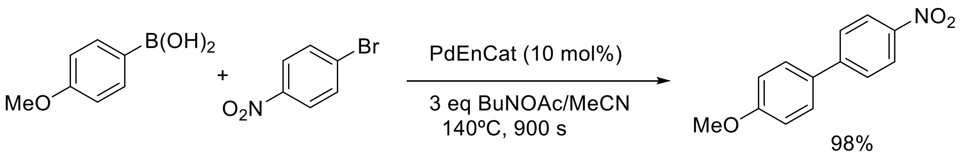


Scheme 2. Oxidation of alcohols using Magtrieve™ under microwaves.

Moreover, most of the observed effects in catalysis are due to the presence of "hot spots," which are likely very important in heterogeneous media as they form more readily at interfaces. This increases the turnover number (TON), as the catalyst does not deactivate as easily due to the shorter reaction times compared to conventional heating.

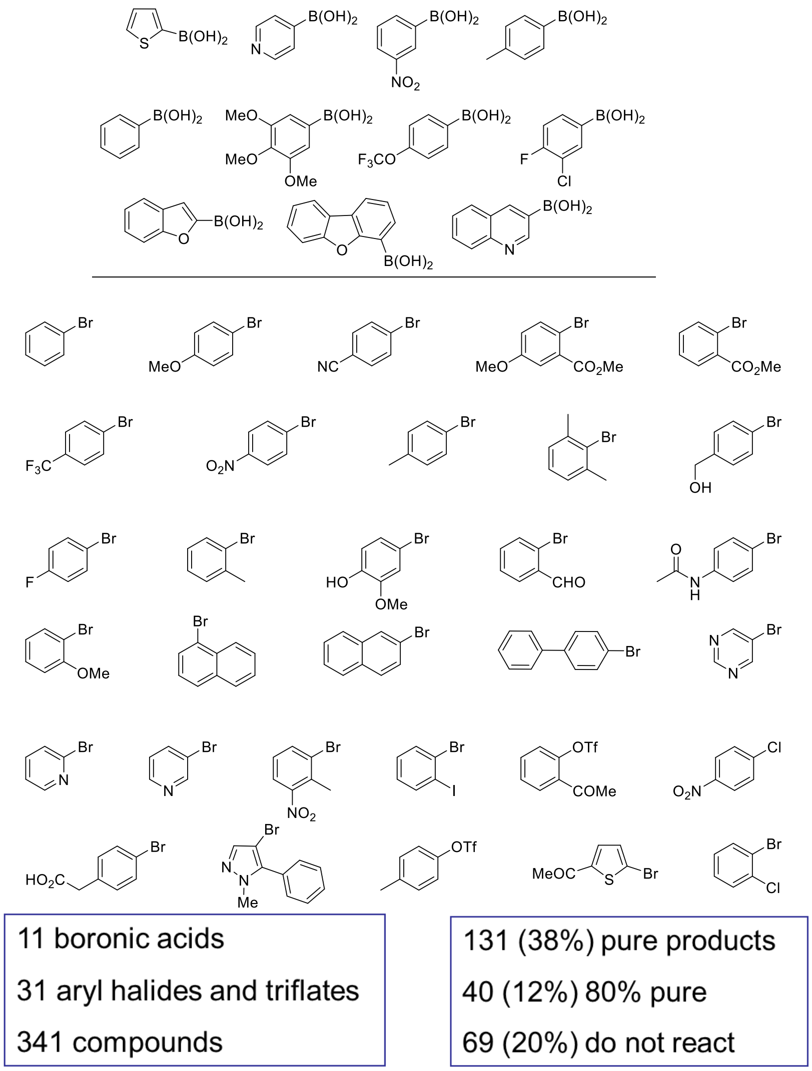
A notable example described by Ley et al. combines selective catalyst heating and the cooling-while-heating method. The authors detail the coupling of boronic acids with halogenated derivatives catalyzed by PdEnCat (palladium encapsulated in polyurea). The use of encapsulated catalysts, compound library preparation, and flow chemistry exemplifies sustainable chemistry.[22]

Using similar conditions to thermal reactions in the microwave (albeit at a slightly higher temperature of 120°C), the reaction time was reduced from 8 hours to just 10 minutes, corresponding to a 48-fold increase in rate. Therefore, the hypothesis is that this enhanced catalytic activity is a direct result of microwave heating. Indeed, the mechanism of molecular interactions leading to heating through the direct coupling of metallic species with microwave irradiation is well-documented as a highly efficient process. Furthermore, several studies have shown that catalysts with integrated or impregnated metal exhibit improved reactivity and prolonged lifespan under microwave heating conditions. These two characteristics are attributed to the selective absorption by metallic particles, which can heat directly without significantly heating the support material due to the drastic difference in their dielectric constants.



Scheme 3. Microwave-assisted Suzuki coupling reaction.

The authors selected a total of 11 boronic acids and 31 aryl halides and triflates, generating a potential matrix of 341 compounds. Of the 341 reactions conducted, 131 (38%) produced products that were pure by both ^{1}H NMR spectroscopy and LC-MS. Another 40 (12%) had purities well above 80%. In all cases, the isolated yields for these reactions were over 80%, with most above 90%. An additional set of 69 combinations (20%) did not fully react during the ten-minute heating period, with their reaction mixtures consisting only of starting materials and product (Figure 19).[22]



11 boronic acids

31 aryl halides and triflates

341 compounds

131 (38%) pure products

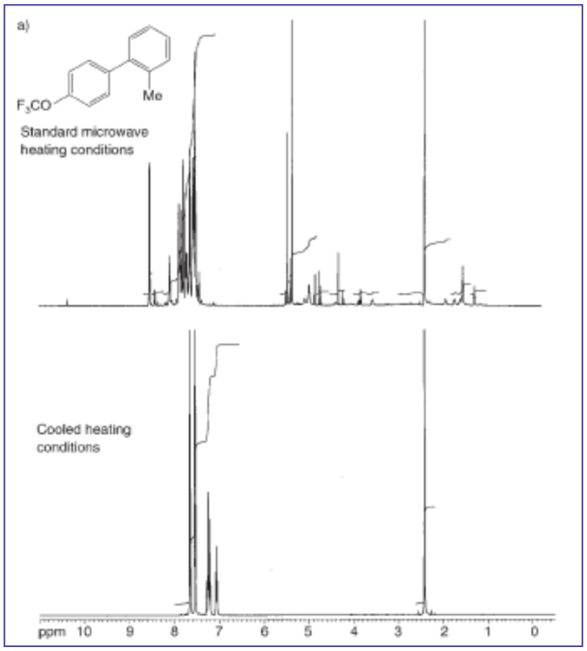
40 (12%) 80% pure

69 (20%) do not react

Figure 19. Suzuki coupling partners employed in library preparation.

Additionally, in this work two sets of substrates that had produced impure products under the standard reaction conditions for the library were heated with simultaneous cooling. The reactions heated at 50 W reached overall temperatures not exceeding 76°C, significantly lower than the 120°C used under standard reaction conditions but using a comparable amount of microwave energy. In both cases, product purity improved dramatically (Figure 20).

The improvement observed under cooling conditions can be explained by selective heating of the catalyst where the reaction occurs. The final product is extracted into the solvent, which is at a lower temperature, reducing decomposition.



MW standard conditions
50 W, 15 min, 120ºC
Purity, 48%

MW cooling conditions
50 W, 15 min, 76ºC
Purity >98%

Increased product purity

Figure 20. Improvement of product purity with Cooling-While-Heating Microwave Heating. Reproduced from ref. 22 with permission.

Recently, Zhang et al. reviewed the use of different methodologies for hydrogen production. The authors highlight the improvements in heating rate transfer, selective heating, and high heating efficiency.[23]

Microwaves can selectively heat the target position in the reaction mixture due to the disparity in microwave absorption of different materials. With this property, a carbon-based catalyst, as an absorber, heats up without the energy loss resulting from heat conduction and convection compared to conventional heating. However, it must be emphasized that microwave irradiation has application constraints:

1. A hotspot with a temperature difference of approximately 200°C higher than the bulk must be formed to enhance mass diffusion; otherwise, the kinetics will not significantly improve.
2. The reaction kinetics must be mass-transfer-controlled. In the case of decalin, which is not mass-transfer-controlled, microwave assistance cannot promote reaction kinetics.
3. The reactant should be chosen from non-polar species that absorb almost no energy from microwave irradiation.

To further intensify the system, a Dewar-type reactor and ionic liquid can be used. Future research should introduce and evaluate more LOHC (Liquid Organic Hydrogen Carrier) species in the microwave dehydrogenation system so that microwave irradiation gains more universal applicability.

An important topic in the dehydrogenation of the organic hydride MCH (methylcyclohexane) using microwave radiation is that the presence of a Pd/AC catalyst bed heated to approximately 340°C in around 2 min resulted in more than 94% dehydrogenation of methylcyclohexane.[24]

In contrast, using conventional heating with a ceramic heater required approximately 35 min. for the catalyst bed to reach the necessary temperature for efficient dehydrogenation, even when the reactor was insulated to suppress heat loss. Microwave heating led to hydrogen evolution in much shorter times with a considerable energy saving (approximately 75%) in electrical energy.

The microscopic temperature distribution of the Pd/AC catalyst and MCH from the simulation is illustrated in the drawings of Figure 21. The advantageous effect of microwaves in increasing species transport (Figure a; for T_cat >>> T_MCH) during the dehydrogenation reaction lies in the temperature gradient and mass transfer, whose direction is opposite to that of conventional heating (Figure b; for T_cat <<< T_MCH). In the case of MCH dehydrogenation under microwave heating, the heat transfer generated from the Pd/AC catalyst to the surrounding species also induced the driving force for mass transfer in the same direction. This phenomenon has two possible effects: (i) promoting the desorption of product species (toluene) from the active sites of the catalyst, thereby facilitating mass transfer in the system and (ii) preventing strong contiguous adsorption of the hydrocarbon (MCH) on the active sites, which would decrease coke formation and deposition. Species transport in the system under microwave heating was more effective than under conventional heating, leading to an increase in the overall reaction rate, consistent with the microwave heating effect that enhances MCH dehydrogenation (Figure 21).[24]

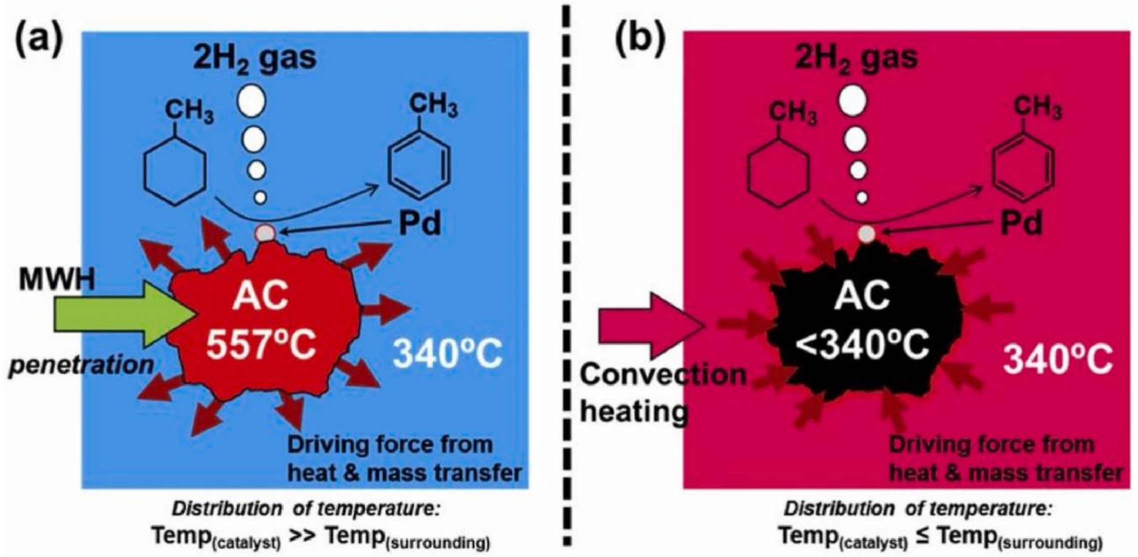


Figure 21. Reaction process within the catalyst: (a) Microwave heating, (b) Conventional heating. Reproduced from ref. 24 with permission.

2.5. Thermal shock by microwaves

Hayasho et al. used microwaves for exfoliation of graphite through what they call “thermal shock”. The concept is illustrated in the Figure 22. First, graphite absorbs microwaves, while ice does not. Therefore, graphite is placed in ice. Second, the graphite is irradiated with microwaves. Only the graphite absorbs the microwaves and is simultaneously cooled by the ice. Additionally, due to the characteristics of multimode microwaves, the electromagnetic field changes randomly. This implies that heating and cooling occur alternately. Finally, these alternating cycles are expected to cause the graphite to repeatedly expand and contract, subjecting it to repeated thermal shocks, similar to the phenomenon that occurs when heated glass is rapidly cooled. This thermal shock became the driving force for exfoliation (Figure 22).[25]

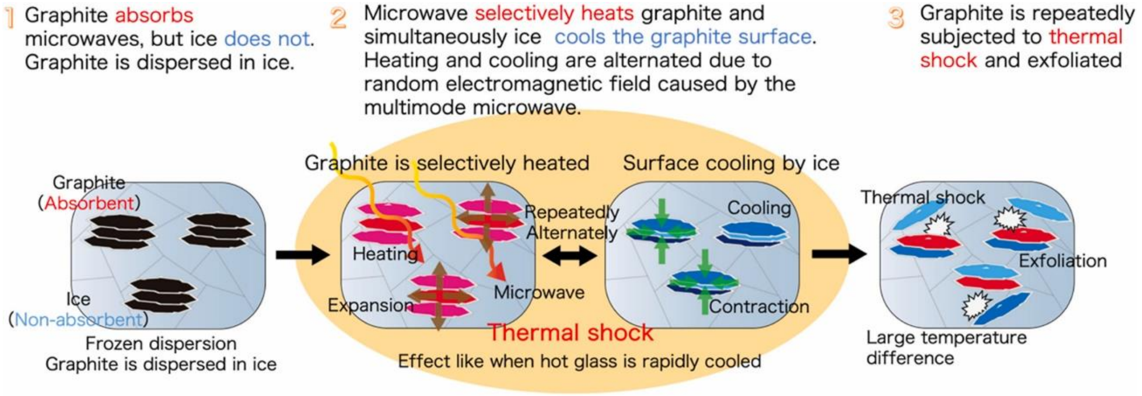


Figure 22. Thermal shock in the exfoliation of graphite using microwaves, Reproduced from ref. 25 with permission.

2.6. Heat (energy) accumulation

Stiegman et al. suggest a thermal effect based on energy accumulation and applies it to reactions such as the Claisen transposition. The authors consider that specific rate enhancements in homogeneous organic reactions can be achieved by microwaves and, under certain conditions, can be very pronounced effects.

The observed rate enhancement can generally be rationalised from Huang and Richert's model as a result of selective heating of the dipolar reactant and the concomitant accumulation of excess energy in the domains around the absorbing molecule.

This mechanism is unique to the way microwave radiation heats molecules and has no parallel in conventional convective heating. Importantly, this mechanism in no way implies non-thermal effects, which, in their opinion, are highly improbable.[26]

The results have been the subject of discussion with those of Kappe.[27-29]

3. Computational Calculations

Our approach has been the use computational calculations in microwave reactions since we consider that it is experimentally impossible to separate thermal effects from non-thermal effects since both have the same origin, coming from the interaction of the wave with the material.[30]

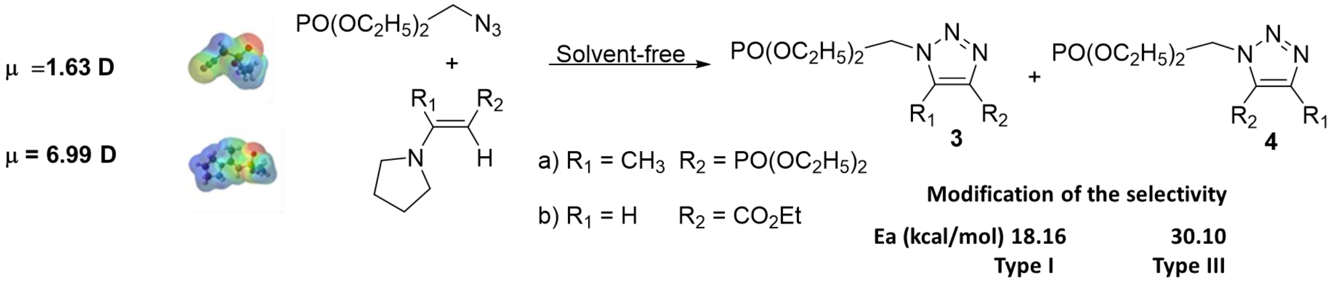
By means of computational calculations, it is possible to determine the thermodynamic parameters, activation energies, etc., directly related to thermal effects and parameters more closely related to non-thermal effects, such as polarity or polarizability. Thus, predictive models can be designed, and simple computational calculations can be used to predict whether a reaction will be enhanced by microwave radiation.

By calculating the enthalpy and activation energy of previously described reactions it was possible to classify the reactions into 6 types. Type I reactions ($Ea < 20$ Kcal mol^{-1} and $\Delta H < 0$) occur easily and are not enhanced by microwaves. Type II reactions ($Ea < 20$ Kcal mol^{-1} and $\Delta H > 0$), III ($Ea = 20\text{-}30$ Kcal mol^{-1} and $\Delta H < 0$) and IV ($Ea = 20\text{-}30$ Kcal mol^{-1} and $\Delta H > 0$). Type V reactions ($Ea > 30$ Kcal mol^{-1} and $\Delta H < 0$) only occur and are enhanced using acceptors while type VI reactions ($Ea > 30$ Kcal mol^{-1} and $\Delta H > 0$) do not occur (Table 3).

Table 3. Conclusions of computational calculations on thermal effects

Reaction	Energy of Activation	Enthalpy (sign)	Conclusions
Type I	< 20 kcal mol^{-1}	< 0	Not improved
Type II		> 0	Improved
Type III	20-30 kcal mol^{-1}	< 0	Improved
Type IV		> 0	Improved
Type V	> 30 kcal mol^{-1}	> 0	Improved with susceptors
Type VI		> 0	Do not occur

The cycloaddition of one azide with the enamines showed in Scheme 4 under classical conditions leads exclusively to the 1,2,3-triazole **3**. This is a type I reaction that should not be enhanced with microwaves. However, with microwaves, there is a modification of selectivity since the corresponding regioisomer **4** is also obtained. Computational calculations show that the formation of the minor regioisomer follows a type III reaction that should be improved with microwaves.[30]

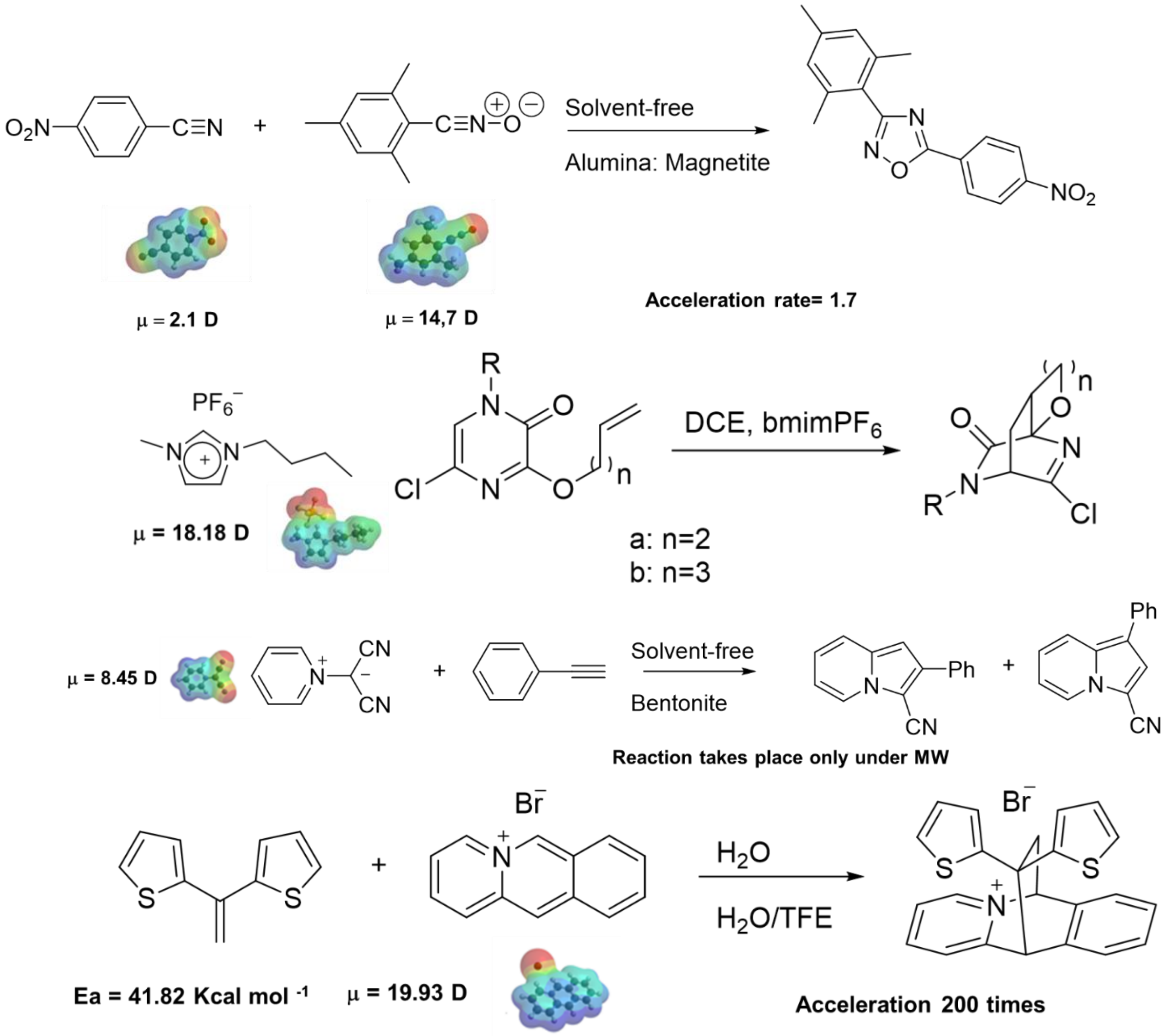


Scheme 4. Cycloaddition reaction of azidomethylphosphonate and functionalized enamines.

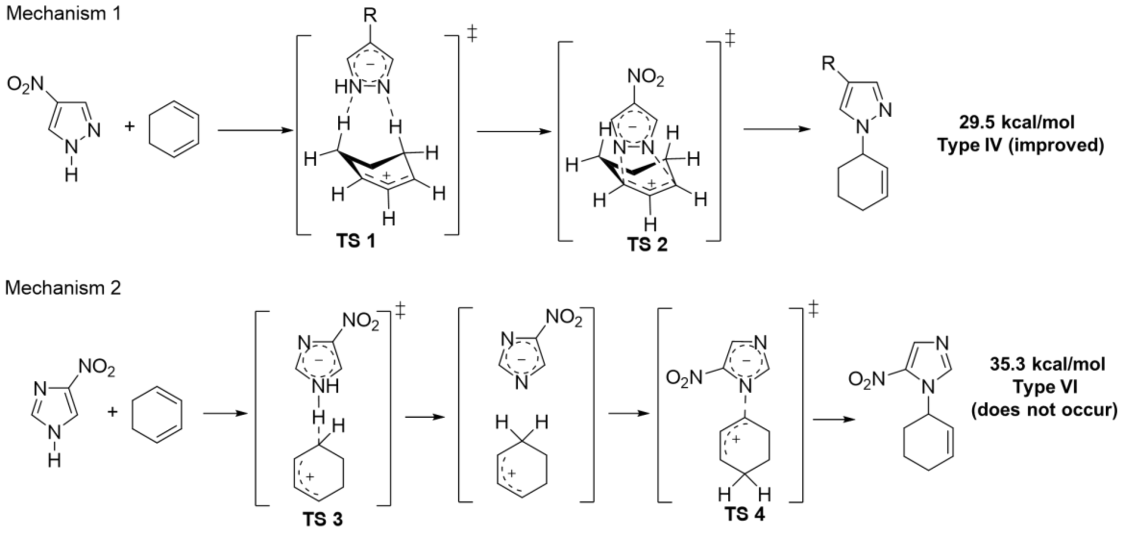
Other examples of type II-V reactions show that reactions can be facilitated with microwaves if there is an agent that efficiently absorbs the radiation, reactants, solvent, catalyst, susceptor, etc. (Scheme 5).

Finally, it is interesting to highlight the results of the reaction of nitroazoles with cyclohexadiene. The reaction of 4-nitropyrazole surprisingly led to the addition product. However, the more nucleophilic 4-nitroimidazole did not react. Under classical conditions, neither of the two reactions occurred.

Computational calculations showed that the reaction occurred via protonation of the diene followed by addition of the azole. In the case of 4-nitropyrazole, the protonation and addition occur in a concerted manner due to the proximity of the two nitrogens. Thus, it was a type IV reaction that should be improved with microwaves, as observed experimentally. In the case of 4-nitroimidazole, the reaction occurs in two steps with the formation of an intermediate, because the two nitrogens are more separated, the concerted reaction is not possible. In this case, the activation energy is higher, being a type VI reaction that should not occur (Scheme 6).[30]



Scheme 5. Microwave-assisted reactions are facilitated by an agent efficiently absorbing the radiation.



Scheme 6. Computed mechanisms for the reactions of 4-nitropyrazole or 4-nitroimidazole with cyclohexadiene.

In conclusion, simple computational calculations allow predicting when a reaction will be improved with microwaves through thermal effects. For this, it must be reactions of type II-V, and there must be some polar component in the reaction that facilitates the absorption of radiation and its transformation into heat.

Conclusions

Microwave dielectric heating has clearly different characteristics from conventional heating. Heat transmission does not occur through conduction or convection but through dielectric losses. This makes it a more selective heating method, as it significantly depends on the properties of the material. Another notable difference is that heating is volumetric where consideration of penetration depth is also fundamental.

Although the electric component is considered responsible for heating in most cases, the magnetic component can be important in some materials. In both cases, the polarization mechanisms responsible for heating must be considered.

All this leads us to the possibility of taking advantage of its differential characteristics to obtain results that cannot be easily achieved through conventional heating. “Impossible” reactions, modifications of selectivity (chemo-, regio-, stereoselectivity), reactions with thermally sensitive reagents or products, etc.

The review has shown some notable examples of how the thermal effects of radiation can be utilized. Likewise, it has demonstrated how computational calculations can be used as a predictive tool for these effects. It is not an exhaustive review of results but a selection of important and characteristics examples of each of the differential effects that be used in the practice for everyone that wants to take advantage of this methodology.

Acknowledgements

References

1. https://www.yardimcikaynaklar.com/mikrodalga-radyo-dalgalari-ve-gama-isinlarinin-bilim-ve-teknolojideki-kullanim-alanlari/ Accesed 24/07/2024
2. Stuerga, D. Microwave–Materials Interactions and Dielectric Properties: From Molecules and Macromolecules to Solids and Colloidal Suspensions. In *Microwaves in Organic Synthesis*; De la Hoz, A., Loupy, A., Ed.; Wiley, 2012; Chapter 1, 1-56. https://doi.org/10.1002/9783527651313.ch1
3. A. Zlotorzynski, A. *Critical Rev. Anal. Chem.* **1995**, *25*, 43-76. https://doi.org/10.1080/10408349508050557
4. Xie, Y.; Shi, R.; Fu, B.; Song, C.; Shang, W.; Tao, P.; Deng, T. *NanoRes.* **2024**. https://doi.org/10.1007/s12274-024-6672-8
5. Belkhir, K.; Riquet, G.; Becquart, F. *Adv. Polymer Technol.* **2022**, 3961233. https://doi.org/10.1155/2022/3961233
6. De la Hoz, A.; Díaz-Ortiz, A.; Moreno, A. *Chem. Soc. Rev.* **2005**, *34*, 164-178. https://doi.org/10.1039/B411438H
7. Schanche, J.-S. *Molecular Diversity* **2003**, *7*, 291-298.

https://doi.org/10.1023/B:MODI.0000006866.38392.f7

8. Navarro, M. C.; Díaz-Ortiz, A.; Prieto, P.; de la Hoz, A. *Appl. Mathematical Model.* **2019**, *66*, 680-694. https://doi.org/10.1016/j.apm.2018.09.035
9. Baghurst, D. R.; Mingos, D. M. P. *J. Chem. Soc. Chem. Commun.* **1992**, 674-677. https://doi.org/10.1039/C39920000674
10. Chemat, F.; Esveld, E. *Chem. Eng. Technol.* **2001**, *24*, 735-744. https://doi.org/10.1002/1521-4125(200107)24:7<735::AID-CEAT735>3.0.CO;2-H
11. Strauss, C. R.; Rooney, D. W. *Green Chem.* **2010**, *12*, 1340-1344. https://doi.org/10.1039/C0GC00024H
12. Tsai, Y.-C.; Coles, B. A.; Compton, R. G.; Marken, F. *J. Am. Chem. Soc.* **2002**, *124*, 9784-9788. https://doi.org/10.1021/ja026037w
13. Bogdal, D.; Bednarz, S.; Lukasiewicz, M. *Tetrahedron* **2006**, *62*, 9440-9445. https://doi.org/10.1016/j.tet.2006.07.038
14. Bowman, M. D.; Leadbeater, N. E.; Barnard, T. M. *Tetrahedron Lett.* **2008**, *49*, 195-198. https://doi.org/10.1016/j.tetlet.2007.10.097
15. Horikoshi, S.; Osawa, A.; Abe, M.; Serpone, N. *J. Phys. Chem. C* **2011**, *115*, 23030-23035. https://doi.org/10.1021/jp2076269
16. Gutmann, B.; Schwan, A. M.; Reichart, B.; Gspan, C.; Hofer, F.; Kappe. C. O. *Angew. Chem. Int Ed.* **2011**, *33*, 7636–7640. https://doi.org/10.1002/anie.201100856
17. Chen, W.; Gutmann, B.; Kappe, C. O. *ChemistryOpen* **2012**, *1*, 39-48. https://doi.org/10.1002/open.201100013
18. Xie, Y.; Shi, R.; Fu, B.; Song, C.; Shang, W.; Tao, P.; Deng, T. *NanoRes.* **2024**. https://doi.org/10.1007/s12274-024-6672-8
19. Zhao, Z.; Shen, X.; Li, H.; Liu, K.; Wu, H.; Li, X.; Gao, X. *Angew. Chem. Int. Ed* **2022**, *61*, e202114340. https://doi.org/10.1002/anie.202114340
20. Raner, K. D.; Strauss, C. R.; Trainor, R. W.; Thorn, J. S. *J. Org. Chem.* **1995**, *60*, 2456-2460. https://doi.org/10.1021/jo00113a028
21. Bogdal, D.; Lukasiewicz, M.; Pielichowski, J.; Miciak, A.; Bednarz, Sz. *Tetrahedron* **2003**, *59*, 649-653. https://doi.org/10.1016/S0040-4020(02)01533-8
22. Baxendale, I. R.; Griffiths-Jones, C. M.; Ley, S. V.; Tranmer, G. K. *Chem. Eur. J.* **2006**, *12*, 4407-4416. https://doi.org/10.1002/chem.200501400
23. Yang, Y.; Wu, Z.; Li, R.; Wang, H.; Ren, J.; Li, B.; Yang, F.; Zhang, Z. *Results in Engineering* **2023**, *19*, 101394. https://doi.org/10.1016/j.rineng.2023.101394
24. Horikoshi, S.; Kamata, M.; Sumi, T.; Serpone, N. *Int. J. Hydrogen Energy* **2016**, *41*, 12029-12037. https://doi.org/10.1016/j.ijhydene.2016.05.139
25. Ebato, Y.; Hayashi, Y.; Takizawa, H. *Clean. Eng. Technol.* **2023**, *17*, 100681. https://doi.org/10.1016/j.clet.2023.100681
26. Chen, P.-K.; Rosana, M. R.; Dudley, G. B.; Stiegman, A. E. *J. Org. Chem.* **2014**, 79, 7425-7436. https://doi.org/10.1021/jo5011526
27. Kappe, C. O.; Pieber, B.; Dallinger, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 1088-1094. https://doi.org/10.1002/anie.201204103
28. Dudley, G. B.; Stiegman, A. E.; Rosana, M. R. *Angew. Chem. Int. Ed.* **2013**, *52*, 7918-7923. https://doi.org/10.1002/anie.201301539

29. Kappe, C. O. *Angew. Chem. Int. Ed.* **2013**, *52*, 7924-7928.
https://doi.org/10.1002/anie.201304368
30. Rodriguez, A. M.; Prieto, P.; de la Hoz, A.; Díaz-Ortiz, A.; Martín, R.; García, J. I. *ChemistryOpen* **2015**, *4*, 308-317.
https://doi.org/10.1002/open.201402123

Authors' Biographies

Ángel Díaz-Ortiz obtained his PhD in 1988. After postdoctoral research at a pharmaceutical company (Laboratorios Alter S.A.) he joined the Faculty of Chemistry at the University of Castilla-La Mancha (UCLM) as an Assistant Professor, becoming full Professor in 2010. His current research interests include Microwave Radiation and its employment in sustainable synthetic processes, Chemistry-on-flow, Synthesis of heterocyclic systems with applications in Supramolecular Chemistry and Crystal Engineering, and Design and synthesis of aggregates of heterocyclic compound with applicability of optical waveguides and OFETs.

Antonio de la Hoz is Professor in Organic Chemistry in the University of Castilla-La Mancha. He obtained his Ph. D. from the Universidad Complutense in Madrid in 1986 under the supervision of Prof. José Elguero and Carmen Pardo. After postdoctoral research in 1987 with Prof. Mikael Begtrup at the Danmarks Tekniske Høskole he joined the Faculty of Chemistry of the Universidad de Castilla-La Mancha in Ciudad Real in 1988 as an Assistant Professor. In 1993 he worked under the supervision Prof. André Loupy in the Université de Paris-

Sud in Microwave Assisted Organic Chemistry. Prof. de la Hoz has an h index = 51 and has authored more than 200 scientific publications 120 of them related to Microwaves in Organic Synthesis. Dr. de la Hoz has been a foundation member of the Spanish Green Chemistry Network. His current research interests focus on Green methodologies, microwave activation, mechanochemistry, flow methodologies, solvent-free reactions, NMR spectroscopy and the synergy these enabling technologies, and the applications of heterocyclic compounds in material and supramolecular chemistry.