C. Oliver Kappe, Doris Dallinger, and S. Shaun Murphree

Practical Microwave Synthesis for Organic Chemists

Strategies, Instruments, and Protocols

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Contents

Preface

Today, a large body of work on microwave-assisted organic synthesis is available in the published and patent literature. Close to one hundred review articles, several books, and online databases already provide extensive coverage of the subject for the specialist reader. The goal of the present book is to provide an introductory treatise for beginners, a sort of "How To Get Started" guide. Apart from a few articles in the *Journal of Chemical Education*, very little introductory and practical hands-on information on controlled microwave chemistry has been presented in a textbook style format.

This fact has prompted the publication of the present work "*Practical Microwave Synthesis for Organic Chemists – Strategies, Instruments, and Protocols*" which serves both the beginner and the more experienced microwave user. A major motivation for writing this treatise has been the continuous and enthusiastic feedback obtained from scientists during conferences and short courses on microwave synthesis organized by the authors. In particular, the very popular MAOS conference series organized since 2003, in combination with practical hands-on or classroom-style training courses, has led to a collection of questions and comments from the attendees and has stimulated the design and concept for this book. It has been written mainly with the microwave novice in mind. Several chapters are specifically designed for beginners, such as undergraduate or graduate students in academia, or industrial scientists getting started in microwave-assisted organic synthesis.

Following a brief introduction (Chapter 1), Chapter 2 details the basic concepts of microwave dielectric heating theory and provides insight into the current understanding of microwave effects. In Chapter 3 a comprehensive review of most of the commercially available single-mode and multimode microwave reactors for organic synthesis is presented. Chapter 4 provides an extensive overview of the different microwave processing techniques that are available today, while Chapter 5 contains many useful tips for the microwave novice, including a "Frequently Asked Questions" Section. The last chapter of the book (Chapter 6) contains a collection of carefully selected and documented microwave experiments that may also be used by scientists in academia to design a course on microwave-assisted organic synthesis. All examples have been tested by advanced undergraduate students in the course of a special “Microwave Chemistry Lab Course” during the spring of 2007 at the University of Graz.

Writing this book would have been impossible without considerable assistance from all the members of the Christian Doppler Laboratory for Microwave Chemistry (CDLMC) in Graz. All past and present members are acknowledged for their invaluable contributions over the years. Special thanks go to Jennifer M. Kremsner, Toma N. Glasnov, Hana Prokopcová, Bernadett Bacsa, Jamshed Hashim, Tahseen Razzaq and Florian Reder for their help in assembling the practical examples presented in Chapter 6. The students taking part in the “Microwave Chemistry Lab Course” are particularly acknowledged for their engagement and valuable input. In this context the authors wish to thank the Fulbright Commission and the Austrian–American Educational Commission for supporting the international collaboration leading to the development of this practical course. Thanks are also due to the microwave equipment vendors for providing detailed information and high resolution graphics of their instruments. In this context, the support of Alexander Stadler (Anton Paar GmbH), Martin Keil (Biotage AB), Axel Schöner (CEM Corp.) and Mauro Ianelli (Milestone s.r.l.) is acknowledged.

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Microwave Synthesis – An Introduction

While fire is now rarely used in synthetic chemistry, it was not until Robert Bunsen invented the burner in 1855 that the energy from this heat source could be applied to a reaction vessel in a focused manner. The Bunsen burner was later superseded by the isomantle, oil bath or hot plate as a source of applying heat to a chemical reaction. In the past few years, heating chemical reactions by microwave energy has been an increasingly popular theme in the scientific community. Since the first published reports on the use of microwave irradiation to carry out organic chemical transformations by the groups of Gedye and Giguere/Majetich in 1986 [1], more than 3500 articles have been published in this fast moving and exciting field, today generally referred to as microwave-assisted organic synthesis (MAOS) [2, 3]. In many of the published examples, microwave heating has been shown to dramatically reduce reaction times, increase product yields and enhance product purities by reducing unwanted side reactions compared to conventional heating methods. The advantages of this enabling technology have, more recently, also been exploited in the context of multistep total synthesis [4] and medicinal chemistry/drug discovery [5], and have additionally penetrated related fields such as polymer synthesis [6], material sciences [7], nanotechnology [8] and biochemical processes [9]. The use of microwave irradiation in chemistry has thus become such a popular technique in the scientific community that it might be assumed that, in a few years, most chemists will probably use microwave energy to heat chemical reactions on a laboratory scale. The statement that, in principle, any chemical reaction that requires heat can be performed under microwave conditions has today been generally accepted as a fact by the scientific community.

The short reaction times provided by microwave synthesis make it ideal for rapid reaction scouting and optimization of reaction conditions, allowing very rapid progress through the “hypotheses–experiment–results” iterations, resulting in more decision points per unit time. In order to fully benefit from microwave synthesis one has to be prepared to fail in order to succeed. While failure could cost a few minutes, success would gain many hours or even days. The speed at which multiple variations of reaction conditions can be performed allows a morning discussion of “What should we try?” to become an after lunch discussion of “What were the results?” Not surprisingly, therefore, many scientists, both in academia and in industry, have turned to microwave synthesis as a frontline methodology for their projects.

Arguably, the breakthrough in the field of MAOS on its way from laboratory curiosity to standard practice started in the pharmaceutical industry around the year 2000. Medicinal chemists were among the first to fully realize the true power of this enabling technology. Microwave synthesis has since been shown to be an invaluable tool for medicinal chemistry and drug discovery applications since it often dramatically reduces reaction times, typically from days or hours to minutes or even seconds [5]. Many reaction parameters can therefore be evaluated in a few hours to optimize the desired chemistry. Compound libraries can then be rapidly synthesized in either a parallel or (automated) sequential format using microwave technology [5]. In addition, microwave synthesis often allows the discovery of novel reaction pathways, which serve to expand “chemical space” in general, and “biologically-relevant, medicinal chemistry space”, in particular.

In the early days of microwave synthesis, experiments were typically carried out in sealed Teflon or glass vessels in a domestic household microwave oven without any temperature or pressure measurements [1]. Kitchen microwave ovens are not designed for the rigors of laboratory usage: acids and solvents corrode the interiors quickly and there are no safety controls. The results were often violent explosions due to the rapid uncontrolled heating of organic solvents under closed vessel conditions. In the 1990s several groups started to experiment with solvent-free microwave chemistry (so-called dry-media reactions), which eliminated the danger of explosions [10]. Here, the reagents were pre-adsorbed onto either a more or less microwave transparent inorganic support (i.e., silica, alumina or clay) or a strongly absorbing one (i.e., graphite), that additionally may have been doped with a catalyst or reagent. Particularly in the beginning of MAOS, the solvent-free approach was very popular since it allowed the safe use of domestic microwave ovens and standard open vessel technology. While a large number of interesting transformations using dry-media reactions have been published in the literature [10], technical difficulties relating to non-uniform heating, mixing, and the precise determination of the reaction temperature remained unsolved, in particular when scale-up issues needed to be addressed.

Alternatively, microwave-assisted synthesis was, in the past, often carried out using standard organic solvents under open vessel conditions. If solvents are heated by microwave irradiation at atmospheric pressure in an open vessel, the boiling point of the solvent typically limits the reaction temperature that can be achieved. In order to nonetheless achieve high reaction rates, high-boiling microwave absorbing solvents were frequently used in open-vessel microwave synthesis [11]. However, the use of these solvents presented serious challenges during product isolation and recycling of solvent. In addition, the risks associated with the flammability of organic solvents in a microwave field and the lack of available dedicated microwave reactors allowing adequate temperature and pressure control were major concerns. The initial slow uptake of microwave technology in the late 1980s and 1990s has often been attributed to its lack of controllability and reproducibility, coupled with a general lack of understanding of the basics of microwave dielectric heating.

In particular, the use of kitchen microwave ovens in combination with non-reliable temperature monitoring devices led to considerable confusion in the microwave chemistry community in the late 1990s and has given MAOS a bad reputation and the stigma of a "black box" science. The majority of organic chemists at that time were not taking microwave chemistry seriously and the discussion and irritation around the topic of "microwave effects" has probably contributed to this situation [12]. Historically, since the early days of microwave synthesis, the observed rate-accelerations and sometimes altered product distributions compared to oil-bath experiments led to speculation on the existence of so-called "specific" or "non-thermal" microwave effects [13]. Such effects were claimed when the outcome of a synthesis performed under microwave conditions was different from the conventionally heated counterpart at the same apparent temperature. Reviewing the present literature it appears that today most scientists agree that, in the majority of cases, the reason for the observed rate enhancements is a purely thermal/kinetic effect, that is, a consequence of the high reaction temperatures that can rapidly be attained when irradiating polar materials in a microwave field, although clearly effects that are caused by the uniqueness of the microwave dielectric heating mechanism ("specific microwave effects") must also be considered. While for the chemist in industry this discussion may seem futile, the debate on "microwave effects" is undoubtedly going to continue for many years in the academic world. Because of the recent availability of modern dedicated microwave reactors with on-line accurate monitoring of both temperature and pressure, some of the initial confusion on microwave effects has subsided. This can also be attributed, to some extent, to the fact that microwave synthesis today is mostly carried out in solution phase using organic solvents, where the temperature of the reaction mixture can generally be adequately monitored.

Controlled MAOS in sealed vessels using standard solvents – a technique pioneered by Strauss in the mid 1990s [14] – has thus celebrated a steady comeback since the year 2000 and today clearly is the method of choice for performing microwave-assisted reactions. This is evident from surveying the recently published literature in the area of microwave-assisted organic synthesis (Figure 1.1). In addition to the primary and patent literature, many review articles [3–19], several books [2], special issues of journals [20], feature articles [21], online databases [22], information on the world-wide-web [23], and educational publications [24, 25] provide extensive coverage of the subject. Among the about 850 original publications that appeared in 2007 describing microwave-assisted reactions under controlled conditions, a careful analysis demonstrates that in about 90% of all cases sealed vessel processing (autoclave technology) in dedicated single-mode microwave instruments has been employed. A recent survey has, however, found that as many as 30% of all published MAOS papers still employ kitchen microwave ovens [26], a practice banned by most of the respected scientific journals today. For example, the American Chemical Society (ACS) organic chemistry journals will typically not consider manuscripts describing the use of kitchen microwave ovens or the absence of a reaction temperature, as specified in the relevant publication guidelines [27].

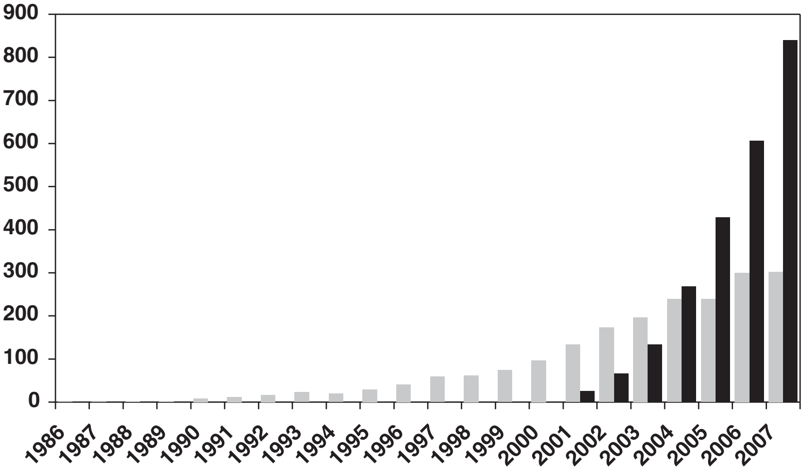

Figure 1.1 Publications on microwave-assisted organic synthesis (1986–2007). Gray bars: Number of articles involving MAOS for seven selected synthetic organic chemistry journals (*J. Org. Chem.*, *Org. Lett.*, *Tetrahedron*, *Tetrahedron Lett.*, *Synth. Commun.*, *Synthesis*, *Synlett*. SciFinder Scholar keyword search on "microwave"). The black bars represent the number of publications (2001–2007) reporting MAOS experiments in dedicated reactors with adequate process control (about 50 journals, full text search: microwave). Only those articles dealing with synthetic organic chemistry were selected.

Recent innovations in microwave reactor technology now allow controlled parallel and automated sequential processing under sealed vessel conditions, and the use of continuous or stop-flow reactors for scale-up purposes. In addition, dedicated vessels for solid-phase synthesis, for performing transformations using pre-pressurized conditions and for a variety of other special applications, have been developed. Today there are four major instrument vendors that produce microwave instrumentation dedicated to organic synthesis. All these instruments offer temperature and pressure sensors, built-in magnetic stirring, power control, software operation and sophisticated safety controls. The number of users of dedicated microwave reactors is therefore growing at a rapid rate and it appears only to be a question of time until most laboratories will be equipped with suitable microwave instrumentation.

In the past, microwave chemistry was often used only when all other options to perform a particular reaction had failed, or when exceedingly long reaction times or high temperatures were required to complete a reaction. This practice is now slowly changing and, due to the growing availability of microwave reactors in many laboratories, routine synthetic transformations are now also being carried out by microwave heating. One of the major drawbacks of this relatively new technology remains the equipment cost. While prices for dedicated microwave reactors for organic synthesis have come down considerably since their first introduction in the late 1990s, the current price range for microwave reactors is still many times higher than that of conventional heating equipment. As with any new technology, the current situation is bound to change over the next several years and less expensive equipment should become available. By then, microwave reactors will have truly become the "Bunsen burners of the twenty first century" and will be standard equipment in every chemical laboratory.

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2
Microwave Theory

The physical principles behind and the factors determining the successful application of microwaves in organic synthesis are not widely familiar to chemists. Nevertheless, it is essential for the synthetic chemist involved in microwave-assisted organic synthesis to have at least a basic knowledge of the underlying principles of microwave–matter interactions and of the nature of microwave effects. The basic understanding of macroscopic microwave interactions with matter was formulated by von Hippel in the mid-1950s [1]. In this chapter a brief summary of the current understanding of microwaves and their interactions with matter is given. For more in-depth discussion on this quite complex field, the reader is referred to recent review articles [2–5].

2.1
Microwave Radiation

Microwave irradiation is electromagnetic irradiation in the frequency range 0.3 to 300 GHz, corresponding to wavelengths of 1 mm to 1 m. The microwave region of the electromagnetic spectrum (Figure 2.1) therefore lies between infrared and radio frequencies. The major use of microwaves is either for transmission of information (telecommunication) or for transmission of energy. Wavelengths between 1 and 25 cm are extensively used for RADAR transmissions and the remaining wavelength range is used for telecommunications. All domestic “kitchen” microwave ovens and all dedicated microwave reactors for chemical synthesis that are commercially available today operate at a frequency of 2.45 GHz (corresponding to a wavelength of 12.25 cm) in order to avoid interference with telecommunication, wireless networks and cellular phone frequencies. There are other frequency allocations for microwave heating applications (ISM (industrial, scientific and medical) frequencies, see Table 2.1) [6], but these are not generally employed in dedicated reactors for synthetic chemistry. Indeed, published examples of organic synthesis carried out with microwave heating at frequencies other than 2.45 GHz are extremely rare [7].

From comparison of the data presented in Table 2.2 [8], it is obvious that the energy of the microwave photon at a frequency of 2.45 GHz (0.0016 eV) is too low to cleave

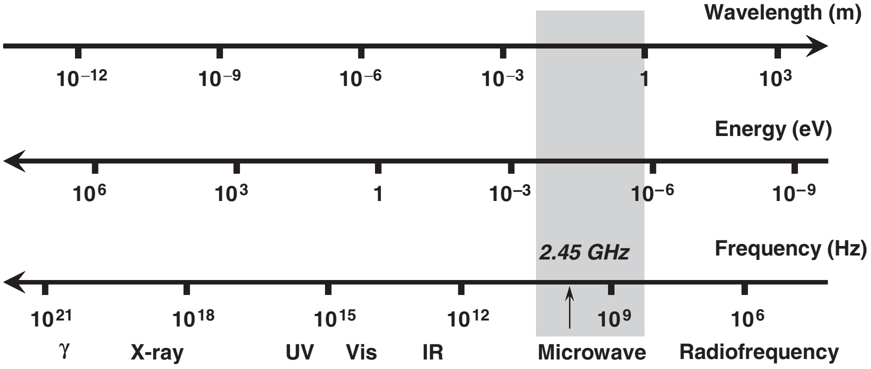

Figure 2.1 The electromagnetic spectrum.

Table 2.1 ISM microwave frequencies (data from Ref. [6]).

Frequency (MHz)	Wavelength (cm)
433.92 ± 0.2%	69.14
915 ± 13	32.75
2450 ± 50	12.24
5800 ± 75	5.17
24 125 ± 125	1.36

Table 2.2 Comparison of radiation types and bond energies (data from Refs. [6, 8]).

Radiation type	Frequency (MHz)	Quantum energy (eV)	Bond type	Bond energy (eV)
Gamma rays	3.0×10^{14}	1.24×10^{6}	C−C	3.61
X-rays	3.0×10^{13}	1.24×10^{5}	C=C	6.35
Ultraviolet	1.0×10^{9}	4.1	C−O	3.74
Visible light	6.0×10^{8}	2.5	C=O	7.71
Infrared light	3.0×10^{6}	0.012	C−H	4.28
Microwaves	2450	0.0016	O−H	4.80
Radiofrequencies	1	4.0×10^{-9}	hydrogen bond	0.04–0.44

molecular bonds and is also lower than Brownian motion. It is therefore clear that microwaves cannot “induce” chemical reactions by direct absorption of electromagnetic energy, as opposed to ultraviolet and visible radiation (photochemistry).

2.2
Microwave Dielectric Heating

Microwave chemistry is based on the efficient heating of materials by “microwave dielectric heating” effects [4, 5]. Microwave dielectric heating is dependent on the

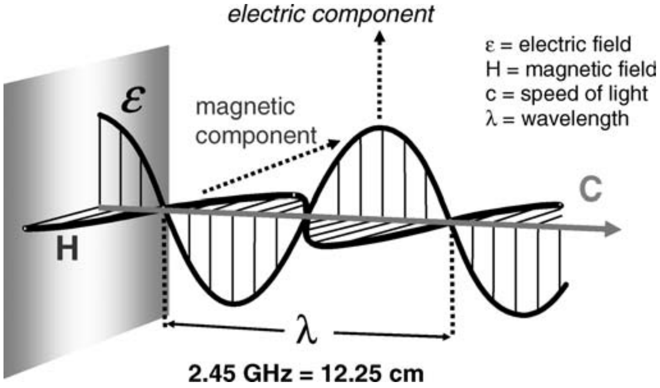

Figure 2.2 Electric and magnetic field components in microwaves.

ability of a specific material (e.g. a solvent or reagent) to absorb microwave energy and convert it into heat. Microwaves are electromagnetic waves which consist of an electric and a magnetic field component (Figure 2.2). For most practical purposes related to microwave synthesis it is the electric component of the electromagnetic field that is of importance for wave–material interactions, although in some instances magnetic field interactions (e.g. with transition metal oxides) can also be of relevance [9].

The electric component of an electromagnetic field causes heating by two main mechanisms: dipolar polarization and ionic conduction. The interaction of the electric field component with the matrix is called the dipolar polarization mechanism (Figure 2.3a) [4, 5]. For a substance to be able to generate heat when irradiated with microwaves it must possess a dipole moment. When exposed to microwave

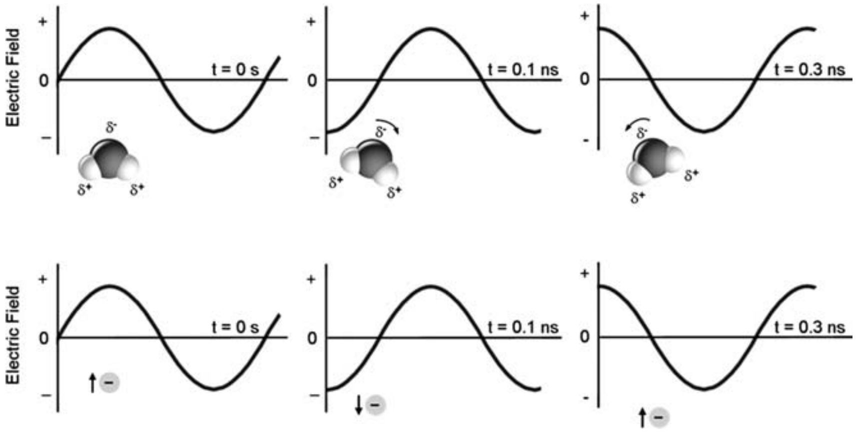

Figure 2.3 (a) Dipolar polarization mechanism. Dipolar molecules try to align with an oscillating electric field. (b) Ionic conduction mechanism. Ions in solution will move in the electric field.

frequencies, the dipoles of the sample align in the applied electric field. As the field oscillates, the dipole field attempts to realign itself with the alternating electric field and, in the process, energy in the form of heat is lost through molecular friction and dielectric loss. The amount of heat generated by this process is directly related to the ability of the matrix to align itself with the frequency of the applied field. If the dipole does not have enough time to realign (high frequency irradiation) or reorients too quickly (low frequency irradiation) with the applied field, no heating occurs. The allocated frequency of 2.45 GHz, used in all commercial systems, lies between these two extremes and gives the molecular dipole time to align in the field but not to follow the alternating field precisely. Therefore, as the dipole reorients to align itself 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. In summary, field energy is transferred to the medium and electrical energy is converted into kinetic or thermal energy, and ultimately into heat. It should be emphasized that the interaction between microwave radiation and the polar solvent, which occurs when the frequency of the radiation approximately matches the frequency of the rotational relaxation process, is not a quantum mechanical resonance phenomenon. Transitions between quantized rotational bands are not involved and the energy transfer is not a property of a specific molecule but the result of a collective phenomenon involving the bulk [4, 5]. The heat is generated by frictional forces occurring between the polar molecules whose rotational velocity has been increased by the coupling with the microwave irradiation. It should also be noted that gases cannot be heated under microwave irradiation since the distance between the rotating molecules is too far. Similarly, ice is also (nearly) microwave transparent, since the water dipoles are constrained in a crystal lattice and cannot move as freely as in the liquid state.

The second major heating mechanism is the ionic conduction mechanism (Figure 2.3b) [4, 5]. During ionic conduction, as the dissolved charged particles in a sample (usually ions) oscillate back and forth under the influence of the microwave field, they collide with their neighboring molecules or atoms. These collisions cause agitation or motion, creating heat. Thus, if two samples containing equal amounts of distilled water and tap water, respectively, are heated by microwave irradiation at a fixed radiation power, more rapid heating will occur for the tap water sample due to its ionic content. Such ionic conduction effects are particularly important when considering the heating behavior of ionic liquids in a microwave field (see Section 4.5.2). The conductivity principle is a much stronger effect than the dipolar rotation mechanism with regard to the heat-generating capacity.

A related heating mechanism exists for strongly conducting or semiconducting materials such as metals, where microwave irradiation can induce a flow of electrons on the surface. This flow of electrons can heat the material through resistance (ohmic) heating mechanisms [10]. In the context of organic synthesis this becomes important for heating strongly microwave absorbing materials, such as thin metal films (Pd, Au) (see Section 4.8.4), graphite supports (see Section 4.1) or so-called passive heating elements made out of silicon carbide (see Section 4.6).

2.3
Dielectric Properties

The heating characteristics of a particular material (e.g. a solvent) under microwave irradiation conditions are dependent on the dielectric properties of the material. The ability of a specific substance to convert electromagnetic energy into heat at a given frequency and temperature is determined by the so-called loss tangent, $\tan\delta$. The loss factor is expressed as the quotient, $\tan\delta = \varepsilon''/\varepsilon'$, where ε'' is the dielectric loss, indicative of the efficiency with which electromagnetic radiation is converted into heat, and ε' is the dielectric constant describing the polarizability of molecules in the electric field. A reaction medium with a high $\tan\delta$ is required for efficient absorption and, consequently, for rapid heating. Materials with a high dielectric constant, such as water (ε' at 25 °C = 80.4), may not necessarily also have a high $\tan\delta$ value. In fact, ethanol has a significantly lower dielectric constant (ε' at 25 °C = 24.3) but heats much more rapidly than water in a microwave field due to its higher loss tangent ($\tan\delta$: ethanol = 0.941, water = 0.123). The loss tangents for some common organic solvents are summarized in Table 2.3 [11]. In general, solvents can be classified as high ($\tan\delta > 0.5$), medium ($\tan\delta$ 0.1–0.5), and low microwave absorbing ($\tan\delta < 0.1$). Other common solvents without a permanent dipole moment, such as carbon tetrachloride, benzene and dioxane, are more or less microwave transparent. It has to be emphasized that a low $\tan\delta$ value does not preclude a particular solvent from being used in a microwave-heated reaction. Since either the substrates or some of the reagents/catalysts are likely to be polar, the overall dielectric properties of the reaction medium will, in most cases, allow sufficient heating by microwaves. Furthermore, polar additives (such as alcohols or ionic liquids) or passive heating elements can be added to otherwise low-absorbing reaction mixtures in order to increase the absorbance level of the medium (see Sections 4.5.2 and 4.6).

The loss tangent values are both frequency and temperature dependent. Figure 2.4 shows the dielectric properties of distilled water as a function of frequency at

Table 2.3 Loss tangents ($\tan\delta$) of different solvents (2.45 GHz, 20 °C; data from Ref. [11]).

Solvent	tan δ	Solvent	tan δ
Ethylene glycol	1.350	*N*,*N*-dimethylformamide	0.161
Ethanol	0.941	1,2-dichloroethane	0.127
Dimethylsulfoxide	0.825	Water	0.123
2-propanol	0.799	Chlorobenzene	0.101
Formic acid	0.722	Chloroform	0.091
Methanol	0.659	Acetonitrile	0.062
Nitrobenzene	0.589	Ethyl acetate	0.059
1-butanol	0.571	Acetone	0.054
2-butanol	0.447	Tetrahydrofuran	0.047
1,2-dichlorobenzene	0.280	Dichloromethane	0.042
1-methyl-2-pyrrolidone	0.275	Toluene	0.040
Acetic acid	0.174	Hexane	0.020

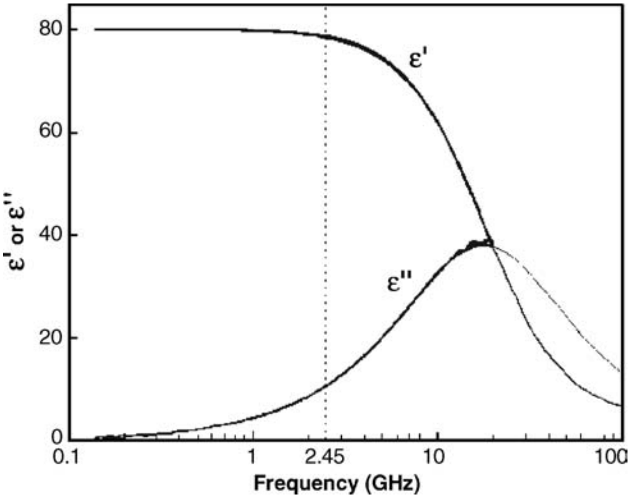

Figure 2.4 Dielectric properties of water as a function of frequency at 25 °C [12].

25 °C [1, 4, 5]. It is apparent that appreciable values of the dielectric loss ε″ exist over a wide frequency range. The dielectric loss ε″ goes through a maximum as the dielectric constant ε′ falls. The heating, as measured by ε″, reaches its maximum around 18 GHz, while all domestic microwave ovens and dedicated reactors for chemical synthesis operate at a much lower frequency, 2.45 GHz. The practical reason for the lower frequency is the necessity to heat food efficiently throughout its interior. If the frequency is optimal for a maximum heating rate, the microwaves are absorbed in the outer regions of the food, and penetrate only a short distance ("skin effect") [4].

According to definition, the penetration depth is the point where 37% (1/*e*) of the initially irradiated microwave power is still present [6]. The penetration depth is inversely proportional to tan δ and therefore depends critically on factors such as temperature and irradiation frequency. Materials with relatively high tan δ values are thus characterized by low values of penetration depth and therefore microwave irradiation may be totally absorbed within the outer layers of these materials. For a solvent such as water ($\tan\delta = 0.123$ at 25 °C and 2.45 GHz), the penetration depth at room temperature is only of the order of a few centimeters (Table 2.4). Beyond this penetration depth, volumetric heating due to absorption of microwave energy becomes negligible. This means that, during microwave experiments on a larger scale, only the outer layers of the reaction mixture may be directly heated by microwave irradiation via dielectric heating mechanisms. The inner part of the reaction mixture will, to a large extent, be heated by conventional heat convection and/or conduction mechanisms. Issues relating to the penetration depth are therefore critically important when considering the scale-up of MAOS (see Section 4.8).

The dielectric loss and loss tangent of pure water and most other organic solvents decrease with increasing temperature (Figure 2.5). The absorption of microwave

Table 2.4 Penetration depth of some common materials (data from Ref. [10]).

Material	Temperature (°C)	Penetration depth (cm)
Water	25	1.4
Water	95	5.7
Ice	−12	1100
Polyvinylchloride	20	210
Glass	25	35
Teflon	25	9200
Quartz glass	25	16 000

radiation in water therefore decreases at higher temperatures. While it is relatively easy to heat water from room temperature to 100 °C by 2.45 GHz microwave irradiation, it is significantly more difficult to further heat water to 200 °C and beyond in a sealed vessel. In fact, supercritical water ($T > 374\,°C$) is transparent to microwave irradiation (see Section 4.5.1).

Most organic materials and solvents behave similarly to water, in the sense that the dielectric loss ε'' will decrease with increasing temperature [2–5]. From the practical point of view this may be somewhat inconvenient, since microwave heating at higher temperatures may often be compromised. On the other hand, from the standpoint of safety, it should be stressed that the opposite situation may lead to a scenario where a material will become a stronger microwave absorber

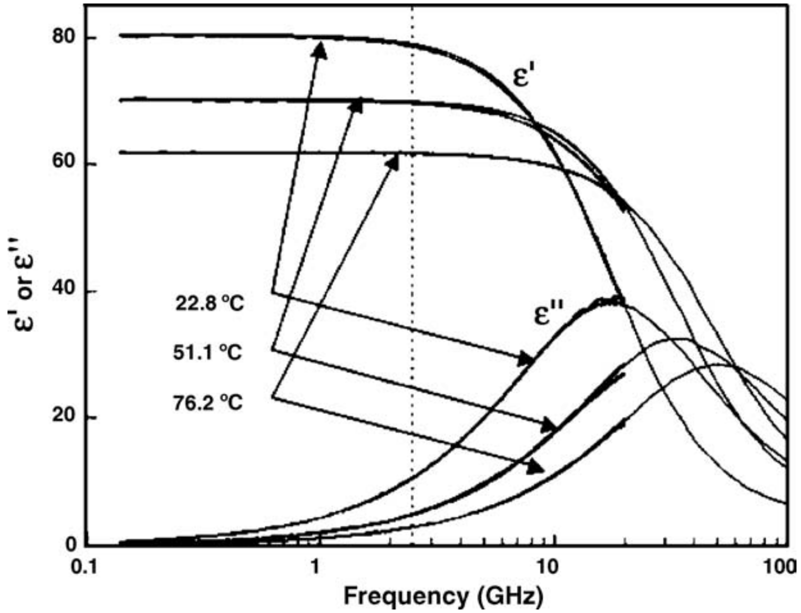

Figure 2.5 Dielectric properties of water as a function of temperature and frequency [12].

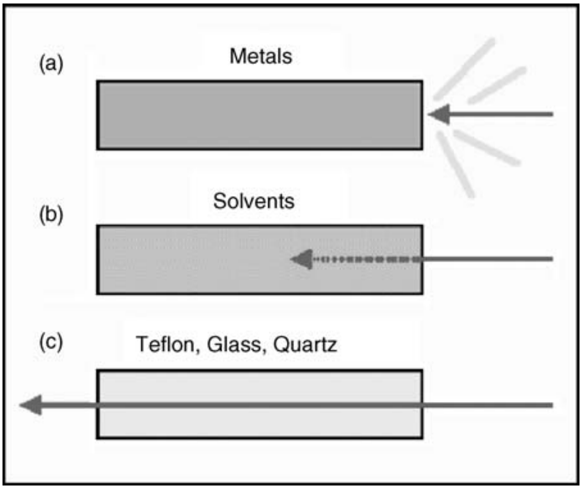

Figure 2.6 Interaction of microwaves with different materials. (a) Electrical conductors, (b) absorbing materials (tan δ 0.05–1), (c) insulators (tan δ < 0.01).

with increasing temperature. This is the case for some inorganic/polymeric materials [4], and will lead to the danger of a thermal runaway during microwave heating.

In summary, the interaction of microwave irradiation with matter is characterized by three different processes: absorption, transmission and reflection (Figure 2.6). Highly dielectric materials, like polar organic solvents, lead to a strong absorption of microwaves and consequently to a rapid heating of the medium (tan δ 0.05–1, Table 2.3). Non-polar microwave transparent materials exhibit only small interactions with penetrating microwaves ($\tan\delta < 0.01$, Table 2.5) and can thus be used as construction materials (insulators) for reactors because of their high penetration depth values (Table 2.4). If microwave radiation is reflected by the material surface, there is no, or only small, coupling of energy into the system. The temperature increases in the material only marginally. This holds true especially for metals with high conductivity, although in some cases resistance heating for these materials can occur.

Table 2.5 Loss tangents (tan δ) of low-absorbing materials (2.45 GHz, 25 °C; data from Ref. [10]).

Material	tan δ ($\times 10^{-4}$)	Material	tan δ ($\times 10^{-4}$)
Quartz	0.6	Plexiglass	57
Ceramic	5.5	Polyester	28
Porcelain	11	Polyethylene	31
Phosphate glass	46	Polystyrene	3.3
Borosilicate glass	10	Teflon	1.5