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The electrodeless discharge lamp: a prospective tool for photochemistry
Part 3. The microwave photochemistry reactor

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Abstract

A simple and original microwave photochemical reactor is described in detail. It consists of an electrodeless discharge lamp placed into the reaction vessel in a modified domestic microwave oven. The microwave field generates ultraviolet radiation by the lamp at the same time when it interacts with the reaction mixture. The construction, experimental set-ups, applications, and safety precautions are discussed.

Keywords: Photochemistry; Microwave; Electrodeless discharge lamp; Laboratory equipment

1. Introduction

During the past decade, microwave (MW) chemistry certainly became one of the important fields of modern organic chemistry [1,2]. Microwaves generate rapid intense heating of polar substances, usually causing reductions in reaction times and, in many cases, higher chemical yields. Chemical processes occurring under microwave radiation are believed to be affected by superheating, polarization, dielectric properties, hot spot formation, nuclear spin rotation, and spin alignment [3–5].

The fact that an electrodeless discharge lamp (or microwave lamp, MWL) generates ultraviolet (UV) radiation when placed into the microwave field has been known for a long time [6–11]. Low powered and low-pressure electrodeless lamps were utilized in spectroscopy and analytical chemistry four decades ago [12,13]. However, their application to organic photochemistry was shown for the first time by us in three publications [14–16]. We reported on the studies in an original photochemical reactor consisting of an MWL placed into the reactor vessel of a commercial microwave oven. The MW field generated a UV discharge in the lamp with the resulting, simultaneous UV and MW irradiation of the sample. Such a simple arrangement brings a unique possibility to study photochemical reactions under extreme thermal conditions. In addition to our investigations, Chemat et al. [17] recently described an MW-UV reactor in which the UV source was external.

In this work, we wish to describe details of working with our MW-UV reactor, necessary modifications to a domestic microwave oven for *microwave photochemistry* experiments, and safety precautions. The paper reviews our current knowledge of this field as well as the industrial applications.

2. Modifications to the microwave ovens

Our modifications to a domestic microwave oven [18] are similar to those described for microwave chemistry experiments [19–22]. Several commercially available ovens [23] were modified according to Fig. 1. In a typical design, at least four holes were drilled in the oven walls: two 30 mm holes, one for a condenser tube in the oven top and the other in the side for an IR pyrometer, and two 20 mm ports for a glass tube with circulating water (inlet and outlet). External aluminum tubes of the same diameter (∼10 cm long) were attached to the holes in order to eliminate possible MW leaking. Special attention was paid to the opening for the pyrometer, which is directed towards the reaction vessel. A part of the oven bottom was replaced by a round aluminum plate (200 mm diameter), carefully attached to the framework to allow magnetic stirring. The opening for the IR pyrometer can serve as the external source of UV irradiation. When a higher intensity of UV radiation, or a defined wavelength

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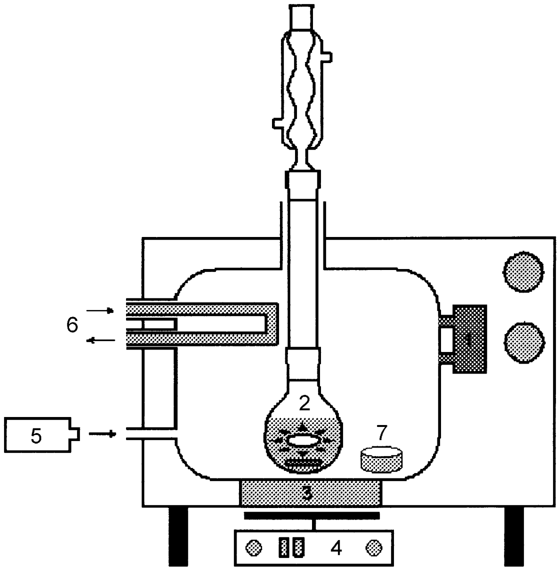

Fig. 1. A modified MW oven for microwave photochemistry experiments: (1) magnetron; (2) reaction mixture with MWL and a magnetic stir bar; (3) aluminum plate; (4) magnetic stirrer; (5) infrared pyrometer; (6) circulating water in a glass tube; (7) solid absorber inside the oven cavity.

range is needed, a high-pressure mercury lamp with an optical filter can be attached to the side oven window.

Water can conduct microwaves outside the oven, thus it is necessary that the equipment should be checked for leaks. In the event of MW leakage, a solid absorber is the only safe choice.

3. Electrodeless discharge lamps

The electrodeless discharge mercury lamps (MWL) [24] were made of quartz or Simax (Pyrex equivalent) tubings, filled with mercury and argon, and sealed under a 20 Torr vacuum [25]. Quartz lamps are suitable for irradiation at wavelengths longer than 254 nm, while Simax absorbs most UV irradiation below 280 nm. The size of our lamps varied from 10×20 to $20 \times 50\,\mathrm{mm}^2$, but this size range is not a limiting factor. The spectral characteristics of the electrodeless lamp resemble those of high-pressure mercury lamps and are known [26]. The lamp gives over three times as much UV radiation as the conventional electrode lamp [6]. In addition to UV and VIS radiation, MWL produces heat.

4. The photochemical microwave reactor

Fig. 2. Photochemistry in a microwave oven.

The typical experiment (shown in Fig. 2) consisted of a reaction vessel (25–1000 ml) with a reaction mixture, equipped with a Teflon-covered magnetic stir bar and MWL (larger lamps usually floated in the liquids while smaller ones sank). Such an arrangement allowed the irradiation of the whole volume of the solution by UV light. The vessel was connected to a very efficient water-cooled condenser by a 100–300 mm long glass tube. The microwave power was adjusted to a maximal value of the particular oven (800–900 W) [23], which guaranteed continuous MW radiation. The circulating cool water or some amounts of a solid, MW absorbing, material (basic Al_2O_3, molecular sieve, etc.) were used in those cases when a small quantity (<50 ml) of a polar liquid or non-absorbing (non-polar) liquids for microwave photochemical experiments were used. It removed the excess microwave power and/or prevented the magnetron from being destroyed by overheating. Since MW absorbers may lower the MW power of the reactor, the same amount of material is essential for good experimental reproducibility.

The temperature of a liquid was monitored by an IR pyrometer [27] or by a fiber-optic probe [28]. The lamp was initiated in non-polar solutions usually in several seconds when it warmed up [15]. Each liquid started to boil very quickly because of the heat produced by the lamp. Polar liquids (e.g. water, ethanol, or acetonitrile), when used in higher amounts, often prevented initiation of the lamp because they absorb most of the microwave power [15,16]. On the other hand, the MWL has *always* to be placed in a position, in which the solvent cools it down efficiently. Lamp overheating causes failure of the lamp emission [14,15].

When the presence of MWL in the reaction mixture affects the course of the reaction or when the reaction mixture

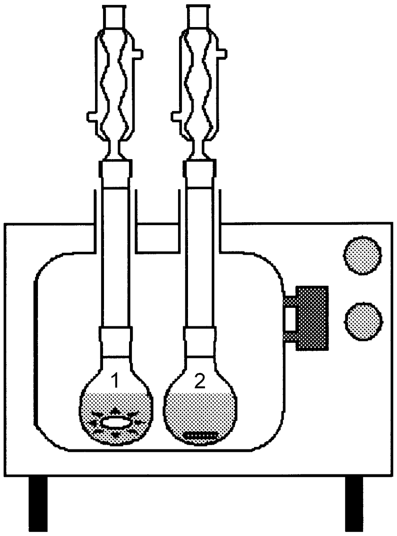

Fig. 3. An arrangement with two reflux apparatuses: (1) UV source; (2) vessel with a reaction mixture.

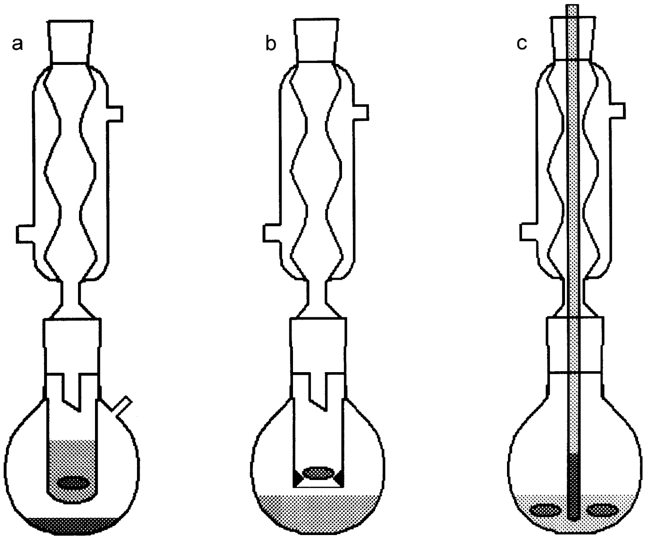

Fig. 4. Experimental arrangements with MWL.

absorbs most of the MW power causing termination of the lamp UV discharge, a different experimental arrangement is necessary. An oven modification that allows the installation of two reflux set-ups next to each other is one of the possibilities (Fig. 3). The first vessel with MWL serves as the source of UV radiation. Hexane or some other non-polar solvents, that are transparent over 254 nm, are ideal cooling media for the lamp. The spectral output of this UV source naturally depends on the quality of the glass of the vessel and MWL. The reaction mixture to be photolyzed is placed into the vessel of the second set-up. The disadvantage of this arrangement is the lower photochemical efficiency because the UV source is placed outside the reaction mixture. Here the size or number of MWLs may increase the radiation intensity [15].

Other possibilities of experimental arrangements are shown in Fig. 4. Set-up (a) is suitable only for the solid-state photochemistry of compounds that are involatile or for photochemistry on solid supports. The reaction vessel has a pinhole for pressure equalization; potential gaseous compounds should be vented to the fume hood by a Teflon tube. The MWL is placed above the reaction mixture, thus only a thin layer of the solid material is recommended. The top layer of the solid may absorb all the radiation. When the material is overheated by MW radiation, its temperature can be lowered by solid CO_2 or liquid nitrogen. Apparatus (b) has been described in our previous paper [15]. The MWL is placed above the reaction solution so that the refluxing liquid cools it down. A much lower photochemical efficiency, when the MWL is outside the solution, was reported. The third arrangement (c) consists of a thin long test tube immersed into the vessel with one or more MWLs in a non-polar liquid. Here the choice of glass material and physical properties of the liquid is significant. Since the reaction mixture in the test tube is partially cooled by the boiling solvent, less volatile hydrocarbons (such as hexadecane) may be applied to increase the temperature. Volatile material in the test tube is trapped inside the condenser or in an additional condenser attached to the test tube.

Other commercially available microwave reactors are also suitable for microwave photochemistry experiments. We successfully used [15,16] the microwave monomode reactor Synthewave 402 (Prolabo) [29] equipped with an IR pyrometer, quartz reaction vessel, and a cooling system. This equipment was also adapted for applications with an external UV source by Chemat et al. [17].

5. Safety considerations

Microwave-enhanced chemistry introduces unique safety considerations that are not encountered by the chemist in non-microwave methods [30]. Control of heating of the reaction mixture and the subsequent course of the reaction might be complicated by the rapid heat transfer mechanism. Thus, careful planning of the experiments is strongly advised when the results are uncertain. In addition, microwave photochemistry operates with harmful ultraviolet radiation and direct exposure should be avoided. The microwave equipment must operate within the safety limits prescribed locally in the country of installation. A generally accepted limit on the safe stray leakage of microwave power density is $10\,\mathrm{mW/cm^2}$ at 2450 MHz measured at a 50 mm distance from the equipment [31]. It is extremely important that the equipment be checked for leaks, especially around the modified area. Working with superheated flammable and toxic solvents in a microwave reactor needs special evaluation.

It is well known that, in addition to other methods (e.g. the photolysis of $^3O_2$ using a photosensitizing dye) [32], *singlet oxygen* is generated by microwave discharge through an oxygen stream [33–35]. It is highly probable that the synergic effect of MW and UV radiation will increase the singlet oxygen concentration in the MW cavity, especially in the presence of a photosensitizer. Since singlet oxygen is responsible for much of the physiological damage caused by reactive oxygen species [36] it is advisable to place the modified oven under a fume hood.

6. Applications

We recently described a number of photochemical systems that were studied in our microwave photochemical reactor. The reactor has been studied in terms of the operating MW power and MWL heating capabilities [15] or the MWL quality and the scale of the experiment [16]. In addition, the efficiencies of several photochemical experiments under MW conditions were compared to those using a conventional UV lamp [14,16]. The advantages and disadvantages of MWL application have been formulated — the electrodeless lamp was presented as a very simple, economic, and efficient tool for photochemistry [16].

There are a number of patents and papers that describe possible practical applications of microwave photochemistry. Lautenschläger suggested the apparatus for initiating and promoting chemical processes [9]. The MW-UV reactor could also serve as an efficient sterilizer of, e.g. contact lenses or the interior space of a microwave oven [37–39] or as an apparatus for the treatment of waste water and pollutants [40–45]. It was recently suggested that microwave-assisted photodegradation of pollutants may be of great interest in the future [46]. Microwave-produced singlet oxygen degradations of polymers has also been reported [47,48].

Dry etching methods for etching semiconductors [49], plasma processing [50], or treating of photoresists [51–54] are other applications. In addition, studies of the dynamic behavior of photochemically generated radical pairs under a microwave field have been reported [55–57].

Since our modifications to the domestic microwave oven are very simple and accessible to a broad spectrum of chemists, *microwave photochemistry* could find its way into a conventional chemical laboratory.

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