

Microwaves in Organic Synthesis

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19 Microwaves in Photochemistry

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19.1 Introduction

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

Microwave (MW) energy is a nonclassical energy source, with ultrasound, high pressure, mechanical activation, or plasma discharge. Since first reports of the use of MW heating to accelerate organic chemical transformations [1, 2], numerous articles have been published on the subject of microwave-assisted synthesis and related topics – microwave chemistry has certainly become an important field of modern organic chemistry [3–14]. Microwave activation increases the efficiency of many chemical processes and can simultaneously reduce formation of the byproducts obtained from conventionally heated reactions. Chemical processes performed under the action of microwave radiation are believed to be affected in part by superheating, hot-spot formation, polarization, and spin alignment [6, 7, 12]. The existence of a specific nonthermal microwave effect in homogeneous reactions has been a matter of controversy in recent years [10, 13, 15–18].

Microwave heating has already been used in combination with other unconventional activation processes. Such combinations might have a synergic effect on reaction efficiencies or, at least, enhance them by summing the individual effects. Application of MW radiation to ultrasound-assisted chemical processes has recently been described by some authors [19–21]. Mechanical activation has also been successfully combined with MW heating to increase the chemical yields of several reactions [22]. There have also been attempts to affect *photochemical* reactions by use of other sources of nonclassical activation, for example ultrasound [23, 24].

Combined chemical activation by use of two different types of electromagnetic radiation, microwave and ultraviolet–visible, is covered by the discipline described in this chapter. The energy of MW radiation is substantially lower than that of UV

radiation, certainly not sufficient to disrupt the bonds of common organic molecules. We therefore assume that, essentially, photoinitiation is responsible for a chemical change and MW radiation subsequently affects the course of the subsequent reaction. The objective of microwave-assisted photochemistry is frequently, but not necessarily, connected with the *electrodeless discharge lamp* (EDL) which generates UV radiation when placed in the MW field.

This chapter gives a complete picture of our current knowledge of microwave-assisted photochemistry and contains recent and updated information not included in the preceding edition [25]. It provides the necessary theoretical background and some details about synthetic and other applications, the technique itself, and safety precautions. Although microwave-assisted photochemistry is a newly developing discipline of chemistry, recent advances suggest it has a promising future.

19.2 Ultraviolet Discharge in Electrodeless Lamps

The electrodeless discharge lamp (EDL) [26] consists of a glass tube (“envelope”) filled with an inert gas and an excitable substance and sealed under a lower pressure of a noble gas. A low frequency electromagnetic field (radiofrequency or MW, 300–3000 MHz) can trigger gas discharge causing emission of electromagnetic radiation. This phenomenon has been studied for many years [27] and was already well understood in the nineteen-sixties [28]. The term “electrodeless” means the lamps lack electrodes within the envelope. Meggers [28] developed the first EDL using the mercury isotope ^{198}Hg in 1942 (Fig. 19.1); its earliest application was in absorption spectroscopy [29]. EDL are usually characterized by higher emission intensity than cathode lamps, lower contamination, because of the absence of the electrodes [30], and a longer lifetime [31]. The lamps have been used as light sources in a variety of applications, and in atomic spectrometers [32].

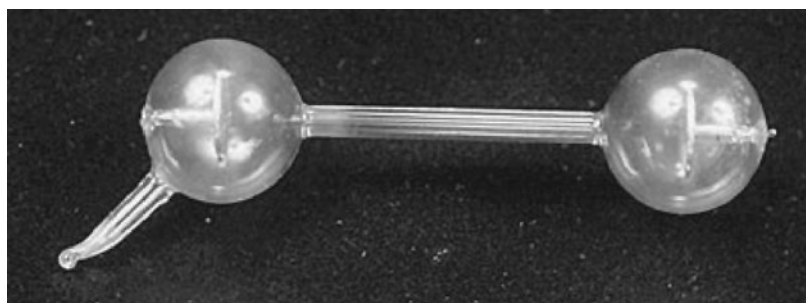


Fig. 19.1. The electrodeless mercury lamp made by William F. Meggers. With permission from the National Institute of Standards and Technology, Technology Administration, US Department of Commerce.

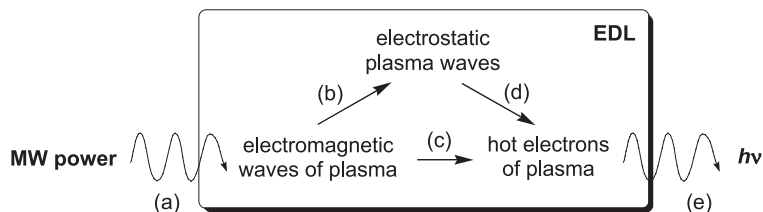


Fig. 19.2. Block diagram illustrating operation of the EDL: (a) energy flows from a MW source into the plasma chamber; (b) collisional or collisionless transformation; (c) normal or nonlinear wave absorption; (d) collisional or collisionless dumping; (e) collisional excitation of atoms and ions followed by emission. Adapted from Ref. [33].

19.2.1

Theoretical Aspects of the Discharge in EDL

The theory of EDL operation, as it is currently understood, is shown in Figs. 19.2 [33] and 19.3 (an example of a mercury EDL, or Hg EDL). Free electrons in the fill (i.e. electrons that have become separated from the environment because of the ambient energy) accelerate as a result of the energy of the electromagnetic (EM) field. They collide with the gas atoms and ionize them to release more electrons. Repetition of this causes the number of electrons to increase significantly over a short period of time, an effect known as an “avalanche”. The electrons are gener-

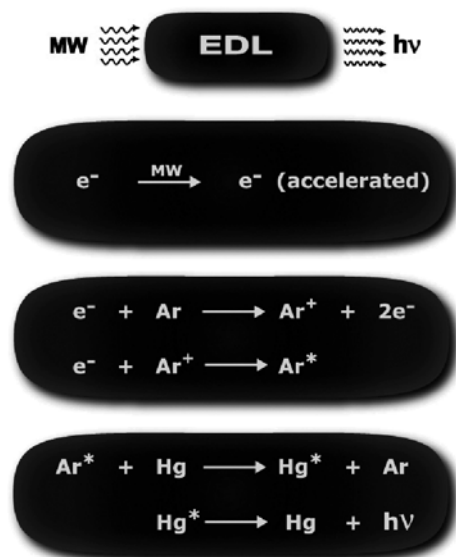


Fig. 19.3. The principle of operation of the mercury EDL and the emission of energy as UV–visible radiation.

ated by processes including *collisional* or *collisionless* transformation of EM waves, and *normal* or *nonlinear wave absorption* [30]. The energetic electrons collide with the heavy-atom particles present in the plasma, exciting them from the ground state to higher energy levels. The excitation energy is then released as EM radiation with spectral characteristics which depend on 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 IR [34].

19.2.2

The Fundamentals of EDL Construction and 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 is made of a scaled (usually quartz) tube envelope, which contains an inert gas (for example a noble gas) and an excitable substance (e.g., Hg, Cd, Na, Ga, In, Tl, Sc, S, Se, or Te) [35]. The envelope material must be impermeable to gases, an electrical insulator, and chemically resistant to the filling compounds at the temperature of operation.

Historically four basic methods have been used to excite discharges without electrodes [36–40]. In the first method, known 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 at a second external (coaxial) electrode. This discharge is similar to arc discharge in an electrode lamp, but needs a higher current. The second method of exciting EDL, with MW power (typically 2450 MHz), is to place the bulb in the path of radiation from a directional antenna. The *microwave discharge* is excited by both electric and magnetic components of the EM field. Because free propagation of the MW power occurs, however, emission is often inherently inefficient. This method is used for excitation of EDL inside a microwave oven. The third method is called the *traveling wave discharge* – a gap between the external electrodes provides the electric field that launches a surface wave discharge. The fourth method uses *inductive coupling* of the EDL, and the system can be compared with 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 approximately 50 kHz [41].

The construction of microwave-excited EDL is relatively straightforward but there are several operating conditions in their preparation which must be considered to produce an intense light source. The desired characteristics and requirements for EDL are high intensity, high stability, long lifetime, and, to a lesser extent, low cost and high versatility. In practice, it is very difficult to meet all these characteristics simultaneously.

The performance of EDL depends strongly on many preparation and operating conditions [35]:

- *The inert gas.* The arc chamber contains a buffer noble gas (usually Kr, Xe, or Ar) which is inert to the extent that it does not adversely affect the lamp operation.

Helium has higher thermal conductivity than other noble gases and, therefore, higher thermal conduction loss is observed [42]. The inert gas easily ionizes at low 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 requires a higher input power to establish the discharge. In general, the recommended pressure of the filling gas is between 0.266 and 2.66 kPa (2–20 Torr) at the operating temperature, which is usually much higher than that of a conventional electrode lamp. Use of argon was regarded as the best compromise between high EDL radiance and long lifetime. Air and nitrogen cannot be used because of their quenching properties in microwave plasmas, similar to water vapor.

- *Choice of fill material* initiating the discharge is very important. Together with a standard mercury fill it is often desirable to incorporate an additive in the fill material with a low ionization potential and sufficient vapor pressure (Cd, S, Se, Zn) [43, 44]. One category of low-ionization-potential materials is the group of alkali metals or their halides (LiI, NaI) but other elements, for example Al, Ga, In, or Tl [45, 46] or Be, Mg, Ca, Sr, La, Pr, or Nd [27, 42, 47], can be used. Other metal-containing compounds have been used to prepare EDL, including amalgams of Cd, Cu, Ag, and Zn. Multi-element EDL have been prepared using combinations of elements (e.g. Li–Na–K, As–Sb, Co–Ni, Cr–Mn, Bi–Hg–Se–Te, Cd–Zn, Ga–In, Se–Te) [48]. The spectral output from each individual element is very sensitive to temperature [49]. It has been found that no interelement interferences occur in the lamp.
- *Temperature of the lamp.* Operation at a high power or high temperatures can increase emission intensity but, at the same time, reduce the lamp lifetime and lead to broadening of the atomic line profile, because of self-absorption and self-reversal effects. It has been found that the optimum operating temperature for mercury filling is 42 °C (for the 254 nm line) [35]. The output is reduced when the temperature is beyond the optimum.
- *The dimensions and properties of the lamp envelope* are based on the discovery that the volume of Hg is critical for effective UV operation [50]. Higher Hg pressures result in the need to use higher microwave power levels. To focus the MW field efficiently into the EDL, a special Cd low-pressure lamp with a metal antenna (a molybdenum foil) was developed for experiments in MW-absorbing liquids [51]. The envelope material must be impermeable to gases, an electrical insulator, and chemically resistant to the filling compounds at the temperature of operation. High quality quartz is the most widely used lamp envelope material but early manufacturers of EDL used glass, Vycor, or Pyrex [52].
- *The nature and characteristics of the EM energy-coupling device* are discussed in Section 19.2.2. For coupling of the MW energy to EDL, cavities (e.g. Broida-type or Evenson-type) and antennas (Raytheon) have been used. Optimum conditions for a lamp operation in one type of a MW cavity will by no means be optimum for operation in a different cavity, however. The results obtained in one MW oven will not, therefore, necessarily be the same as those from other tested cavities.
- *The frequency and intensity* of EM energy is determined by the type of a device.

Microwave energy is widely used for excitation of EDL because it is usually more efficient than radiofrequency energy for generation of intense light. Microwave radiation for excitation of gas discharges is usually generated by use of a fixed-frequency (2.45 GHz) magnetron oscillator.

19.2.3

EDL Manufacture and Performance Testing

Although general procedures of EDL manufacture are available in the literature [52–57], many minor details critical for proper lamp function are often omitted. The investigator who wants to make an EDL is thus faced with a very large amount of information dispersed in the literature and finds it very difficult to reproduce these procedures to develop EDL with the properties desired. An experimental vacuum system for EDL (Hg, HgI₂, Cd, I₂, KI, P, Se, S) manufacture has recently been designed by Církva and coworkers (Fig. 19.4) [58]. The technique is very simple and enables the preparation of EDL in a conventional chemistry laboratory. Examples of EDL are shown in Fig. 19.5. EDL performance is tested to prepare the lamps for spectral measurements [58]. A typical experimental system for such testing comprises a round-bottomed flask, placed in a MW oven, containing *n*-heptane and equipped with fiber-optic temperature measurement, a spectral probe, and a Dimroth condenser (Fig. 19.6).

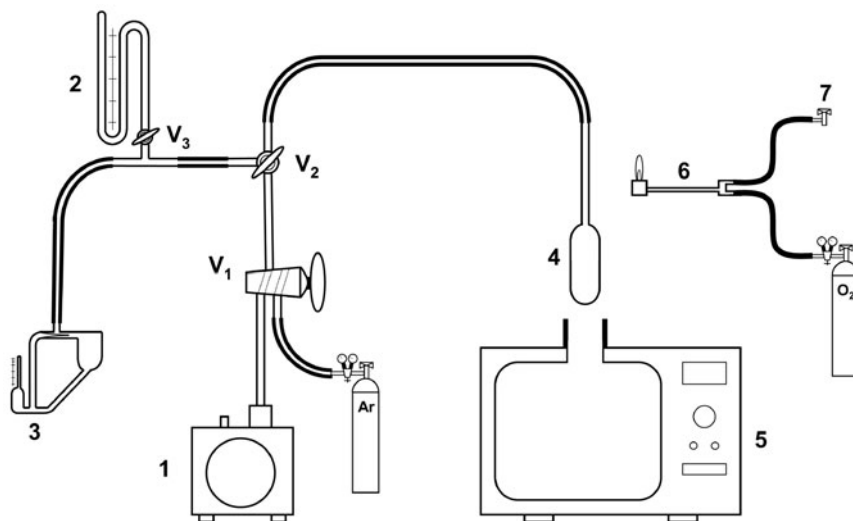


Fig. 19.4. A vacuum system for manufacture of EDL. 1, rotary vacuum pump; 2, mercury manometer; 3, tilting-type McLeod pressure gauge; 4, EDL blank; 5, modified microwave oven; 6, glass-working burner; 7, natural gas; V₁–V₃ are stopcocks. Adapted from Ref. [58].

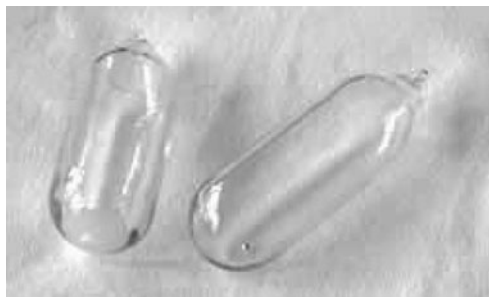


Fig. 19.5. Hg and S EDL for photochemical applications.

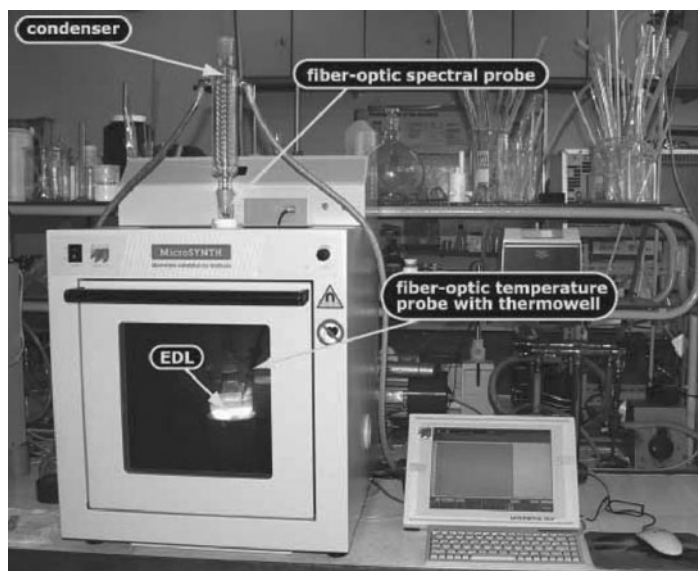


Fig. 19.6. Testing EDL performance in a Milestone MicroSYNTH Labstation.

19.2.4

Spectral Characteristics of EDL

The spectral characteristics of EDL are of general interest in microwave-assisted photochemistry experiments. The right choice of EDL envelope and fill material can be very useful in planning an efficient course of the photochemical process without the need to filter out the undesirable part of the UV radiation by use of other tools, for example glass or solution filters or monochromators [59, 60].

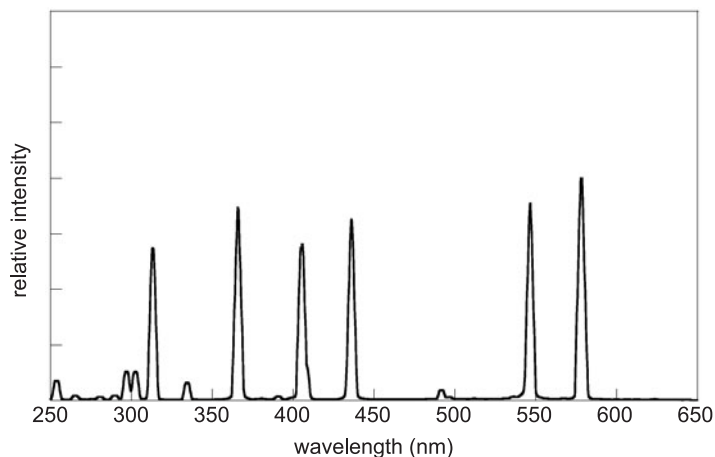


Fig. 19.7. The emission spectrum of an Hg EDL in *n*-decane (quartz envelope; argon atmosphere). With permission from Elsevier Science [60].

Whereas atomic fills usually furnish line emission spectra, molecular fills give continuous emission bands [61]. The total emission output of the most common lamp – the mercury EDL (Hg EDL) – in the region 200–600 nm is approximately the same as that of the electrode lamp with the same power input [62]. The distribution of the radiation is, however, markedly different, as a result of much higher Hg pressure and the greater number of atoms present in the plasma. EDL emit over three times as much UV and over a half as much IR as a conventional lamp [63]. It has been noted that EDL and electrode lamps provide different spectra when the fill contains a rare-earth material but similar spectra when a non-rare-earth fills are used [64]. Addition of material had very substantial effects on the spectral distributions of EDL [62].

Müller, Klán, and Církva have reported the emission characteristics of a variety of EDL containing different fill materials (for example Hg, HgI₂, Cd, I₂, KI, P, Se, or S) in the region 250–650 nm [60]. Whereas distinct line emission peaks were obtained for the mercury (Fig. 19.7), cadmium, and phosphorus (Fig. 19.8) fills, the iodine, selenium, and sulfur-containing EDL (Fig. 19.9) emitted continuous bands. Sulfur-containing EDL have been proposed for assisting phototransformations of environmental interest, because the emission flux is comparable with that of solar radiation. In addition, the EDL spectra could easily be modified by the choosing a suitable EDL envelope glass material, temperature, MW output power, or solvent, according to the needs of a photochemical experiment [59]. The relative intensities of the individual emission peaks in Hg EDL were found to be very dependent on temperature (35–174 °C); the short-wavelength bands (254 nm) were suppressed with increasing temperature (in decane). The emission spectra of quartz and Pyrex

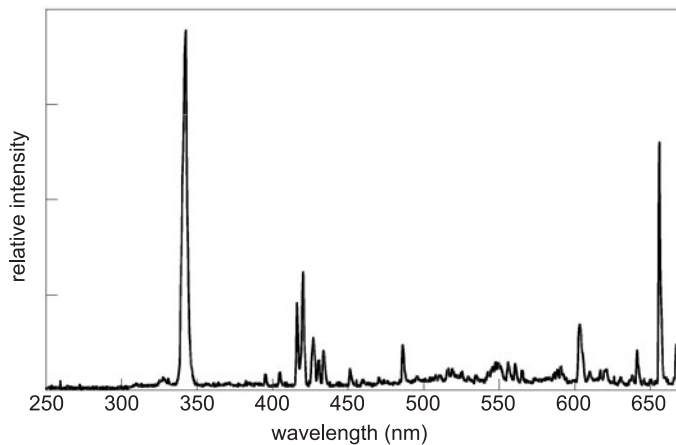


Fig. 19.8. The emission spectrum of a P EDL in *n*-decane (Pyrex envelope; argon atmosphere). With permission from Elsevier Science [60].

Hg EDL in *n*-hexane are compared in Fig. 19.10 (Pyrex absorbs most of the UV radiation below 290 nm). Most lamps emitted less efficiently below 280 nm than a standard Hg lamp. Table 19.1 summarizes characteristics, reported in the literature, of EDL filled with a variety of compounds.

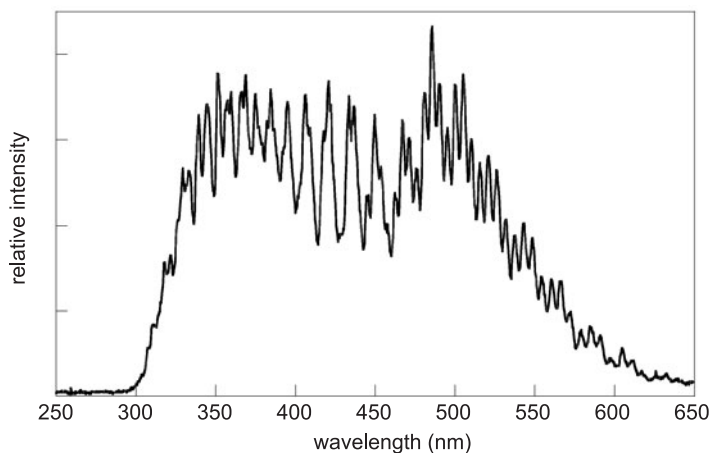


Fig. 19.9. The emission spectrum of an S EDL (quartz envelope; argon atmosphere). With permission from Elsevier Science [60].

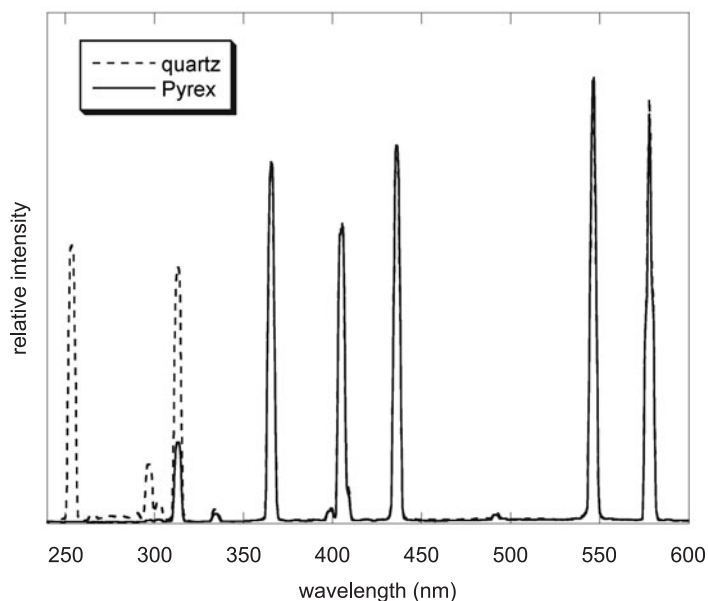


Fig. 19.10. The emission spectrum of a quartz and Pyrex Hg EDL. With permission from Elsevier Science [59].

19.3

Photochemical Reactor and Microwaves

The photochemical reactor used for microwave-assisted experiments is an essential tool for experimental work. Such equipment enables simultaneous irradiation of the sample with both MW and UV-visible radiation. The idea of using an electrodeless lamp, in which the discharge is powered by the MW field, for photochemistry was born half a century ago [53, 62]. 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 with the construction of a high-intensity source of UV radiation for atomic fluorescence flame spectrometry [88–90].

Gunning, Pertel, and their coworkers reported the photochemical separation of mercury isotopes [92–95] in a flow reactor which consisted of a microwave-operated discharge lamp [52, 96] cooled by a flowing film of water. A filter cell and a circulation system, to prevent heating of the filter solution and the cell, were placed concentrically and coaxially with the lamp. A similar reactor, for small-scale laboratory photolysis of organic compounds in the solution or gas phase, has been proposed by Den Besten and Tracy [91]. In this arrangement the EDL was placed in a reaction solution and was operated by means of an external microwave field from a radio or microwave-frequency transmitter (Fig. 19.11). The quantum output of the lamp was controlled by changing the output of the trans-

Tab. 19.1. Filling compounds and wavelengths of EDL emission.

Filling material (filling gas)	Excited species	Main emission bands, λ [nm]	Refs
Hg (Ar)	Hg	185, 254, 297, 313, 365, 405, 436, 546, 577, 579	35, 36, 50, 51, 60, 64–66
Cd (Ar)	Cd	229, 327, 347, 361, 468, 480, 509, 644	35, 51, 60, 67
SnI ₂ (Ar)	SnI ₂	400–850, 610	68, 69
SnBr ₂ (Ar)	SnBr ₂	400–850	70
BiI ₃ (Ar)	BiI ₃	300–750	71
FeCl ₂ (Ar)	Fe	248, 272, 358, 372–376	35
Zn (Ar)	Zn	214, 330, 468	35, 51, 72
CuCl (Ar)	Cu	325, 327	35
NaI (Xe, Kr)	Na	589	73, 74
Mg, H ₂ (Ar)	MgH	518, 521, 480–560	75
AlBr ₃ (Ne)	AlBr	278	76
AlCl ₃ (Ne)	AlCl	261	77, 78
Ga, GaI ₃ (Ar)	Ga	403, 417, 380–450	65, 72
InI ₃ (Ar)	In	410, 451	72
TlI (Ar)	Tl	277, 352, 378, 535	35, 72
P (Ar)	P	325, 327, 343	60
PCL ₄ (Kr)	P ₂	380	79
S (Ar)	S	320–850, 525	45, 60, 80–82
Se (Ar, Xe)	Se	370–850, 545	60, 81–84
Te (Xe)	Te	390–850, 565	81, 82, 84
Ar (Ar)	Ar ₂	126, 107–165, 812	34, 85
Ar, Cl ₂ (Ar)	ArCl	175	34, 85
Xe, Cl ₂ (Xe)	XeCl	308	34, 85
B ₂ O ₃ , S (Kr)	B ₂ S ₃	812	86
I ₂ (Ar)	I ₂	342	60
I ₂ , HgI ₂ (Ar)	I	183, 206	87

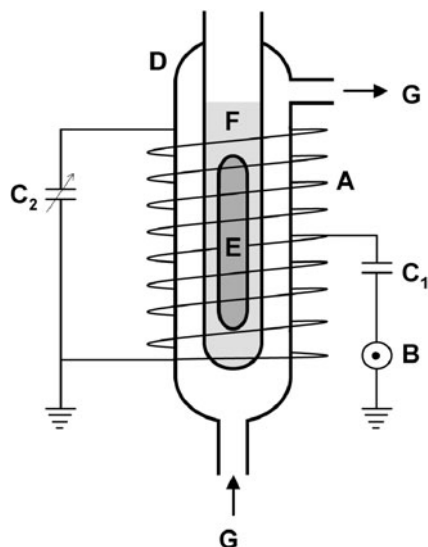


Fig. 19.11. Apparatus for electrodeless UV irradiation. A, antenna; B, transmitter; C₁, capacitor; C₂, variable capacitor; D, jacketed flask; E, EDL; F, reaction mixture; G, circulating coolant. Adapted from Ref. [91].

mitter 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 in the solution was quite advantageous, because the full quantum output was used. The authors recommended keeping the sample temperature lower, because EDL produce a substantial amount of heat.

The use of a domestic microwave oven appeared in a patent [97], according to which gaseous reactants were irradiated with microwave and UV-visible radiation to produce desired photoproducts (the EDL was positioned inside the MW cavity, although outside the reaction vessel). Several similar reactors have been proposed for UV sterilization [98–100] or for treatment of waste water containing organic pollutants [101–103].

Čírkva and Hájek have proposed a simple application of a domestic microwave oven for microwave-assisted photochemistry experiments [105]. In this arrangement the EDL (the MW-powered lamp for this application was specified as a microwave lamp or MWL) was placed in a reaction vessel located in the cavity of an oven. The MW field generated a UV discharge inside the lamp that resulted in simultaneous UV and MW irradiation of the sample. This arrangement provided the unique possibility of studying photochemical reactions under extreme thermal conditions [106].

Klán, Literák, and coworkers published a series of papers that described the scope and limitations of this reactor [104, 107–109]. In a typical design (Figs. 19.12 and 19.13), four holes were drilled into the walls of a domestic oven – one

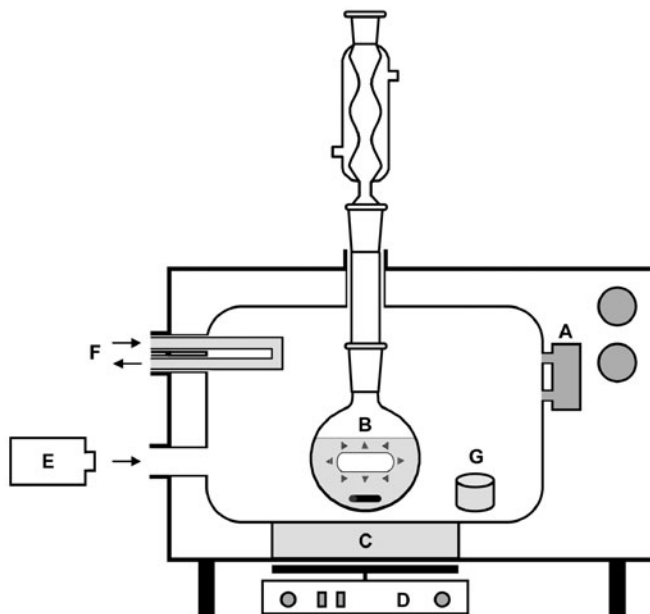


Fig. 19.12. A modified MW oven for microwave-assisted photochemistry experiments. A, magnetron; B, reaction mixture with EDL and magnetic stir bar; C, aluminum plate; D, magnetic stirrer; E, infrared pyrometer; F, circulating water in a glass tube, G, dummy load inside the oven cavity. With permission from Elsevier Science [104].



Fig. 19.13. Photochemistry in a microwave oven (the EDL floats on the liquid surface).

Tab. 19.2. Advantages and disadvantages of EDL applications in photochemistry. Adapted from Ref. [108].

Advantages

Simultaneous UV and MW irradiation of the sample
 Possibility of performing photochemistry at high temperatures
 Good photochemical efficiency – the EDL is “inside” the sample
 Simplicity of the experimental arrangement and a low cost of the EDL
 Easy method of EDL preparation in the laboratory
 Use of a commercially available microwave oven
 “Wireless” EDL operation
 Choice of the EDL material might modify its spectral output

Disadvantages

Technical difficulties of performing experiments at temperatures below the solvent b.p.
 Greater safety precautions
 EDL overheating causes lamp emission failure
 Polar solvents absorb MW radiation, thus reducing the UV output efficiency of the EDL

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. Part of the oven bottom was replaced with an aluminum plate to enable magnetic stirring. The opening for the 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 means of a long glass tube. The circulating cool water or different amounts of a MW-absorbing solid material (dummy load – basic Al_2O_3 , molecular sieve, etc.) were used when a small quantity of a nonabsorbing or poorly absorbing sample was used. This material removed excess microwave power and prevented the magnetron from being destroyed by overheating. The EDL had always to be placed in a position in which the solvent cooled it efficiently, because lamp overheating might cause failure of lamp emission. Intense IR output from the lamp triggered immediate boiling of all solvents including nonpolar (MW-transparent) liquids [107, 108]. Polar solvents, on the other hand, absorbed most of MW radiation, resulting in reduced UV output efficiency. Table 19.2 depicts the most important advantages and disadvantages of EDL applications.

Chemat and his coworkers [110] have proposed an innovative combined MW–UV reactor (Fig. 19.14) based on a commercially available MW reactor, the Synthe-wave 402 (Prolabo) [8]. This is 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 mechanically stirred and its temperature was monitored by means of an IR pyrometer. The reaction systems were irradiated by means of an external source of UV radiation (a 240-W medium-pressure mercury lamp).

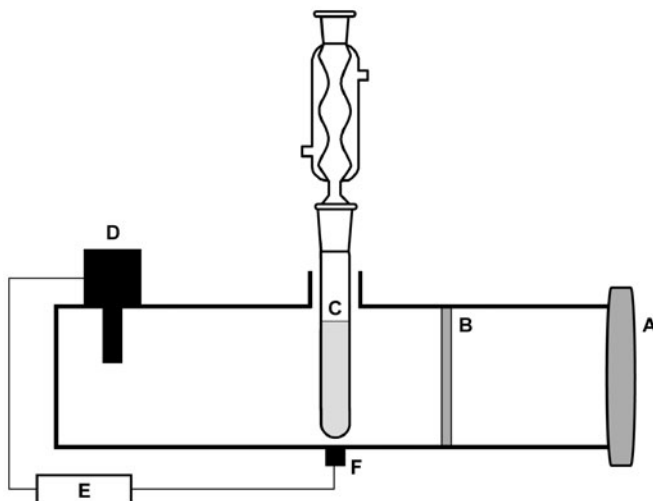


Fig. 19.14. Reactor for microwave-assisted photochemistry based on the Synthrowave 402 (Prolabo). A, medium-pressure Hg lamp; B, window opaque to MW radiation; C, reaction mixture; D, magnetron; E, regulator; F, IR sensor. Adapted from Ref. [110].

Similar photochemical applications in a Synthrowave reactor using either an external or an internal UV source have been reported by Louerat and Loupy [111].

A microwave-assisted, high-temperature, and high-pressure UV digestion reactor has been developed by Florian and Knapp [51] for analytical purposes. The apparatus contained an immersed electrodeless discharge lamp operating as a result of the MW field in the oven cavity (Fig. 19.15). An antenna, fixed to the top of the EDL enhanced the EDL excitation efficiency. Another interesting MW–UV reactor has been designed by Howard and his coworkers [112]. A beaker-shaped electrodeless discharge lamp, placed in a modified domestic MW oven has been used for mineralization of organophosphate compounds. The samples in quartz tubes were positioned in a carousel inside an open UV beaker; they were thus efficiently photolyzed from the whole surface of the beaker.

Microwave irradiation has also been used for heterogeneous photocatalytic oxidation of solutions of a variety of organic compounds in aqueous TiO_2 dispersions [113, 114] or ethylene in the gas phase using a TiO_2 – ZrO_2 mixed oxide [115]. The microwave photocatalytic reactors consisted either of an external UV source irradiating the sample placed inside the MW cavity [114–117], in a manner similar to that shown in Fig. 19.14, or of EDL in the cavity and powered by microwaves [115, 118]. Horikoshi, Hidaka, and Serpone have proposed a flow-through quartz photoreactor for photocatalytic remediation of aqueous solutions (Fig. 19.16) under the action of irradiation from a 1.5-kW microwave generator [119–121]. The incident and reflected MW radiation was determined and the circulating dispersion

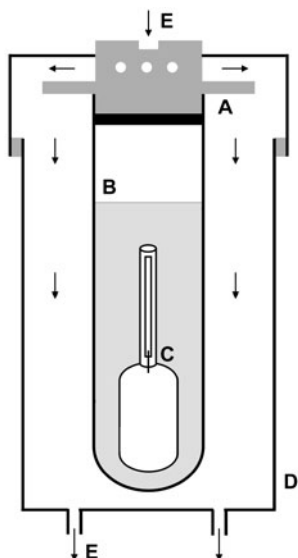


Fig. 19.15. Simplified schematic diagram of a high-pressure digestion vessel with EDL. A, plug and seal; B, quartz pressure reaction vessel with a sample solution; C, EDL with an antenna; D, PEEK vessel jacket with a screw cap; E, air flow. Adapted from Ref. [51].

was tempered in a cooling device. Either conventional or electrodeless mercury lamps were employed as sources of UV radiation [121]. A similar microwave-stimulated flow-through UV reactor was designed for disinfection of drinking, waste, and feed waters [122].

Čírkva and coworkers have studied a flow MW photoreactor containing a glass

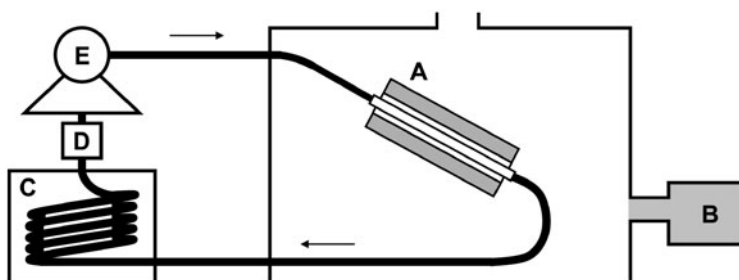


Fig. 19.16. Experimental setup of a flow-through quartz photoreactor used for photocatalytic decomposition in aqueous TiO_2 dispersions using cylindrical electrodeless mercury discharge lamps. A, cylindrical EDL

with a quartz pipe with the sample solution in a microwave cavity; B, a microwave generator; C, cooling circulator device; D, thermometer; E, peristaltic pump. Adapted from Ref. [119].

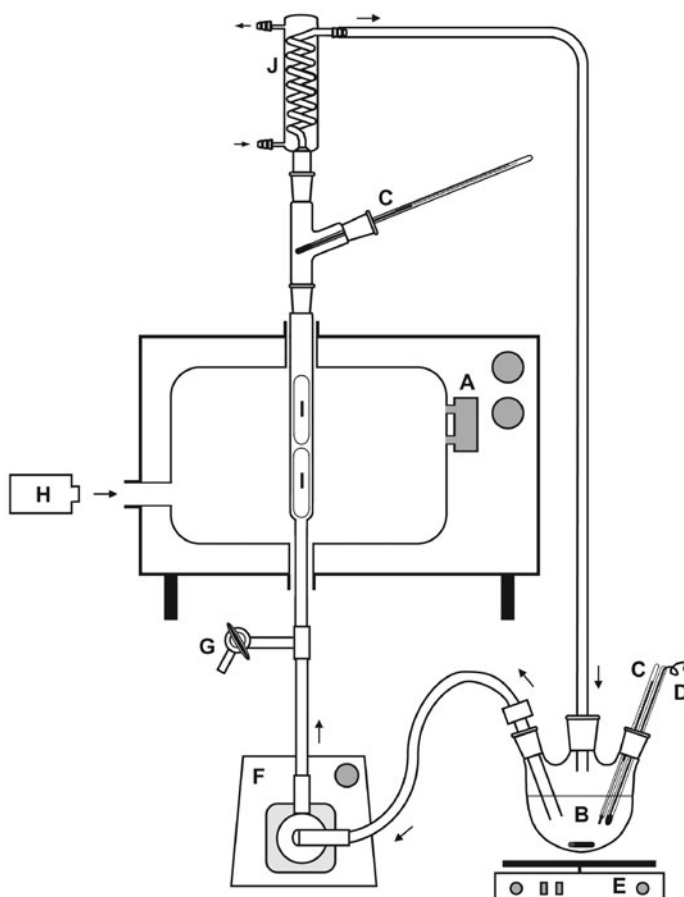


Fig. 19.17. A flow microwave photoreactor. A, microwave oven with magnetron; B, reaction mixture with magnetic stir bar; C, thermometer; D, pH meter with glass electrode; E, magnetic stirrer; F, PTFE membrane pump; G, outlet; H, spectrometer with a fiber-optic probe; I, glass tube with quartz Hg EDL; J, condenser [123].

tube with quartz Hg EDL (254 nm emission) inside a microwave oven, a PTFE membrane pump, a container flask, a cooling condenser, thermometers, and a pH meter with a glass electrode (Fig. 19.17) [123]. Photohydrolysis of chloroacetic acid to hydroxyacetic acid and hydrogen chloride was chosen as model reaction; the course of the reaction was followed by monitoring the change of pH of the solution. The conversion was optimized as a result of a trade-off between the thermal dependence of the quantum yield (which increased with increasing temperature) and the thermal dependence of a relative intensity of a short-wavelength band (which increased with decreasing temperature).

Microwave-enhanced chemistry introduces unique *safety considerations* not encountered by the chemist in other fields of chemistry [124]. Careful planning of

all experiments is strongly advised, especially when the results are uncertain, because control of the reaction temperature might be complicated by rapid heat-transfer. It is, furthermore, well known that electronically excited singlet oxygen, capable of causing serious physiological damage, is generated by microwave discharge through an oxygen stream [125]. The combined effect of MW and UV irradiation could increase the singlet oxygen concentration in the MW cavity, particularly in the presence of a photosensitizer.

19.4 Interactions of Ultraviolet and Microwave Radiation with Matter

Although microwave chemistry has already received widespread attention from the chemical community, considerably less information is available about the effect of microwave radiation on photochemical reactions. Photochemistry is the study of the interaction of ultraviolet or visible radiation ($E = 600\text{--}170 \text{ kJ mol}^{-1}$ at $\lambda = 200\text{--}700 \text{ nm}$) with matter. The excess energy of electronically excited states significantly alters species reactivity – it corresponds, approximately, to typical reaction activation energies helping the molecules overcome activation barriers. The microwave region of the electromagnetic spectrum, on the other hand, lies between infrared radiation and radio frequencies. Its energy ($E = 1\text{--}100 \text{ J mol}^{-1}$ at $\nu = 1\text{--}100 \text{ GHz}$) is approximately 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 with 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 (thus generating heat). Additional (secondary) effects of microwaves include ionic conduction (ionic migration in the presence of an electric field) or spin alignment.

Simultaneous UV–visible and MW irradiation of molecules, which does not necessarily cause any chemical change, might affect the course of a reaction by a variety of mechanisms at *each* step of the transformation. From many possibilities, let us present a simplified model describing two main distinct pathways (Fig. 19.18). The first route, more probable, is a photochemical reaction starting with a ground state molecule **M**, which is electronically excited to **M***, transformed into an intermediate (or a transition state) **I**, and, finally, a product **P**. Virtually every step may

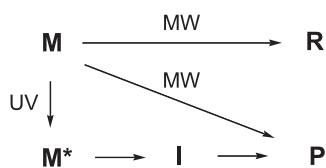


Fig. 19.18. Simplified model of nonsynergistic effects of UV and MW radiation on a chemical reaction.

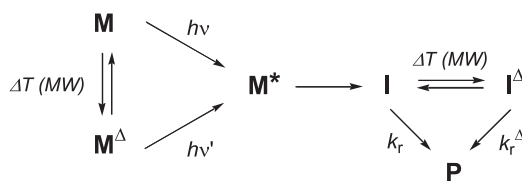


Fig. 19.19. A simplified model of the synergistic effect of UV and MW radiation on a chemical reaction, where Δ denotes “hot” molecules, and k_r and k_r^Δ are the rate constants of the processes leading eventually to the same product P .

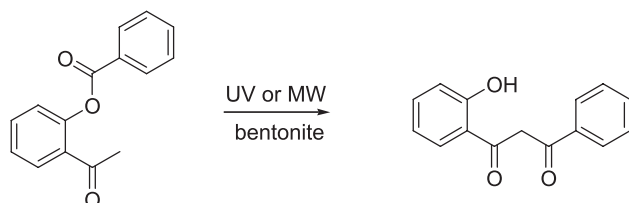
be complicated by a parallel microwave-assisted reaction enabling a different chemical history. There is a theoretical possibility that MW radiation affects the electronically excited molecule M^* or a short-lived transition state. In such circumstances the lifetime of the species should be long enough to interact with this low-frequency radiation. The second pathway becomes important when MW initiate a “dark” chemical reaction (essentially through polar mechanisms), competitive with or exclusive to a photochemical pathway, yielding a different (R) or the same (P) product. Figure 19.18 depicts a model in which MW and UV effects are easily distinguishable – it is assumed there is no synergistic effect during a single step of the transformation.

Let us, on the other hand, assume that the efficiency of a photoreaction is altered by microwave induction. In an example shown in Fig. 19.19 microwave *heating* affects the excitation energy of the starting ground-state molecule. The individual effects of both types of electromagnetic radiation simultaneously affect a single chemical step in which the ground-state molecules M and M^Δ (a MW-heated molecule) are being excited. If, furthermore, the intermediates I and I^Δ react with different rate constants, the total observed rate constant of the reaction, k_{obs} , is proportional to the sum $k_{\text{obs}} \approx (\chi k_r + \chi^\Delta k_r^\Delta)$, where χ and χ^Δ represent the populations of I and I^Δ .

19.5 Photochemical Reactions in the Microwave Field

19.5.1 Thermal Effects

Baghurst and Mingos have hypothesized that superheating of polar solvents at atmospheric pressure, so that average temperatures are higher than the corresponding boiling points, is a result of microwave dissipation over the whole volume of a liquid [126]. With the absence of nucleation points necessary for boiling, heat loss occurs at the liquid–reactor wall or at liquid–air interfaces. Many reaction efficiency enhancements reported in the literature have been explained as the effect



Scheme 19.1

of superheating when the reactions were essentially performed in sealed vessels without any stirring [127–131]; this effect is also expected in microwave-assisted photochemistry experiments in condensed media. Gedye and Wei [16], for example, have observed enhancements of the rate of several different thermal reactions by factors of 1.05 to 1.44 in 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 nonthermal effects. Stadler and Kappe reported similar results in an interesting study of the MW-mediated Biginelli reaction [15].

Chemat et al. [110] reported 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 19.1). The reaction, performed in the reactor shown in Fig. 19.14, was subject to a substantial activation effect under simultaneous UV and MW irradiation; this corresponded at least to the sum of the individual effects (Fig. 19.20). The rearrangement was not studied in further detail, however. Such competitive processes can be described by the diagram in Fig. 19.18, because the product obtained from both types of activation was the same.

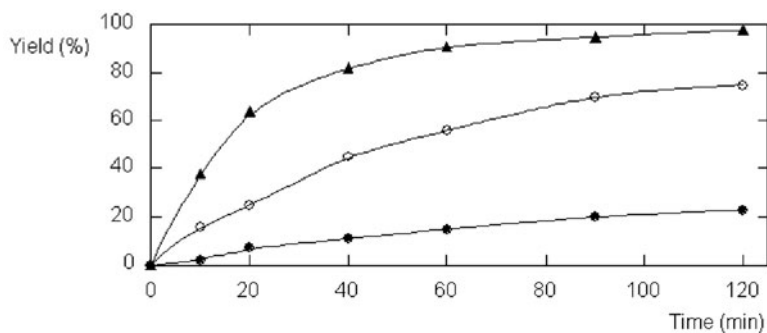
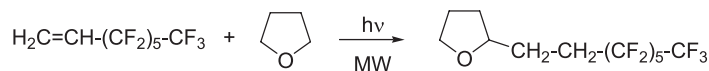


Fig. 19.20. Reaction yields in the rearrangement of 2-benzoyloxyacetophenone induced by microwave heating (●), ultraviolet irradiation (○), or simultaneous UV and MW irradiation (▲). Adapted from Ref. [110].

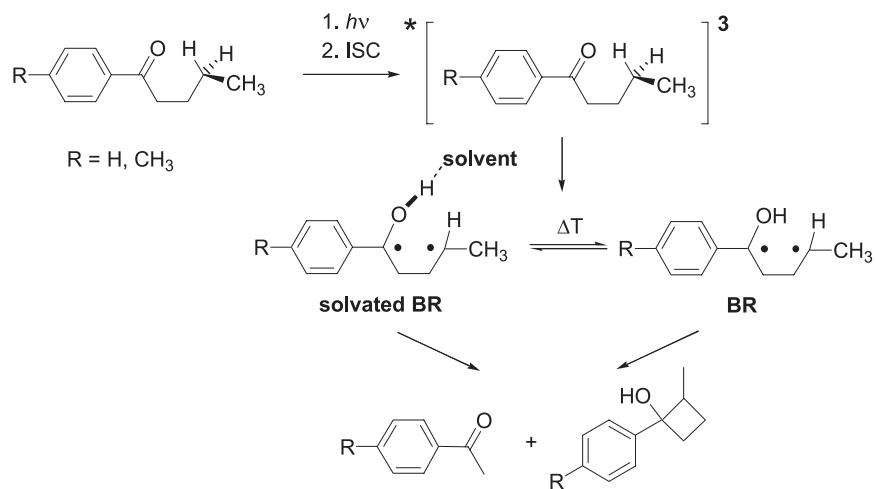


Scheme 19.2

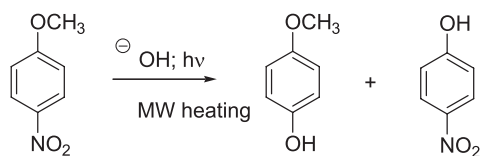
Čírkva and Hájek have studied the photochemically or microwave-induced addition of tetrahydrofuran to perfluorohexylethene (Scheme 19.2) [105]. Whereas the thermal reaction was too slow, photochemical activation was very efficient, with no apparent thermal effects of MW radiation. Combined UV and MW radiation (Fig. 19.12) has principally been used to initiate EDL operation in the reaction mixture. Another illustration of the MW–UV-assisted reaction has been demonstrated by Nüchter et al. [22] on dehydrodimerization reactions of some hydrocarbons.

Klán et al. [109] successfully evaluated MW superheating effects in polar solvents by use of a temperature-dependent photochemical reaction. It is known that quantum efficiencies of the Norrish type II reaction [132] of *p*-substituted valerophenones depend on the presence of a weak base, because of specific hydrogen bonding to the biradical OH group (**BR**; Scheme 19.3) [106, 107]. The efficiency of this reaction was linearly dependent on temperature over a broad temperature range 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 presence of a superheating effect (4–11 °C) for three aliphatic alcohols and acetonitrile as reaction solvents. The results were in a perfect agreement with measurements by use of a fiber-optic thermometer.

Klán et al. recently studied temperature-sensitive, regioselective photochemical nucleophilic aromatic substitution of 4-nitroanisole by the hydroxide anion in



Scheme 19.3

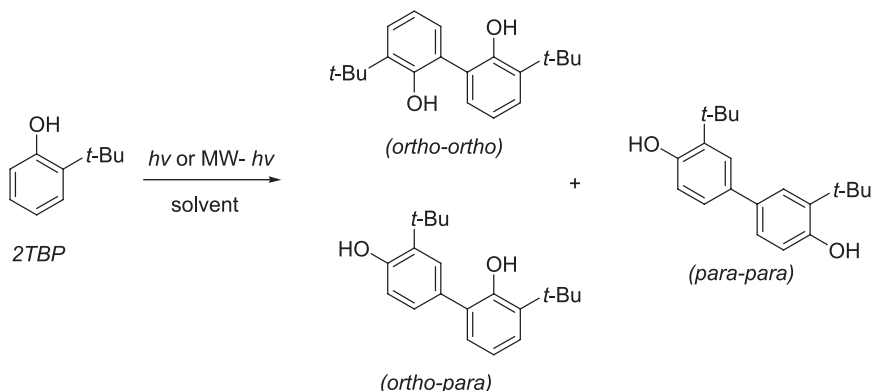


Scheme 19.4

homogeneous solutions by use of microwave heating and an EDL (Fig. 19.12) [133]. The quantum yield for formation of one product (4-methoxyphenol) was found to be independent of temperature, in contrast with that for formation of 4-nitrophenol, suggesting the occurrence of a temperature-dependent process after partitioning between replacement of the nitro and methoxy groups (Scheme 19.4). The technique of microwave-assisted photochemistry was proposed in this paper as an efficient and practical tool for organic synthesis. Subsequent investigation of the release of a photoremovable protecting group, the 2,5-dimethylphenacyl chromophore, from the carboxyl moiety, enhanced by MW heating, showed that quantum yields for ester degradation in polar solvents increased by a factor of three when the temperature was increased from 20 to 50 °C [134]. Distribution of the products and reaction conversions of several different photochemical systems, irradiated by use of a conventional UV source and by an EDL in a MW–UV reactor (Fig. 19.12), were compared to elucidate the advantages and disadvantages of this technique [108]. Some reactions, e.g. photolysis of phenacyl benzoate in the presence of triethylamine or photoreduction of acetophenone by 2-propanol, were moderately enhanced by MW heating. Two temperature-sensitive model photochemical reactions, the Norrish Type II reaction and photochemical nucleophilic aromatic substitution of 4-nitroanisole by the hydroxide ion, have recently been studied in high-temperature water (100–200 °C) in a pressurized vessel under microwave heating [135]. The observed chemoselectivity and the ability to increase the solubility of hydrophobic organic compounds in this solvent were found to be promising results for environment-friendly (photo)chemical applications.

Čírkva et al. have recently investigated an effect of UV and combined MW–UV irradiation on the transformation of 2-*tert*-butylphenol (2TBP) in the presence and the absence of sensitizers with different values of singlet and triplet energy, and in the presence of solvents with different polarity [136]. UV or combined UV–MW irradiation of the starting molecules furnished three isomers – 3,3'-di-*tert*-butylbiphenyl-2,2'-diol (ortho–ortho), 3,3'-di-*tert*-butylbiphenyl-2,4'-diol (ortho–para), and 3,3'-di-*tert*-butylbiphenyl-4,4'-diol (para–para) (Scheme 19.5). Their concentration ratios depended on the nature of the solvents and sensitizers used. No significant specific effects of the combined MW–UV radiation on the distribution of the products from 2TBP photolysis were observed.

MW–UV irradiation of 4-*tert*-butylphenol (4TBP) has also been investigated [137]. Photolysis of this compound furnished 4',5'-di-*tert*-butyl-2-hydroxydiphenyl ether (ortho–O) and 5,5'-di-*tert*-butylbiphenyl-2,2'-diol (ortho–ortho), and 2TBP as

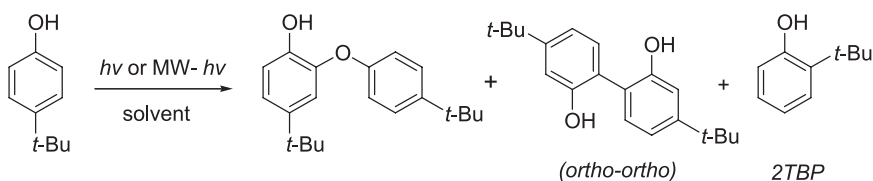


Scheme 19.5

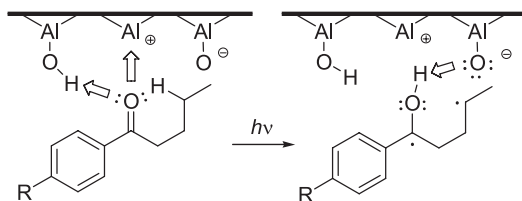
an isomerization by-product (Scheme 19.6). Again, no specific MW effect was observed.

Kunz et al. have studied the hydrogen peroxide-assisted photochemical degradation of EDTA with a microwave-activated ultraviolet source (model UV LAB, UMEX) [138]. The effect of pH and H_2O_2 -EDTA molar concentration ratio on the efficiency of degradation was evaluated. Han et al. investigated enhanced oxidative degradation of aqueous phenol in a UV- H_2O_2 system under the action of microwave irradiation [139]. The experimental results, based on the kinetic study, showed that MW irradiation can enhance both phenol conversion and the TOC removal efficiency by up to 50% or above.

Louerat and Loupy studied some photochemical reactions (e.g. stilbene isomerization) in homogenous solutions and on solid supports such as alumina [111] and the Norrish type II photoreaction of alkyl aryl ketones on alumina or silica gel surfaces has been investigated by Klan et al. [140]. On the basis of on these results, a model in which the short-lived biradical intermediate interacts with the surface, in addition to a polar effect on the excited triplet of ketone, has been proposed (Scheme 19.7). Both acidic and basic sites are present on the amphoteric alumina surface; while the acidic OH groups coordinate to the carbonyl oxygen, the basic groups (O^-) are involved in hydrogen bonding with the OH group of the biradical



Scheme 19.6



Scheme 19.7

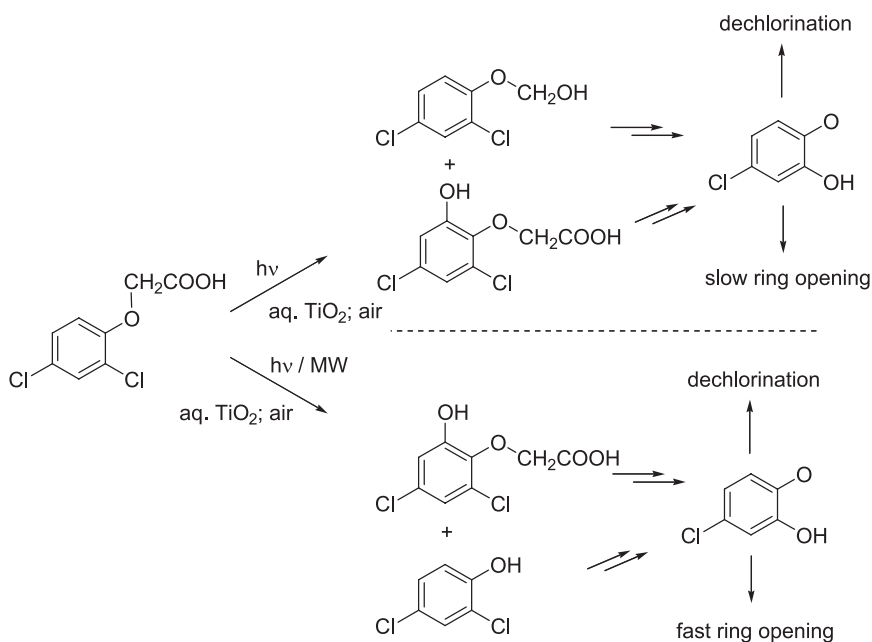
intermediate. The change in the regioselectivity of the reaction as a result of microwave heating was explained in terms of the weakening of such interactions.

19.5.2

Microwaves and Catalyzed Photoreactions

Advanced oxidation processes, for example photocatalysis, have emerged as potentially powerful methods for transforming organic pollutants in aqueous solution into nontoxic substances. Such remediation usually relies on generation of reactive free radicals, especially hydroxyl radicals ($\cdot\text{OH}$) [141]. These radicals react rapidly and usually nonselectively with most organic compounds, either by addition to a double bond or by abstraction of a hydrogen atom, resulting in a series of oxidative degradation reactions ultimately leading to mineralization products, for example CO_2 and H_2O [142].

In the past four years, Horikoshi, Hidaka, and Serpone have published results from a series of studies on environmental remediation of a variety of aqueous solutions by simultaneous MW–UV irradiation in the presence of a TiO_2 catalyst. They have clearly shown that this integrated illumination technique is superior to simple photocatalysis in the degradation of a variety of organic compounds, e.g. rhodamine-B dye [114, 119, 120, 143], bisphenol-A [117], 2,4-dichlorophenoxyacetic acid [118, 121], and carboxylic acids, aldehydes, and phenols [116]. Microwave radiation has occasionally been used to power an EDL inside the photochemical reactor [119, 120]. The authors suggested that, in addition to thermal effects, nonthermal effects [117, 121, 143] might govern microwave-assisted reactions in the presence of TiO_2 , because combined UV and MW radiation generated more hydroxyl radicals (proved by use of electron spin resonance spectroscopy to detect the radicals) [144]. A solution of 5,5-dimethyl-1-pyrrolidine-*N*-oxide (DMPO; spin trap) containing TiO_2 was subjected to photolysis and/or thermolysis and the number of DMPO- $\cdot\text{OH}$ spin adducts was determined. MW irradiation yielded a small quantity of OH radicals; substantially more were produced by UV irradiation. Combined UV–MW treatment at the same sample temperature generated even more radicals, by a factor of approximately 2. It was suggested this increase was a result of nonthermal interactions between the MW field and the surface of the catalyst. The nature of such interactions, however, remains to be elucidated. It was, moreover, suggested that hydrophilic–hydrophobic changes on the TiO_2 surface as a



Scheme 19.8

result of MW radiation led to changes in the population of the surface hydroxyls [115]. When rhodamine-B, for example, was subjected to photocatalytic destruction in the absence of MW radiation, it was suggested the two oxygen atoms of the carboxylate moiety of the dye were interacting with the positively charged TiO_2 surface [143]. MW-assisted photolysis, however, increased the hydrophobic nature of the TiO_2 , as a result of the MW irradiation, and adsorption might be facilitated by the aromatic rings, eventually causing formation of different degradation intermediates than in the absence of MW. In a different project, the effect of dissolved oxygen and MW irradiation on photocatalytic destruction of 2,4-dichlorophenoxyacetic acid was investigated [121]. The greater efficiency of MW-assisted degradation was ascribed to a nonthermal effect on ring-opening of the aromatic moiety via oxidative reaction (Scheme 19.8).

Heterogeneous catalytic degradation of humic acid in aqueous titanium dioxide suspension under MW–UV conditions was studied by Chemat et al. [110]. Enhancement in this application was reported as substantial – i.e. greater than simple addition of both effects. Zheng et al. [145–147] have recently reported microwave-assisted heterogeneous photocatalytic oxidation of ethylene using porous TiO_2 and SO_4^{2-} - TiO_2 catalysts. Significant enhancement of photocatalytic activity was attributed to the polarization effect of the high-defect catalysts in the MW field. These studies also included modeling of the photodegradation of organic pollutants in the microwave field. TiO_2 - ZrO_2 mixed-oxide catalyst, prepared by sol–gel

processing, has also been used in photocatalytic oxidation of ethylene by Anderson and coworkers [115]. The adsorption experiments demonstrated that MW irradiation removed water from the surface of the catalyst better than when heat was supplied by conductive (conventional) heating. Ai et al. [148] have investigated microwave-assisted photocatalytic degradation of 4-chlorophenol by use of an electrodeless discharge UV system. The effects of pH, irradiation intensity, aeration, and amount of H_2O_2 both on direct photolysis and on TiO_2 photocatalysis were evaluated. It was found that the process proceeds through the same mechanism as in the absence of the catalyst. Zhang and Wang have recently reviewed the effects and mechanisms of microwave-assisted photocatalysis [149].

19.5.3

Intersystem Crossing in Radical Recombination Reactions in the Microwave Field – Nonthermal Microwave Effects

Radical pairs and biradicals are extremely common intermediates in many organic photochemical (and some thermal) reactions. A singlet state intermediate is formed from the singlet excited state in reactions that conserve spin angular momentum whereas the triplet intermediate is obtained via the triplet excited state. Radical pairs in solution coherently fluctuate between singlet and triplet electronic states [150, 151] and the recombination reactions are often controlled by electron–nuclear hyperfine interactions (HFI) on a nanosecond time-scale [152, 153]. Only pairs of neutral radicals with singlet multiplicity recombine. A triplet pair intersystem crosses into the singlet pair or the radicals escape the solvent cage and react independently at a later stage (Fig. 19.21) [154]. The increasing efficiency of triplet-to-singlet interconversion (“mixing” of states) leads to a more rapid recombination reaction and *vice versa*. It is now well established that a *static* magnetic field can affect intersystem crossing in biradicals (magnetic field effect, MFE) and the effect has been successfully interpreted in terms of the radical pair mechanism [155, 156]. This concept enabled explanation of nuclear and electronic spin polarization phenomena during chemical reactions, e.g. chemically induced dynamic nuclear polarization (CIDNP) or reaction yield-detected magnetic resonance (RYDMAR).

An external magnetic field stronger than the hyperfine couplings inhibits (because of Zeeman splitting) singlet–triplet interconversions by isolating the triplets T_{+1} and T_{-1} from the singlet (S); these can, therefore, mix only with T_0 (Fig. 19.21a, b). For the *triplet-born radical pair*, the magnetic field reduces the probability of radical recombination. 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 excess population from the T_{+1} or T_{-1} states back to a mixed state. Application of a strong magnetic field to the *singlet-born radical pair* leads to an increase in the probability of recombination that can, however, also be controlled by microwave irradiation [156].

This microwave-induced spin dynamics can be regarded as an archetypal *non-thermal* MW effect. Because the radical pair is usually created via a photochemical

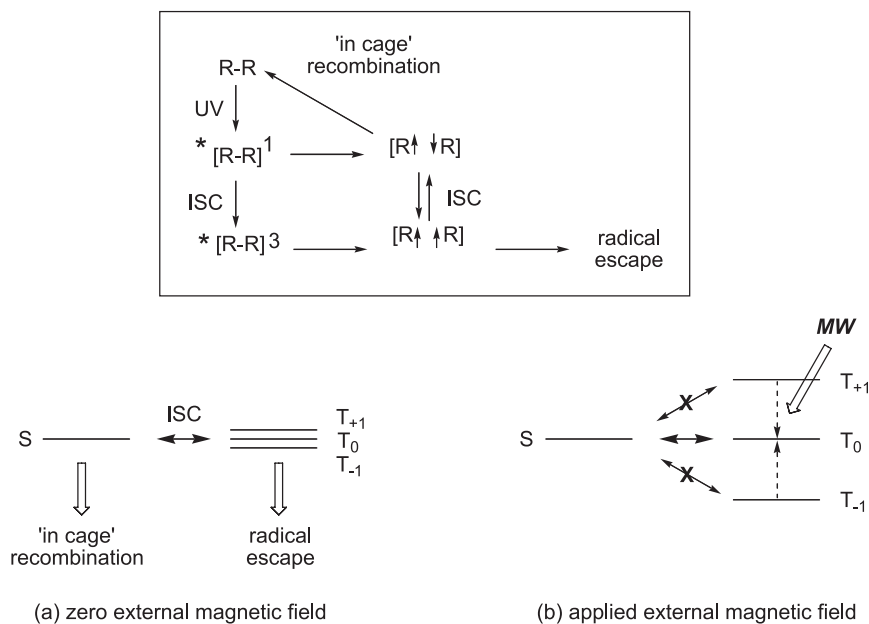


Fig. 19.21. Schematic illustration of magnetic field and MW effects in radical-pair chemistry.

pathway, the topic should certainly be included in this chapter. The literature offers many examples that span photobiology, photochemistry, and photophysics. Wasielewski et al. [157], for instance, showed that the duration of photosynthetic charge separation could be controlled by use of microwave radiation. It was, moreover, possible to observe the dynamics of radical-pair processes involving primary bacterial photochemistry [158]. Okazaki et al. [159] reported the possibility of controlling chemical reactions by inducing the ESR transition of the intermediate radical pair in the photoreduction of anthraquinone micellar solution under the action of an external magnetic field and simultaneous MW irradiation. A similar study with a bifunctional molecule was reported by Mukai et al. [160]. Research in this field is very well covered by several reviews and books [155, 156, 161, 162]. Weak static magnetic fields, smaller than an average hyperfine coupling, also affect radical pair recombination yields [163, 164]. This effect is opposite to the effect of a strong field [165, 166]. The effect of a magnetic field on singlet oxygen production in a biochemical system was reported recently [167].

Until recently, 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 [168]. Hore and coworkers [169–171] recently described this effect, denoted 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 pairs (pyrene anion and dimethylaniline cation) in solution has been reported [172]. Triplet–singlet interconversions as a result of HFI are relatively efficient in a zero applied magnetic field (to be more precise, in the Earth’s field of $\sim 50 \mu\text{T}$). All the states are almost degenerate, assuming separation of the radicals is such that their electronic exchange interaction is negligible [155]. Jackson and his coworkers [173] 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 of 0.1–3.0 mT, the oscillating magnetic field effect, enhancing the conversion of the singlet state to the triplet (as was observed for weak static fields), is expected in the *radiofrequency* region (3–80 MHz) [170]. Canfield et al. calculated the effects and proved them experimentally on the radical pairs involved in coenzyme B₁₂-dependent enzyme systems [174–176]. Other theoretical studies have appeared in recent years [172, 177, 178]. Whether electromagnetic fields affect animal and human physiology is still open question. It has, for instance, been suggested that radiofrequency fields might disorient birds [179]. Detailed experimental studies of OMFE in the microwave region have not yet been performed. Hoff and Cornelissen [180] have reasoned that triplet-state kinetics could be affected by a pulse of resonant microwaves rather than by equilibrium methods in the zero static field.

According to the OMFE model a weak oscillating magnetic field (the magnetic interactions are much smaller than the thermal energy of the molecule [177]) has no effect on equilibrium constants or activation energies; it can, however, exercise immense *kinetic* control over the reaction of the radicals [177]. The simplified kinetic scheme in Fig. 19.22 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 cleavage (k_{cl}) to the triplet radical pair. The oscillating magnetic field affects state mixing of the radical pair (k_{TS} and k_{ST}). The probability that the triplet radical pair

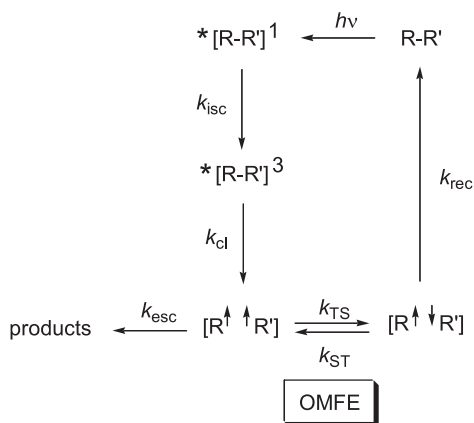


Fig. 19.22. The oscillating magnetic field effect (OMFE) in the triplet-state radical-pair reaction.

will form the products is given by the efficiency of radical escape from the solvent cage (k_{esc}) and of triplet-to-singlet intersystem crossing (k_{TS}). The recombination reaction is very rapid when the tight radical pair reaches the singlet state.

19.6 Applications

19.6.1 Analytical Applications

In addition to analytical applications in which microwaves serve as a power source for the electrodeless discharge lamps (Section 19.2), the first successful use of combined MW–UV irradiation for efficient degradation of a variety of samples before a subsequent analytical application has been reported. Florian and Knapp [51] have proposed a novel MW–UV, high-temperature–high-pressure digestion procedure for decomposition of interfering dissolved organic carbon as a part of trace element analysis of industrial and municipal wastewater or other liquid samples. Very efficient and rapid mineralization was obtained in an original reactor (Fig. 19.15) because of the very high temperature (250–280 °C). The high temperature also enabled dissolution of solid organic matrices by use of dilute 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. Efficient decomposition of organophosphate compounds, with the aim of the colorimetric phosphate determination, has been achieved by Howard et al. in a novel beaker-shaped electrodeless MW–UV lamp [112]. Although no details of the organophosphate decomposition mechanism have been presented, the authors suggested two possible pathways. In addition to direct photodegradation, much of the decomposition resulted from photochemical generation of hydroxyl and oxygen radicals from dissolved O_2 in the samples. The concentration of OH radicals could be enhanced by addition of hydrogen peroxide. In addition, Sodre et al. have proposed a new procedure for digestion of natural waters, based on a microwave-activated photochemical reactor, in their speciation studies of copper–humic substances [181].

19.6.2 Environmental Applications

Photodegradation [182] and microwave thermolysis [183] of pollutants, toxic agents or pathogens in waste water, often in combination with a solid catalyst (e.g., TiO_2), are two important methods for their removal. Results from environmentally relevant studies of the combined use of MW and UV [97, 101–103] have already appeared in the scientific literature and the topic is also covered by several

patents. Photochemical oxidation is a process in which a strong oxidizing reagent (ozone or hydrogen peroxide) is added to water in a UV-ionizing reactor, resulting in the generation of highly reactive hydroxyl radicals ($\cdot\text{OH}$). The first-generation techniques used commercial EDL (high pressure Hg–Xe lamps) immersed in the water tanks. The lamps deteriorated rapidly, however, leading to poor production of hydroxyl radicals. The second-generation technique incorporated manual cleaning mechanisms and use of a polymer coating (PTFE) on the quartz sleeve, additional oxidizers (ozone), and catalytic additives (TiO_2) to enhance the rate of an OH radical production [184]. A novel UV-oxidation system used a highly efficient EDL combined with a simple coaxial flow-through reactor [103]. 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 vessel. An H_2O_2 solution was injected into the liquid being treated and thoroughly mixed by means of an in-line mixer, just before the mixture entered the reactor vessel. It was found by Lipsky et al. that photooxidation of humic acids causes changes in their absorption and luminescence properties that might be of a great importance in environmental photophysics and photochemistry [185]. Aqueous aerated alkaline solutions of the acids were irradiated with a mercury EDL in a flow system and analyzed by means of fluorescence, absorption, and chemiluminescence techniques. Campanella et al. reported minor but positive enhancement of the efficiency of photocatalytic degradation of *o* and *p*-chlorophenol in aqueous solutions by microwave heating [113]. The success of these model chemical systems suggested extension to other environmentally interesting compounds, e.g. sodium dodecylbenzenesulfonate or organophosphate pesticides. It has been suggested that microwave-assisted photodegradation of pollutants may be of great interest in the future. Several other research groups, for example those of Chemat [110], Zheng [145], Ai [148], and Hidaka and Serpone [116, 118, 121] have demonstrated improvement of degradative efficiency when microwave radiation is coupled with photocatalytic degradation of pollutants in aqueous solutions, as already described in Section 19.5.2. Spherical or cylindrical EDL have been used to remediate fluids, directly or by excitation of photocatalyst surfaces, which may be located on the lamps themselves or on structures which permeable to the fluids [186].

Noncatalytic remediation of aqueous solutions of a variety of aromatic compounds by microwave-assisted photolysis in the presence of hydrogen peroxide has recently been studied by Klan and Vavrik [187]. The combined degradation effect of UV and MW radiation was always larger than the sum of the isolated effects. It was concluded that this overall increase in efficiency is essentially because of thermal enhancement of subsequent oxidation reactions of the primary photoreaction intermediates. Optimization revealed that this effect is particularly significant for samples containing low concentrations of H_2O_2 , although a large excess of H_2O_2 was essential for complete destruction in most experiments. The degradation profiles of the techniques used in the degradation of 4-chlorophenol are com-

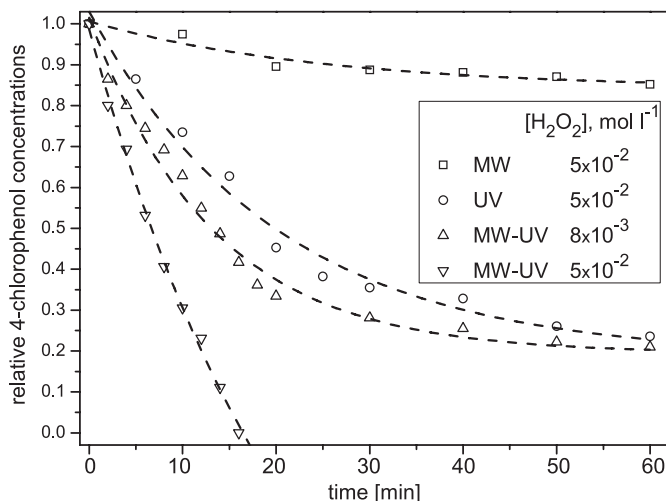


Fig. 19.23. Degradation of 4-chlorophenol ($c = 10^{-3} \text{ mol L}^{-1}$) in the presence of H_2O_2 (the concentrations are shown in the inset) in water under given conditions: microwave heating (MW), photolysis at 20°C (UV), and MW-assisted photolysis (MW-UV). With permission from Elsevier Science [187].

pared in Figure 19.23, which also suggests possible optimum degradation conditions. The results from this work showed that simultaneous MW-UV- H_2O_2 remediation could be an attractive alternative to conventional oxidation or photocatalytic degradation methods for environmental remediation of polluted wastewaters.

Sterilization techniques for 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 chemical modification of DNA in bacteria (usually dimerization of thymine). 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 [188]. An apparatus using a mercury EDL for surface sterilization or disinfection of objects such as bottles, nipples, contact lenses, or food has been proposed by LeVay [98] and Okuda [189]. An apparatus for continuous sterilization of bottle corks and textiles has also been described [190–192]. The sterilization performance of a microwave-powered commercial UV lamp designed to generate active oxygen species for destruction of microorganisms has also been reported [193].

In addition, ozone treatment can be used in combination with UV exposure to sanitize or disinfect a variety of substances [99, 100, 194–197]. Another application of EDL (containing Hg, Cd-Ar, or Kr) for disinfection of aqueous solutions has recently been reported by Michael [198].

19.6.3

Other Applications

Simultaneous use of UV and MW irradiation has found widespread use in industry. The techniques are based on the conventional UV lamps or MW-powered electrodeless lamps [33].

Photolithography is a technique used for manufacture of semiconductor devices (e.g. transistors or integrated circuits). In the process the image of an optical mask is copied, by use of UV radiation, on to 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. Application of shorter wavelengths (190–260 nm) results in greater depth of focus, i.e. sharper printing. The first EDL applied were made from a material known as commercial water-containing natural quartz [199]. It was found that transmission of the envelope at vacuum UV wavelengths falls off sharply with time. The lamps developed later from water-free quartz [66] were much more transparent. Excimer lamps used for photoetching and microstructuring of the polymer surface have been developed for applications in standard MW ovens [85].

A photochemical apparatus for generating superoxide radicals ($O_2^{\cdot-}$) in an oxygen-saturated aqueous sodium formate solution by means of an EDL has been described [200]. An interesting method for initiating and promoting chemical processes by irradiation of starting gaseous materials in the EM field under a lower pressure has been proposed by Lautenschläger [97]. EDL (containing GaI_3 , InI_3 , or AlI_3) with a “blue” output are now often used for dental purposes or for curing polymers. High-power microwave lamps (H and D bulb, fusion UV curing system) have been used for polymerization of maleimide derivatives [201]. The very small size of the lamps makes them particularly useful for supplying light to an optical fiber or light pipe [202]. Another example of microwave photochemical treatment of solutions at different wavelengths has been described by Moruzzi, who used MW for promotion of photochemical reactions [203].

19.7**Concluding Remarks**

Understanding, on the molecular scale, of processes relevant to microwave-assisted photochemistry has not yet reached the maturity of other topics in chemistry. Such a challenge is somewhat ambitious, because of several difficulties. Although some obstacles have been overcome, study of the effects of microwaves on photochemical reactions requires a special approach. Microwave-assisted photochemistry involves highly reactive, electronically excited molecules which are exposed to a different kind of reactivity-enhancing stimulation. Microwave heating strongly interferes with possible nonthermal effects that cannot be easily separated in mechanistic studies. One solution seems to be investigation of the spin dynamics of photochemically generated radical pairs. Many photochemical reactions could be

affected by a MW treatment if they pass through polar intermediates, e.g. ions or ion-radicals. Application of EDL simplifies the technical procedure, especially in organic synthesis, environmental chemistry, and analysis.

In this review we have discussed how the concept of microwave-assisted photochemistry has become important in chemistry. Although still at the beginning, detailed analysis of past and current literature confirms explicitly the usefulness of this method of chemical activation. The technique is already established in industry and we hope it will also find its way into conventional chemical laboratories.

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