# Chapter 14

# Microwave Photochemistry

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## Content

# 14.1 Introduction

Chemistry under extreme or non-classical conditions is currently a dynamically developing issue in applied research and industry. Alternatives to conventional synthetic or waste treatment procedures may increase production efficiency or save the environment by reducing the use or generation of hazardous substances in the chemical production.

*Microwave* energy belongs to non-classical energy sources together with ultrasound, high pressure, mechanical activation, or plasma discharge [1]. Since the first reports on the use of MW heating to accelerate organic chemical transformations [2,3], over 1000 articles have been published in the area of microwave-assisted synthesis and related topics. Microwave chemistry certainly became one of the important fields of modern organic chemistry [4-13]. Microwave activation increases efficiencies of many chemical processes at the same time as it can reduce formation of by-products, otherwise obtained from conventionally heated reactions. Chemical processes performed under microwave radiation are believed to be affected in part by superheating, hot spots formation, polarization, and spin alignment [7,8,13]. The existence of a "specific microwave effect" in homogeneous reactions, i. e. non-thermal effect, has been a matter of controversy during the past decade [11,14-17].

Microwave heating has been already utilized in combination with some other (non)conventional activation processes. Such a combination may have a synergic effect on the reaction efficiencies or, at least, enhance them by summing up the individual effects. An application of MW radiation on ultrasound-assisted chemical processes has been recently described by some authors [18,19]. Mechanical activation was also successfully combined with MW heating to increase chemical yields of several reactions [1].

On the other hand, there have been attempts to affect *photochemical* reactions by other sources of non-classical activation, e.g., ultrasound [20,21]. A combined chemical activation by two distinctive kinds of electromagnetic radiation, microwave (MW) and ultraviolet (UV)/visible (VIS), is covered by the field simply called *microwave photochemistry*. Energy of MW radiation is considerably lower than that of UV radiation, i.e. it is not sufficient to disrupt bonds of common organic molecules. We can therefore anticipate that it is essentially photoinitiation what is responsible for a chemical change and MW radiation subsequently affects the course of the reaction. The objective of microwave photochemistry is frequently, but not irreplaceably, connected to the electrodeless discharge lamp (EDL) which generates UV radiation when placed into the MW field.

This chapter covers a complete picture of current knowledge about microwave photochemistry. It provides the necessary theoretical background and some details about synthetic and other applications as well as the technique and safety precautions. Despite of the fact that microwave photochemistry is a newly developing discipline of chemistry; the recent advances suggest its promising future.


# 14.2 Ultraviolet Discharge in Electrodeless Lamps

The electrodeless discharge lamp (EDL) [22] consists of a glass tube ("envelope") that is filled with an inert gas and an excitable substance, and it is sealed under a lower pressure of a noble gas. A high frequency electromagnetic field (radiofrequency or MW: 300-3000 MHz) can trigger gas discharge causing the emission of electromagnetic radiation. This phenomenon has been studied for many years [23] and was already well understood in the 1960s [24]. The term "electrodeless" means that the lamps lack the electrodes within the envelope. Meggers [24] developed the first EDL using the mercury isotope $^{198}$Hg in 1942 (Fig. 14.1) and its earliest application appeared in the field of absorption spectroscopy [25]. EDL is usually

characterized by higher emission intensity than that of the hollow cathode lamps, a lower contamination due to the absence of the electrodes [26], and a longer lifetime [27].
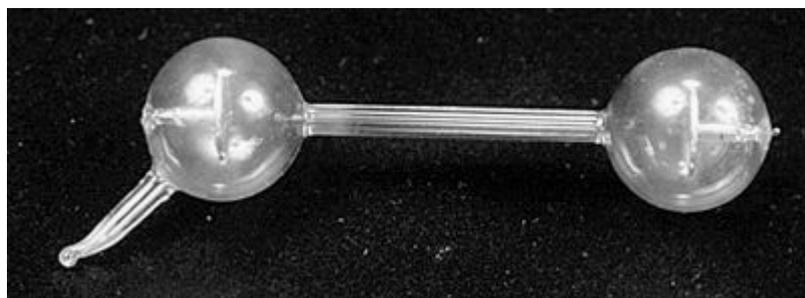


**Fig. 14.1** The electrodeless mercury lamp made by Williams F. Meggers. With permission from the National Institute of Standards and Technology, Technology Administration, U.S. Department of Commerce.

### 14.2.1 Theoretical aspects of the discharge in EDLs

The theory of EDL operation, as it is presently understood, is shown in the block diagram in Fig. 14.2 [28]. Free electrons in the fill (i.e. electrons that have separated from a noble gas due to the ambient energy) accelerate as a result of the electromagnetic (EM) field energy. They collide with the gas atoms and ionize them to release more electrons. The repetitive effect causes the number of electrons increases significantly over a short period of time, an effect otherwise known as an "avalanche". The electrons are generated by processes including the *collisional* or *collisionless* transformation of EM waves, and *normal* or *non-linear wave absorption* [26]. The energetic electrons collide with the heavy-atom particles present in the plasma, thus exciting them from a ground state to higher energy levels. The excitation energy is then released as EM radiation with the spectral characteristics according to the composition of the envelope. The excited molecular or atomic species in the plasma can emit photons over very broad portion of the EM spectrum, ranging from x-rays to the IR [29].
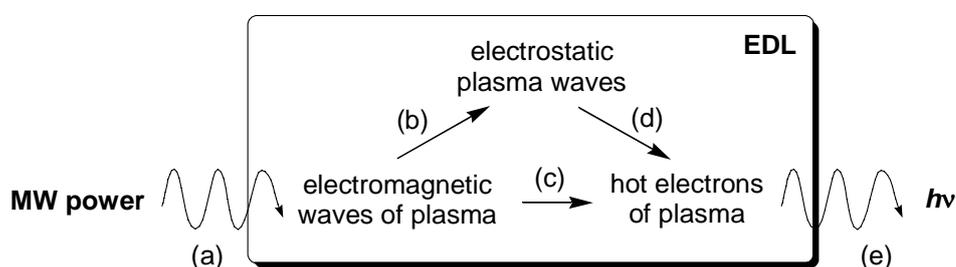


**Fig. 14.2** The block diagram illustrating operation of EDL: (a) energy flows from a MW source into the plasma chamber; (b) collisional or collisionless transformation; (c) normal or non-linear wave absorption; (d) collisional or collisionless dumping; (e) collisional excitation of atoms and ions followed by emission. Adapted from [28].

### 14.2.2 The fundamentals for EDL construction and its performance

The EDL system is modular and consists of two basic parts, a gas filled bulb and a power supply with waveguides or external electrodes. A typical EDL consists of a scaled (usually quartz) tube envelope, which contains an inert gas (such as a noble gas) and an excitable substance (e.g. Hg, Cd, Na, Ga, In, Tl, Sc, S, Se, Te) [30]. The envelope material must be impermeable to gases, an electrical insulator, and chemically resistant to the filling compounds at the temperature of operation.

There have been historically four basic methods of exciting discharges without electrodes [31-35]. In the first method, referred as *capacitive coupling*, the electric field lines of the applied EM signal (usually 915 MHz) originate from one external electrode, pass through the gas filled bulb containing the discharge, and terminate on a second external (coaxial) electrode. This discharge is similar to arc discharge in an electrode lamp but it needs a higher current. The second method of exciting EDLs with MW power (typically 2450 MHz) is to place the bulb in the path of radiation from a directional antenna. *Microwave discharge* is excited by both electric and magnetic components of the EM field. However, since a free propagation of the MW power occurs, an inherent inefficiency of the emission is often observed. This method is used for excitation of EDLs inside of a MW oven. The third method is called the *travelling wave discharge*: a gap between the external electrodes provides the electric field that launches a surface wave discharge. The fourth method uses the *inductive coupling* of EDL and the system can be compared to an electrical transformer. An alternating current in the coil causes a changing magnetic field inducing the electric field that drives a current into the plasma. The operating frequency is limited to about 50 kHz [36].

The operating parameters influencing the electrodeless lamp performance are a complex of many variables [30].

(a) *Inert gases*. The arc chamber contains a buffer noble gas (usually Kr, Xe, and Ar) which is inert to the extent that it does not adversely affect the lamp operation. Helium has a higher thermal conductivity than other noble gases and therefore higher thermal conduction loss is observed [37]. The inert gas easily ionizes at a lower pressure but its transition to the thermal arc is slower and the lamp requires a longer warm-up time. Ionization is more difficult at higher pressures and it requires a higher input power to establish the discharge. The pressure in EDLs at operation temperature is generally much higher (5-20 atm) than that of a conventional electrode lamp.

(b) *The choice of the fill material* initiating the discharge is a very important parameter. Together with a standard mercury fill, it is often desirable to incorporate an additive in the fill material that has a low ionization potential [38,39]. One category of low-ionization-potential materials is the group of alkali metals or their halides (LiI, NaI) but some other elements, such as Al, Ga, In, Tl [40,41] or Be, Mg, Ca, Sr, La, Pr, Nd [23,37,42], can be used.

(c) *Dimensions and the properties of the lamp envelope* is based on the discovery that the volume of Hg is critical for the effective UV operation [43]. Higher Hg pressures result in necessity to use a higher MW power levels. To focus efficiently MW field into EDLs, a special Cd low-pressure lamp with a metal antenna (a molybdenum foil) was developed by Florian and Knapp [44].

(d) *The nature and characteristics of the EM energy-coupling device* is discussed in Chap. 14.2.3.

(e) *The frequency and intensity* of EM energy is determined by the type of a device. A standard MW power source operates around 915 or 2450 MHz.

### 14.2.3 Spectral characteristics of EDLs

Spectral characteristics of EDLs are of a general interest for microwave photochemistry. The right choice of the filling material can provide a desirable ultraviolet radiation. Generally, the atomic fills provide the line emission spectra (e.g. of a Hg-EDL shown in Fig. 14.3) and molecular fills give the continuous spectra [45]. The total emission output of Hg-EDL in the region of 200-600 nm is about the same as of the electrode lamp with the same power input [46]. However, the distribution of radiation is markedly different as a result of a much higher Hg pressure and a greater number of atoms that takes part in the plasma. EDL gives over three times as much UV and over two times less IR irradiation than received from a conventional lamp [47]. It has been noted that EDLs and the electrode lamps provide different spectra when the fill includes a rare-earth material but similar spectra when a non-rare-earth fills are used [48]. Addition of some elements (Sn, Pb, Ga) has a very significant effect on the spectral EDL distributions [46]. Most lamps emits less efficiently below 280 nm than a standard Hg lamp (Table 14.1). The advantages of EDLs for MW-photochemistry applications are discussed in the Chapter 14.4.
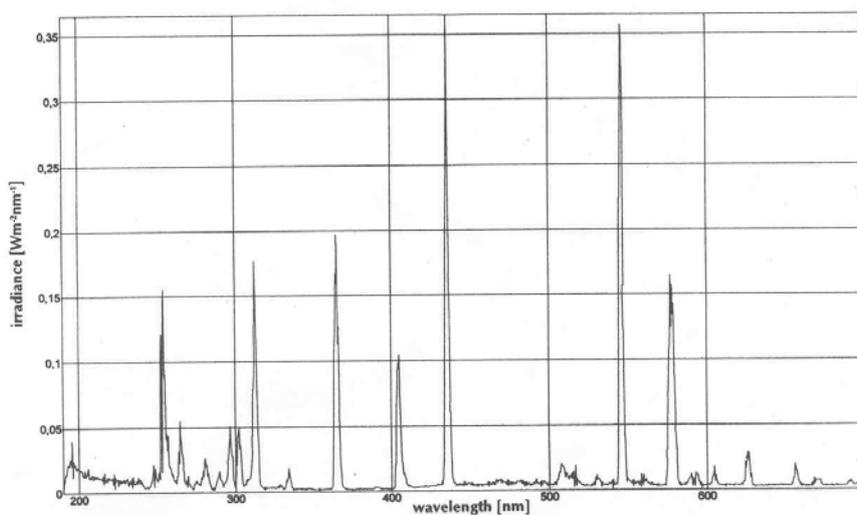


**Fig. 14.3** Emission spectrum of MW-powered Hg-EDL. With permission from [44].

**Table 14.1** Filling compounds and the wavelength of EDL emission

| Filling material (filling gas) | Excited species | Emission bands $\lambda$ [nm] | Reference |
|---|---|---|---|
| Hg (Ar) | Hg | 185, 254, 365, 405, 436, 546 | [30,31,43,44,48-50] |
| Cd (Ar) | Cd | 229, 326 | [30,44,51] |
| $SnI_2$ (Ar) | $SnI_2$ | 400-850, 610 | [52] |
| $FeCl_2$ (Ar) | Fe | 248 | [30] |
| Zn (Ar) | Zn | 214 | [30,44,53] |
| CuCl (Ar) | Cu | 325 | [30] |
| NaI (Xe, Kr) | Na | 589 | [54,55] |
| Mg, $H_2$ (Ar) | MgH | 518, 521, 480-560 | [56] |
| $AlBr_3$ (Ne) | AlBr | 278 | [57] |
| $AlCl_3$ (Ne) | AlCl | 261 | [58,59] |
| Ga, $GaI_3$ (Ar) | Ga | 403, 417, 380-450 | [49,53] |
| $InI_3$ (Ar) | In | 410, 451 | [53] |
| TlI (Ar) | Tl | 277, 535 | [30,53] |
| $PCl_4$ (Kr) | $P_2$ | 380 | [60] |
| S (Ar) | S | 350-850, 525 | [40,61,62] |
| Se (Ar, Xe) | Se | 370-850, 545 | [62-64] |
| Te (Xe) | Te | 390-850, 565 | [62,64] |
| Ar (Ar) | $Ar_2$ | 126, 107-165 | [29,65] |
| Ar, $Cl_2$ (Ar) | ArCl | 175 | [29,65] |
| Xe, $Cl_2$ (Xe) | XeCl | 308 | [29,65] |
| $B_2O_3$, S (Kr) | $B_2S_3$ | 812 | [66] |
| $I_2$, $HgI_2$ (Ar) | I | 206 | [67] |

# 14.3 Microwave photochemical reactor

The microwave photochemical reactor is an essential tool for experimental work in this field. Such an equipment allows simultaneous irradiation of the sample by both MW and UV/VIS radiation. The idea to use an electrodeless lamp (EDL), in which the discharge is powered by the MW field, for photochemistry was born half a century ago [46,68]. The lamp was originally proposed as a source of UV radiation only, without considering the effects of microwaves on photochemical reactions. The first applications of EDL were connected to a construction of a high intensity source of UV radiation for atomic fluorescence flame spectrometry [69-71].
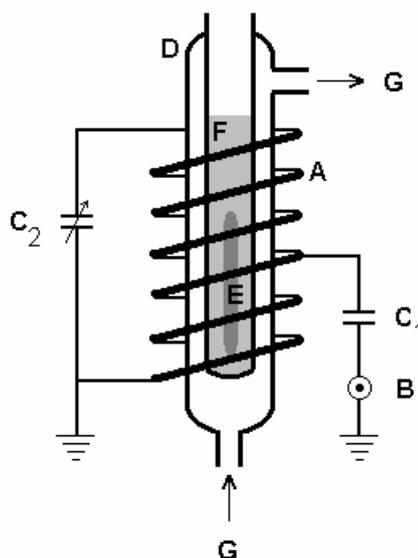
**Fig. 14.4** An apparatus for electrodeless photochemical irradiation. A - antenna; B - transmitter; $C_1$ - capacitor; $C_2$ - variable capacitor; D - jacketed flask; E - EDL; F - reaction mixture; G - circulating coolant. Adapted from [72].

Gunning, Pertel and their coworkers reported on the photochemical separation of mercury isotopes [73-76] in a flow reactor. It consisted of the microwave-operated discharge lamp [77,78] cooled by a flowing film of water. A filter cell and a circulation system, preventing the filter solution and the cell from being heated, were placed concentric and coaxial with the lamp. A similar reactor, for small-scale laboratory photolysis of organic compounds in solution or gas phase, has been proposed by Den Besten and Tracy [72]. In this arrangement, EDL was placed into the reaction solution and was operated by an external microwave field from a radio- or microwave-frequency transmitter (Fig. 14.4). The lamp quantum output was controlled by changing the output of the transmitter or by using a dilute ionic solution circulating through the cooling jacket. For maximum lamp output, a weakly conducting solution has been proposed. Placing EDL into the solution was quite advantageous since the full quantum output was utilized. The authors recommended keeping the sample temperature lower since EDL produces a considerable amount of heat.

Application of a domestic microwave oven appeared in a patent [79], according to which gaseous reactants were irradiated with microwave and UV/VIS radiation to produce desired photoproducts (EDL was positioned inside the MW cavity, although outside the reaction vessel). Several similar reactors were proposed for UV sterilization [80-82] or the treatment of waste water containing organic pollutants [83-85].
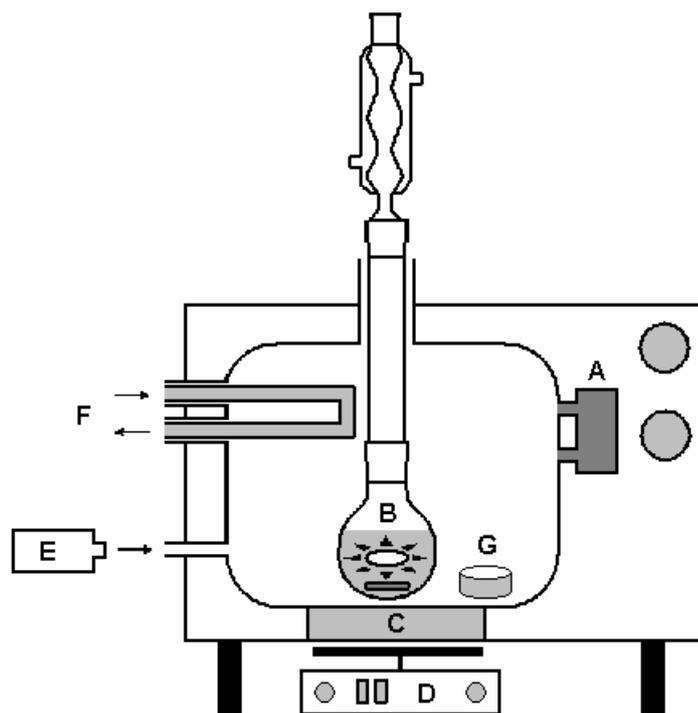
**Fig. 14.5** A modified MW oven for microwave photochemistry experiments. A - magnetron; B - reaction mixture with EDL and a magnetic stir bar; C - aluminum plate; D - magnetic stirrer; E - infrared pyrometer; F - circulating water in a glass tube, G – dummy load inside the oven cavity. Adapted from [86].

Církva and Hájek have proposed a simple application of a domestic microwave oven for microwave photochemistry experiments [87]. In this arrangement, EDL (the MW-powered lamps were in this case specified as microwave lamps or EDLs) was placed into a reaction vessel located in the cavity of an oven. The MW field generated UV discharge inside the lamp that resulted in simultaneous UV and MW irradiation of the sample. This arrangement offered a unique possibility to study photochemical reactions under extreme thermal conditions. Klán et al. published a series of papers that described the scope and limitation of using this reactor [86,88-91]. In a typical design (Fig. 14.5 and 14.6), four holes were drilled into the walls of a domestic oven: one for a condenser tube in the oven top, another in the side for an IR pyrometer, and two ports for a glass tube with circulating water. A part of the oven bottom was replaced by aluminum plate to allow magnetic stirring. The opening for an IR pyrometer could also serve for an external (additional) source of UV radiation. The vessel was connected to a very efficient water-cooled condenser by a long glass tube. The circulating cool water or some amounts of a MW-absorbing solid material (dummy load: basic $Al_2O_3$, molecular sieve, etc.) were used in those cases when a small quantity of non- or poorly absorbing samples for microwave photochemical experiments was used. The material removed the excess microwave power and/or prevented the magnetron from being destroyed by overheating. The EDL has to be always placed in a position, in which the solvent cools it efficiently down because lamp overheating causes failure of the lamp emission. An extensive lamp IR output caused immediate boil of all solvents including non-polar (MW-transparent) liquids [88-90].

On the other hand, polar solvents absorbed most of MW radiation resulting in lowering the UV output efficiency. The Table 14.2 depicts the most important advantages and disadvantages that accompany EDL applications.



**Fig. 14.6** Photochemistry in a microwave oven (EDL floats on the liquid surface).

**Table 14.2** Advantages and disadvantages of EDL application in photochemistry [90].

| **Advantages** |
| --- |
| 1.  A simultaneous UV and MW irradiation of the sample<br>2.  Possibility to carry out photochemistry at high temperature<br>3.  Good photochemical efficiencies (EDL is "inside" the sample)<br>4.  Simplicity of the experiment and a low cost of EDL<br>5.  The use of a commercially available microwave oven<br>6.  A "wireless" EDL operation<br>7.  The choice of the EDL material may modify its spectral output |
| **Disadvantages** |
| 1.  Technical difficulties with experiments at temperatures below the solvent b. p.<br>2.  Higher safety precautions<br>3.  EDL overheating causes the lamp emission failure<br>4.  Polar solvents absorb MW radiation |

Chemat and his coworkers [92] have proposed an innovative MW-UV combined reactor (Fig. 14.7) based on the construction of a commercially available MW reactor Synthewave 402 (Prolabo) [9], a monomode microwave oven cavity operating at 2.45 GHz designed for both solvent and dry media reactions. A sample in the quartz reaction vessel could be magnetically stirred and its temperature was monitored by an IR pyrometer. The reaction systems were irradiated from an external source of UV radiation (a 240-W medium-pressure mercury lamp). Similar photochemical applications in a Synthewave reactor using either an external or internal UV source has been done by Louerat and Loupy [93].
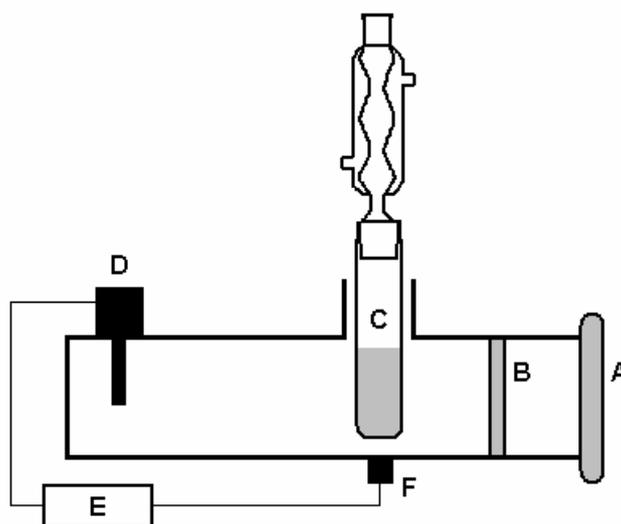


**Fig. 14.7** A reactor for microwave photochemistry derived from Synthewave SW 402 (Prolabo). A - a medium pressure Hg lamp; B - a window hermetic to MW radiation; C - reaction mixture; D - magnetron; E - regulator; F - IR sensor. Adapted from [92].

A microwave-assisted, high-temperature, and high-pressure UV digestion reactor has been developed by Florian and Knapp [44] for analytical purposes. The apparatus consisted of the immersed electrodeless discharge lamp operating thanks to the MW field in the oven cavity (Fig. 14.8). An antenna, fixed on the top of EDL, enhanced the EDL excitation efficiency. Another interesting MW-UV reactor has been shown by Howard and his coworkers [94]. A beaker-shaped electrodeless discharge lamp, placed into a modified domestic MW oven, has been employed for the mineralization of organophosphate compounds. The samples in quartz tubes were positioned in a carrousel inside the open UV-beaker and efficiently photolyzed from the whole surface of the beaker. Microwave-enhanced chemistry introduces unique *safety considerations* that are not encountered by the chemist in other fields of chemistry [95]. Careful planning of all experiments is strongly advised, especially when the results are uncertain, because the control of reaction temperature might be complicated by rapid heat transfer mechanisms. Furthermore, it is well known that electronically excited singlet oxygen, capable of causing a serious physiological damage, is generated by microwave discharge through an oxygen stream [96]. A combined effect of MW and UV irradiation could increase the singlet oxygen concentration in the MW cavity, particularly in the presence of a photosensitizer.
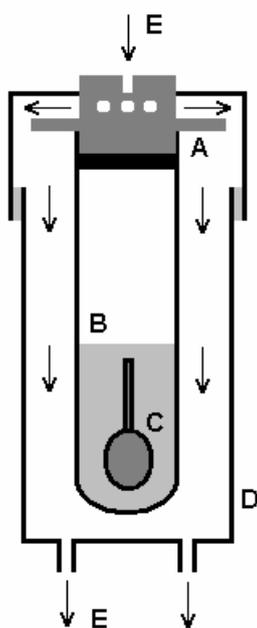
**Fig. 14.8** A simplified scheme of a high-pressure digestion vessel with EDL. A - plug and seal; B - quartz pressure reaction vessel with a sample solution; C - EDL with an antenna; D - vessel jacket with a screw cap; E - air flow. Adapted from [44].

## 14.4. Microwave photochemistry

### 14.4.1 Interactions of ultraviolet and microwave radiation with matter

While microwave chemistry already received widespread appreciation by chemical community, there is considerably less information about the microwave radiation effect on photochemical reactions. Photochemistry is the study of the interaction of ultraviolet or visible radiation ($E$ = 600-170 kJ mol$^{-1}$ at $\lambda$ = 200-700 nm) with matter. The excess energy of electronically excited states significantly alters the reactivity of the species, and it corresponds roughly to typical reaction activation energies helping the molecules to overcome activation barriers. On the other hand, the microwave region of the electromagnetic spectrum lies between infrared radiation and radio frequencies. Its energy ($E$ = 1-100 J mol$^{-1}$ at $\nu$ = 1-100 GHz) is about 3-6 orders of magnitude lower than that of UV radiation (a typical MW kitchen oven operates at 2.45 GHz). Microwave heating is not identical to classical external heating, at least at the molecular level. Molecules with a permanent (or induced) dipole respond to an electromagnetic field by rotating, which results in friction with neighboring molecules (thereby in heat). There are some additional (secondary) effects of microwaves, including ionic conduction (ionic migration in the presence of an electric field) or spin alignment.

A simultaneous UV/VIS and MW irradiation of molecules, which does not necessarily have to cause any chemical change, may affect the course of a reaction by various mechanisms at *each* step of the transformation. From many possibilities, let us present a simplified model describing two main distinct pathways (Fig. 14.9). The first route, more probable, is a photochemical reaction starting with a ground state molecule **M**, which is electronically excited into **M***, transformed into an intermediate (or a transition state) **I**, and

finally a product **P**. Virtually each step may be complicated by a parallel microwave-assisted reaction offering a different chemical history. There is a hypothetical possibility that MW radiation affects the electronically excited molecule **M\*** or a short-lived transition state. In such a case, the lifetime of the species should be long enough to provide a sufficient time for the interaction with this low-frequency radiation. The second pathway becomes important when MW initiate a "dark" chemical reaction (essentially through polar mechanisms), competitive or exclusive to a photochemical pathway, yielding a different (**R**) or same (**P**) product.
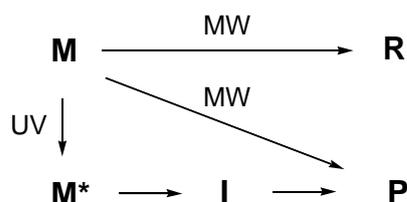


**Fig. 14.9** A simplified model of non-synergic effects of UV and MW radiation on a chemical reaction.

Fig 14.9 represents a model where MW and UV effects are easily distinguishable: it is assumed that there is no synergic effect during a single step of the transformation. On the other hand, let us assume that the quantum efficiency of a photoreaction is altered by microwave induction. In an example shown in Fig. 14.10, microwave *heating* affects the excitation energy of the starting ground state molecule. The individual effects of both types of electromagnetic radiation thus influence a single chemical step in which the MW-heated molecule ($M^\Delta$) is being excited. If the excited molecules **M\*** and $M^{\Delta}*$ decay with different efficiencies to the ground state the quantum yields should be proportional to the ratios ($k_r / k_d$) or ($k_r^\Delta / k_d^\Delta$), respectively. The observed rate constant $k_{obs}$ is then expressed by the sum $k_{obs} \sim (\chi k_r + \chi^\Delta k_r^\Delta)$, where $\chi$ and $\chi^\Delta$ represent the populations of **M\*** and $M^{\Delta}*$.
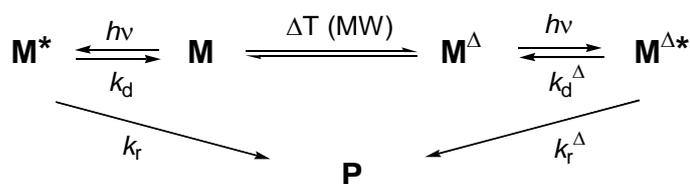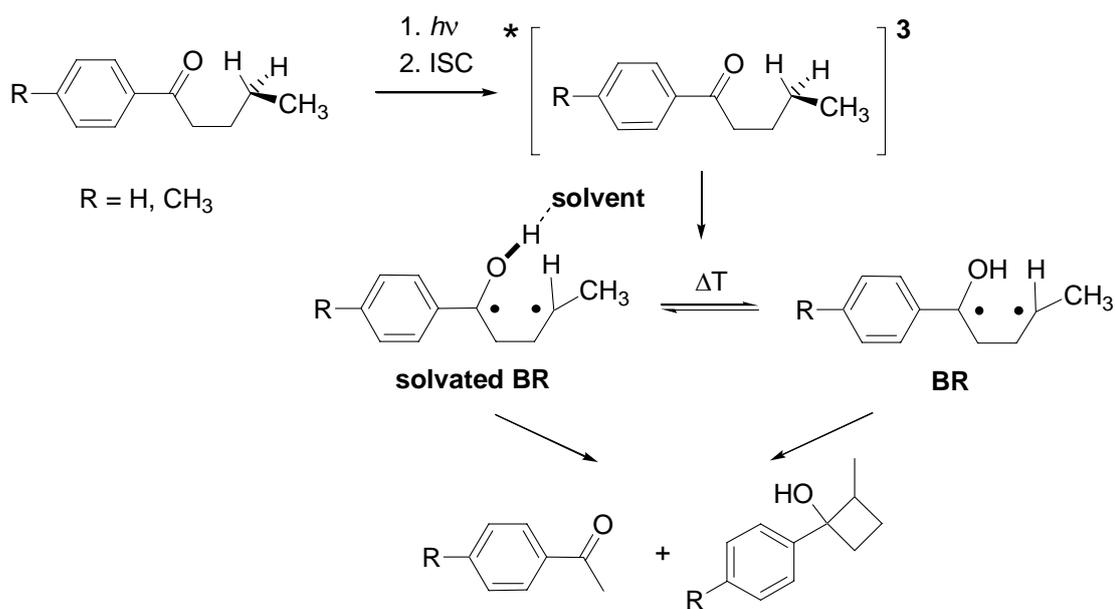


**Fig. 14.10** A simplified model of the synergic effect of UV and MW radiation on a chemical reaction. $M^\Delta$ is the "hot" molecule and $k_d$, $k_d^\Delta$, $k_r$, and $k_r^\Delta$ are the rate constants of the processes leading eventually to the same product **P**.

**Scheme 14.1**

### 14.4.2 Photochemical reactions in the microwave field: thermal effects

Superheating of polar solvents at atmospheric pressure, i.e. having the average temperatures higher than those of the corresponding boiling points, has been explained by Baghurst and Mingos as a result of the microwave dissipation over the whole volume of a liquid [97]. With the absence of nucleation points necessary for boiling, the heat loss occurs at the liquid/reactor wall or liquid/air interfaces. Many reaction efficiency enhancements reported in the literature have been explained by superheating effect when the reactions were essentially carried out in sealed vessels without any stirring [98-102], and this effect is also anticipated in microwave photochemistry experiments in the condensed media. Gedye and Wei [15], for example, have shown that rate enhancements of several different thermal reactions by factors of 1.05-1.44 were observed for experiments accomplished in a domestic-type MW oven but not in a variable-frequency microwave reactor. The enhancement was interpreted as a consequence of solvent superheating or hot-spot formation rather than non-thermal effects. Stadler and Kappe reported similar results in an interesting study of MW-mediated Biginelli reaction [14].



**Scheme 14.2**
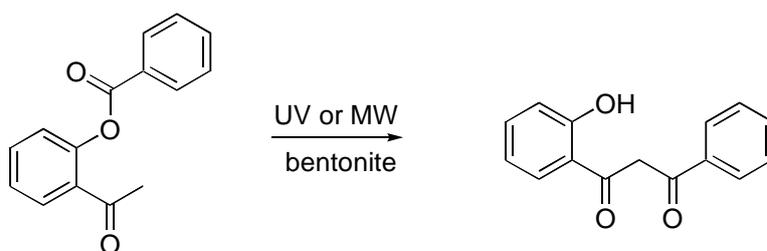
Klán, Literák et al. [91] succeeded in the evaluation of the MW superheating effects in polar solvents using a temperature dependent photochemical reaction. It is known that quantum efficiencies of the Norrish type II reaction [103] of a mixture of some *p*-substituted valerophenones depend on the presence of a weak base, thanks to specific hydrogen bonding to the biradical OH group (**BR**; Scheme 14.1) [88,89]. This reaction provided a linear temperature dependence of the efficiencies over a broad temperature region and the system served as a photochemical thermometer at the molecular level, even for the MW-heated mixtures. The magnitude of the photochemical change in the MW field suggested the existence of superheating effect (4-11 °C) for three aliphatic alcohols and acetonitrile. The results were in a perfect agreement with the measurements using a fiber-optic thermometer.

Chemat and his collaborators [92] reported on the UV- and MW-induced rearrangement of 2-benzoyloxyacetophenone in the presence of bentonite into 1-(*o*-hydroxyphenyl)-3-phenylpropane-1,3-dione in methanol at atmospheric pressure (Scheme 14.2). The reaction, performed in a reactor shown in Fig. 14.7, displayed a significant activation effect under simultaneous UV and MW irradiation, which corresponded at least to the sum of the individual effects (Fig. 14.11). The rearrangement, however, was not studied in further details. Such competitive processes can be described by the scheme in Fig. 14.9; in case that the product obtained from both types of activation is the same.
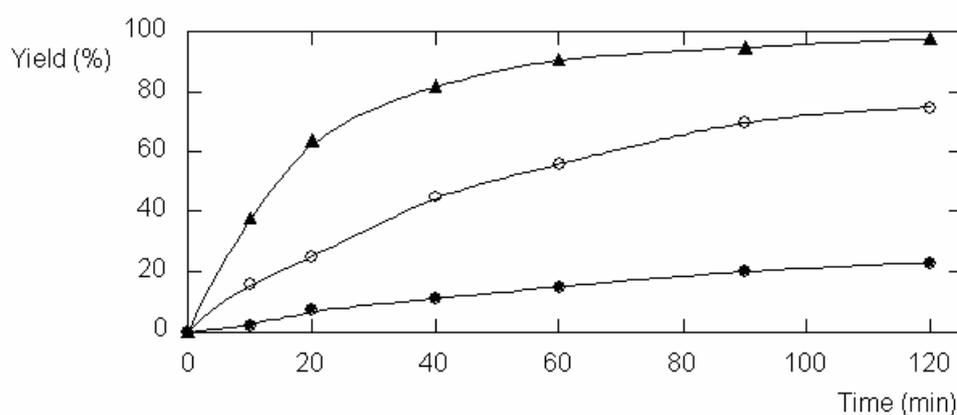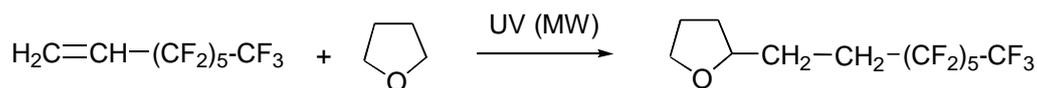


**Fig. 14.11** Reaction yields in the rearrangement of 2-benzoyloxyacetophenone induced by microwave heating (●), ultraviolet irradiation (○), or simultaneous UV and MW irradiation (▲). Adapted from [92].

Církva and Hájek [87] studied a photochemically or microwave-induced addition of tetrahydrofuran to perfluorohexylethene (Scheme 14.3). While the thermal reaction was too slow, photochemical activation was very efficient. No apparent thermal effects of MW radiation were observed. The combined UV/MW radiation has been principally used in order to initiate EDL operation in the reaction mixture (Fig. 14.5). Another illustration of the MW-UV-assisted reaction has been demonstrated by Nüchter et al. [1] on dehydrodimerization reactions of some hydrocarbons. Zheng et al. [104,105] reported on a microwave-assisted heterogeneous photocatalytic oxidation of ethylene using porous $TiO_2$ and $SO_4^{2-}/TiO_2$ catalysts. A significant enhancement of the photocatalytic activity was attributed to the polarization effect of the highly defected catalysts in the MW field.

H$_2$C=CH−(CF$_2$)$_5$-CF$_3$  +  [tetrahydrofuran, O]  →[UV (MW)]  [tetrahydrofuranyl, O]−CH$_2$−CH$_2$−(CF$_2$)$_5$-CF$_3$

**Scheme 14.3**

Product distributions and reaction conversions of several different photochemical systems, irradiated by conventional UV source as well as by EDL in a MW-UV reactor (Fig. 14.5), were compared in order to elucidate the advantages and disadvantages of microwave photochemical reactor [90]. Some reactions, such as photolysis of phenacyl benzoate in the presence of triethylamine or photoreduction of acetophenone by 2-propanol, showed a moderate enhancement by MW heating. On the other hand, photosubstitution reaction of chlorobenzene in methanol exhibited a dramatic increase in efficiency with increasing reaction temperature.

## 14.4.3 Non-thermal microwave effects: the intersystem crossing in radical recombination reactions

Radical pairs and biradicals are extremely common intermediates in many organic photochemical (or some thermal) reactions. A singlet state intermediate is formed from the singlet excited state in reactions that conserve spin angular momentum, while the triplet intermediate is obtained *via* the triplet excited state. Radical pairs in solution coherently fluctuate between singlet and triplet electronic states [106,107] and the recombination reactions are often controlled by electron-nuclear hyperfine interactions (HFI) on a nanosecond time scale [108,109]. Only a pair of the neutral radicals with the singlet multiplicity recombines. A triplet pair intersystem cross into the singlet pair or the radicals escape the solvent cage and react independently at some later stage (Fig. 14.12) [110]. The increasing efficiency of the triplet-to-singlet interconversion ('mixing' of states) leads to a more rapid recombination reaction and *vice versa*. It is now well established that *static* magnetic field can influence the intersystem crossing in biradicals (magnetic field effect, MFE) and the effect has been successfully interpreted in terms of the radical pair mechanism [111,112]. This concept offered explanations of nuclear and electronic spin polarization phenomena during chemical reactions, such as chemically induced dynamic nuclear polarization (CIDNP) or reaction yield detected magnetic resonance (RYDMAR).
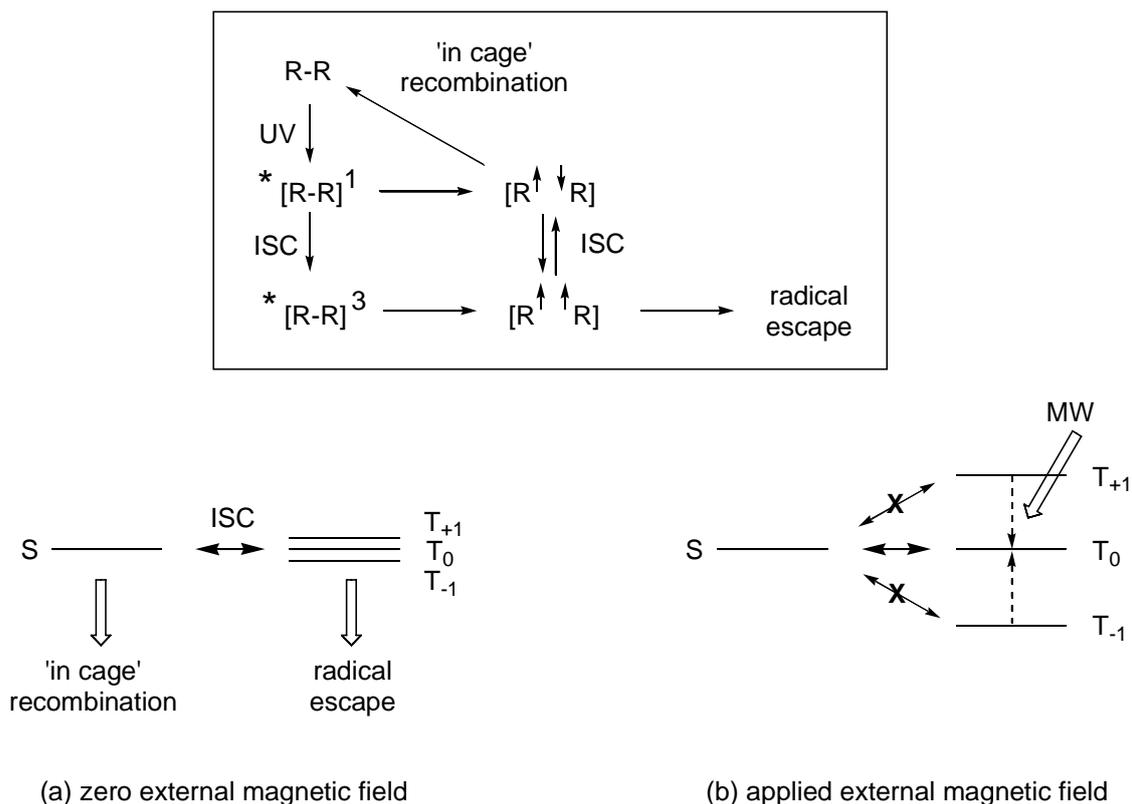
**Fig. 14.12** Schematic illustration of magnetic field and microwave effects in the radical pair chemistry.

An external magnetic field that is stronger than the hyperfine couplings inhibits (due to the Zeeman splitting) the singlet-triplet interconversions by isolating the triplets $T_{+1}$ and $T_{-1}$ from the singlet (S) which can therefore mix only with $T_0$ (Fig. 14.12 a, b). For the *triplet-born pair*, the magnetic field decreases the radical recombination probability. The microwave field, which is in resonance with the energy gaps between the triplet levels ($T_{+1}$ or $T_{-1}$) and $T_0$, transfers the excessive population from the $T_{+1}$ or $T_{-1}$ states back to a mixed state. Application of a strong magnetic field on the *singlet-born radical* pair leads to an increase of the recombination probability that can, however, be also controlled by microwave irradiation [112].

This microwave-induced spin dynamics can be considered as an archetype of a *non-thermal* MW effect. Since the radical pair (biradical) is usually created by a photochemical pathway, the topic certainly deserves to be included into the field of microwave photochemistry. The literature offers many examples that go across photobiology, photochemistry, as well as photophysics. Wasielewski et al. [113], for instance, showed that the duration of photosynthetic charge separation could be controlled with microwave radiation. Moreover, it was possible to observe the dynamics of the radical pair processes that involve the primary bacterial photochemistry [114]. Okazaki and his collaborators [115] reported on a possibility to control chemical reactions by inducing the ESR transition of the intermediate radical pair in the photoreduction of anthraquinone micellar solution under an external magnetic field and simultaneous MW irradiation. A similar study with a bifunctional molecule was reported by Mukai et al. [116]. The research in this field is very well covered by

several reviews and books [111,112,117,118]. Weak static magnetic fields, smaller than an average hyperfine coupling, also influence radical pair recombination yields [119,120]. This effect is opposite to the effect of a strong field [121,122].

Little attention has been devoted to the effects of *time-dependent* magnetic fields (created by electromagnetic waves) in the absence of a strong magnetic field. Hore and his coworkers [123-125] recently described this effect as the *oscillating magnetic field effect* (OMFE) on the fluorescence of an exciplex formed in the photochemical reaction of anthracene with 1,3-dicyanobenzene over the frequency range 1-80 MHz. Another study of the electron-hole recombination of radical ion (pyrene anion and dimethylaniline cation) pairs in solution appeared just recently [126]. The triplet-singlet interconversions due to HFI are relatively efficient in the zero applied magnetic field (to be more precise, in the Earth's field of ~50 μT). All the states are almost degenerate provided that the separation of radicals is large enough that their electronic exchange interaction is negligible [111]. Jackson and his coworkers [127] suggested that the resonance energy of the oscillating field should be tuned to the HFI in one of the radicals. With a typical value of HFI in the radicals 0.1-3.0 mT, oscillating magnetic field effect, enhancing the conversion of the singlet states to triplet (as was observed for weak static fields), is expected in the *radiofrequency* region (3-80 MHz) [124]. Canfield et al. [128-130] calculated the effects and proved them experimentally on the radical pairs involved in coenzyme $B_{12}$-dependent enzyme systems. Other theoretical studies appeared in the past 5 years [126,131,132]. There is still an open question if electromagnetic fields influence animal and human physiology. It has been, for instance, suggested that radiofrequency fields may disorient birds [133]. There are no detailed experimental studies of OMFE in the microwave region yet. Hoff and Cornelissen [134] reasoned in their paper that triplet state kinetics could be affected rather by a pulse of resonant microwaves than by equilibrium methods in the zero static field.
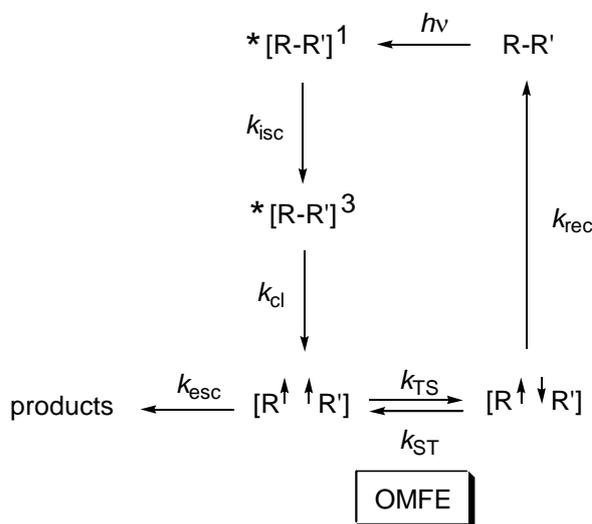


**Fig. 14.13** The oscillating magnetic field effect (OMFE) in the triplet state radical pair reaction.

According to the OMFE model, a weak oscillating magnetic field (the magnetic interactions are much smaller than the thermal energy of the molecule [131]) has no impact on equilibrium constants or activation energies, however, it can have an immense *kinetic* control over the reaction of the radicals [131]. A simplified kinetic scheme in Fig. 14.13 shows the

excitation of a starting material R-R' into the singlet state, which intersystem crosses to the triplet ($k_{isc}$) and is followed by the cleavage ($k_{cl}$) to the triplet radical pair. Oscillating magnetic field influences the state mixing of the radical pair ($k_{TS}$ and $k_{ST}$). The probability that the triplet radical pair will form the products is given by the efficiency of the radical escape from the solvent cage ($k_{esc}$) and the triplet-to-singlet intersystem crossing ($k_{TS}$). The recombination reaction is very fast when the tight radical pair reaches the singlet state.

### 14.4.4 Analytical and environmental applications of microwave photochemistry

In addition to analytical applications, in which microwaves serve as a power source for the electrodeless discharge lamps, there are first successful attempts to use combined MW/UV irradiation for an efficient degradation of various samples prior to application of a subsequent analytical method. Florian and Knapp [44] proposed a novel MW-UV, high-temperature - high-pressure, digestion procedure for the decomposition of interfering dissolved organic carbon as a part of the trace element analysis of industrial and municipal wastewater or other liquid samples. Very efficient and fast mineralization was obtained in an original reactor (Fig. 14.8) due to a very high temperature (250-280 °C). Furthermore, a high temperature also enabled dissolution of solid organic matrixes using diluted mineral acids. A Cd low-pressure electrodeless discharge microwave lamp, strongly emitting at $\lambda = 228$ nm, guaranteed even more efficient degradation than standard mercury UV lamps. The pressurized sealed vessel did not require a separate cooling device to prevent sample evaporation. Besides, an efficient decomposition of organophosphate compounds with the aim of the colorimetric phosphate determination has been applied in a novel beaker shaped electrodeless MW-UV lamp by Howard et al. [94]. Although no details of the organophosphate decomposition mechanism have been presented, the authors reasoned about two possible pathways. In addition to a direct photodegradation reaction, much of the decomposition resulted from the photochemical generation of hydroxyl and oxygen radicals generated from dissolved $O_2$ in the samples. The concentration of OH radicals could be enhanced by the addition of hydrogen peroxide.

Photodegradation [135] or microwave thermolysis [136] of pollutants and toxic agents in waste water are two important methods for their removal, often in combination with a solid catalyst (e.g. $TiO_2$). Therefore, it is expected that a combined MW-UV effect will be even more efficient. Results from the first environmentally relevant studies already appeared in the scientific literature and the topic is also covered by several patents [79,83-85]. Campanella et al. [137] reported on minor but positive enhancements of the photodegradation efficiency of *o*- and *p*-chlorophenol aqueous solutions by microwave heating. Those model chemical systems served for extension the application to other environmentally interesting compounds, such as sodium dodecylbenzenesulfonate or organophosphosphate pesticides. It was suggested that microwave-assisted photodegradation of pollutants may be of great interest in the future. Heterogeneous catalytic degradation of humic acid in aqueous titanium dioxide suspension under MW-UV conditions was studied by Chemat et al. [92]. An enhancement in this case was reported as substantial, i.e. higher than a simple addition of both effects. Zheng and his collaborators [105] investigated the microwave-assisted photocatalytic oxidation of ethylene and trichloroethylene in the presence of water. The reactions also served as a model study for photodegradation of organic pollutants in the microwave field.

# 14.5 Industrial applications

Simultaneous applications of UV and MW irradiation have found widespread use in industry. The techniques are based on the conventional UV lamps as well as MW-powered electrodeless lamp and MW device [28]. The following paragraphs discuss a number of patents and papers that describe industrial microwave photochemistry, such as photolithography, treatment of waste water, sterilization, or industrial photoinduced organic synthesis.

*Photolithography* is a technique for manufacturing of the semiconductor devices (i.e. transistors or integrated circuits). In the process, a pattern of an optical mask is imaged with UV radiation onto a semiconductor wafer coated with a UV-sensitive photoresist. The main goal is to reduce the size of the components and to increase their densities. An application of shorter wavelengths (190-260 nm) results in a greater depth of the focus, i.e. in a sharper printing. The first EDLs applied were made from the material known as commercial water-containing natural quartz [138]. It was found that the transmission of the envelope at vacuum UV wavelengths falls off sharply with time. The lamps developed later from water-free quartz [50] provided a much better transparency. Excimer lamps used for photoetching and microstructuring of the polymer surface have been developed for applications in standard MW ovens [65].

A *photochemical* apparatus for generating superoxide radicals ($O_2^{\bullet-}$) in an oxygen-saturated sodium formate aqueous solution by means of EDL has been described [139]. An interesting method of initiating and promoting chemical processes by irradiation of starting gaseous materials in the EM field under a lower pressure has been proposed by Lautenschläger [79]. EDLs (containing $GaI_3$, $InI_3$, $AlI_3$) with a "blue" output are now often used for dental purposes or curing the polymers. A very small size of the lamps makes it particularly useful in supplying light to an optical fiber or a light pipe [140]. Another example of microwave photochemical treatment of solutions at various wavelengths has been described by Moruzzi [141]. Photooxidation of humic acids caused changes in their absorption and luminescence properties that might be of a great importance for environmental photophysics and photochemistry [142]. Aqueous aerated alkaline solutions of the acids were irradiated with Hg-EDLs in a flow system and analyzed by means of fluorescence, absorption and chemiluminescence techniques.

Microwave photochemistry is generally quite advantageous for removal of a toxic material or pathogens from *wastewater*. Photochemical oxidation is a process in which a strong oxidizing reagent (ozone or hydrogen peroxide) is added to water in an UV-ionizing reactor resulting in generation of highly reactive hydroxyl radicals ($OH^{\bullet}$). The first generation techniques used commercial EDLs (high pressure Hg-Xe lamps) immersed in the water tanks. However, lamps rapidly deteriorated what caused a low production of hydroxyl radicals. The second generation technique incorporated manual cleaning mechanisms and a use of the polymer coating (PTFE) on the quartz sleeve, additional oxidizers (ozone), and catalyzing additives ($TiO_2$) to enhance the rate of the OH radical production [143]. A novel UV-oxidation system used a highly efficient EDL combined with a simple coaxial flow-through reactor design [85]. In this reactor, a liquid containing contaminants (MTBE, 2-propanol, or phenol) was pumped from the bottom and flowed vertically upward through the reactor vessel against gravity. The mercury UV source was mounted above the reactor vessel and the radiation was directed downward through the reactor vessel. A $H_2O_2$ solution was injected into the liquid being treated and thoroughly mixed by an in-line mixer just before the mixture entered the reactor vessel.

The *sterilization* techniques for the intermittent or continuous destruction of pathogens in solid films or in organic and biological fluids, without significantly affecting the properties

or physiological characteristics of the medium, are based on the biocidal synergism of UV and MW irradiation. UV radiation induces a chemical modification of DNA in bacteria (usually due to thymine dimerization). The first apparatus involved a commercial UV emitting lamp with a separate power source inside the chamber of a MW oven and was used for simple sterilization of biological fluids [144]. An apparatus using EDL (Hg-Ar) for surface sterilizing or disinfecting objects, such as bottles, nipples, contact lenses, or food, has been proposed by LeVay [81]. A continuous sterilizing apparatus are also described [145,146]. In addition, ozone treatment may be used in combination with UV exposure to sanitize or disinfect various substances [80,82,147-149]. Another application of EDLs (containing Hg, Cd/Ar or Kr) of water-solution disinfecting has been recently showed by Michael [150].

# 14.6 Concluding remarks

The understanding, at the molecular scale, of the relevant processes implied in the microwave photochemistry has not reached the degree of maturity of other topics in chemistry yet. Such a challenge is somewhat ambitious due to the several difficulties. Although some obstacles have been overcome, the study of a microwave effect on a photochemical reaction requires a special approach. Microwave photochemistry involves highly reactive, electronically excited molecules which are exposed by a different kind of the reactivity-enhancing stimulation. Microwave heating strongly interferes with possible non-thermal effects that cannot be easily separated. One of the solutions seems to be investigations of the spin dynamics of photochemically generated biradicals. On the other hand, many photochemical reactions might be accelerated by MW treatment if undergo through polar transition states and intermediates, such as ion or ion-radical pairs. An application of EDL simplifies the technical procedure, especially in the field of organic synthesis, environmental chemistry or analysis. However, thanks to a lower reproducibility of the experimental results an external UV source would serve better in the mechanistic studies.

Through this review we have demonstrated how the concept of microwave photochemistry already became an important issue in chemistry. Although still in the beginning, a detailed analysis of past and present literature confirms explicitly the usefulness of this way of chemical activation. The field has been already established in the applied industry and we hope that it will find its way also into a conventional chemical laboratory.

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