The electrodeless discharge lamp: a prospective tool for photochemistry Part 4. Temperature- and envelope material-dependent emission characteristics

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Abstract

This work extends our previous research on an original photochemical reactor—the electrodeless discharge lamp (EDL) inside a reaction mixture that generates ultraviolet radiation in the microwave (MW) field. This arrangement was found to be a straightforward solution for homogeneous as well as heterogeneous photochemical experiments that need to be carried out at higher temperatures. Here, we report the emission characteristics (250–600 nm) of EDL as a function of temperature, MW output power of the reactor, EDL envelope material, and properties of solvents used in photochemical reactions. Relative intensities of the individual emission peaks were found to be largely dependent on temperature (in the region of 35–174 °C): the short-wavelength bands (particularly the 254 nm peak) were suppressed with increasing temperature. Solvents absorbing MW significantly reduced the EDL emission intensity. It is concluded that the right choice of EDL envelope material and reaction conditions is essential for an efficient course of a photochemical process in this experimental arrangement.
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1. Introduction

There have been attempts to affect photochemical reactions by other sources of non-classical activation, such as ultrasound [1–3] or magnetic field [4,5]. Photochemistry in the microwave (MW) field [6] presents a combined chemical activation by two distinctive kinds of electromagnetic radiation. Energy of MW radiation ($E = 0.4$–$40\,\mathrm{J\,mol^{-1}}$ at $\nu = 1$–$100\,\mathrm{GHz}$) is considerably lower than that of UV-Vis radiation ($E = 600$–$170\,\mathrm{kJ\,mol^{-1}}$ at $\lambda = 200$–$700\,\mathrm{nm}$), thus insufficient to disrupt bonds of common organic molecules. Microwave heating is not identical to classical external heating, at least at the molecular level [7–10]. 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. Therefore, MW effects on photochemical reactions are expected to be diverse.

The objective of photochemistry in the microwave field is frequently, but not irreplaceably, connected to the electrodeless discharge lamp (EDL), which generates UV radiation when placed into the MW field. We have reported on an original photochemical reactor that takes advantage of an EDL *inside* a reaction mixture (Fig. 1) [11–13]. Such an arrangement was proposed for the first time by Den Besten and Tracy [14], and later applied by Církva and Hájek [15] in experiments using a modified microwave oven. Photochemical applications of a microwave-powered light source in photochemistry were recently described in several articles [16–22]. Knowledge of spectral characteristics of EDL is clearly essential for planning the photochemical experiment. The right choice of a filling and envelope material, glass, and even temperature can dramatically modify the emission spectrum. In the present study, we describe the influence of the EDL properties, the MW output power, and the reaction conditions on the EDL spectral characteristics.

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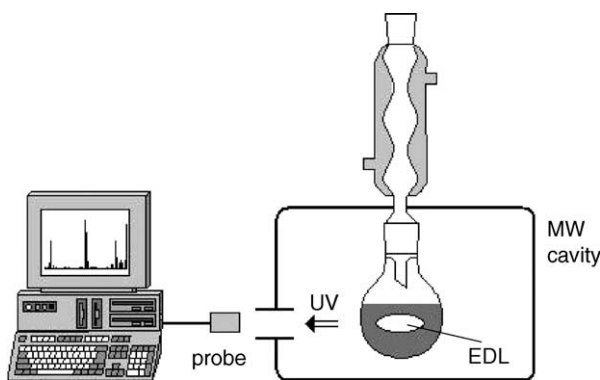*E-mail address:* klan@sci.muni.cz (P. Klán).

Fig. 1. Photochemistry in the MW field (adapted according to Klán et al. [13]).

2. Experimental

2.1. Equipment

The spectral measurements were accomplished in a modified MW oven Whirlpool M401 (900 W), operating at 2450 MHz frequency and described elsewhere [12], which had a window for UV radiation coming from EDL to a spectrometer. Its power was adjusted to the maximum in order to guarantee a continual MW irradiation. Every liquid is immediately boiling since EDL produces a considerable amount of IR radiation. The oven contained an external reflux condenser and a cooling glass spiral for removing redundant MW energy, thus preventing the magnetron from destruction by overheating [13,17]. Some experiments were carried out in a MW instrument Synthewave 402 (Prolabo, equipped with an IR pyrometer, a quartz reaction vessel, and an external spiral reflux condenser). The limit on the safe stray leakage of microwave power density was kept below 5 mW cm^{-2} at 2450 MHz measured in the 50 mm distance from the equipment. The equipment was checked for leaks especially around the modified area [13].

Electrodeless discharge mercury lamps were manufactured in Teslamp (Prague, Czech Republic). The lamps were made of a 9 or 14 mm quartz or Pyrex tubing (of approximately 1 mm thick glass) of the 13–37 mm length, filled with mercury and argon, and sealed under 2.7 kPa vacuum [12]. Pyrex absorbs most of the UV radiation below 290 nm. Gas chromatography was accomplished on a Shimadzu GC-17A apparatus. The UV-Vis spectra of all chemicals were measured on a Shimadzu UV-1601 spectrophotometer.

2.2. Chemicals

Methanol (pure, ML Chemica Co.) was used as received. *n*-Pentane (pure, Lachema Co.) was further purified by distillation and *n*-hexane (SupraSolv, Merck) was used as received. *n*-Heptane (pure, Lachema Co.) was washed with concentrated sulfuric acid and distilled; *n*-decane (pure,

Reachim) was washed with concentrated sulfuric acid and purified through an activated silica-gel column. The quality of all alkanes was checked by the UV-Vis spectrophotometry and GC. The solvent absorbance values (versus air) were negligible throughout the tested range of wavelengths (250–500 nm).

2.3. Spectral measurements

A typical experimental system consisted of a quartz vessel containing a liquid and EDL, equipped with a reflux condenser, and placed to a microwave oven. The AVS-S2000 spectrometer with an optic fiber probe served for measuring and evaluating the emission spectra using the software package AvaSoft (Avantes BV). The spectrum was recorded after the light source was stabilized. The effect of the output power of the MW reactor was investigated in the Synthewave 402 MW instrument because, unlike domestic MW ovens, its power (30–300 W) can be adjusted continuously.

3. Results and discussion

The electrodeless discharge lamp is a glass tube filled with an excitable substance and sealed under a reduced pressure or a noble gas. A high frequency electromagnetic field (radio frequency or MW, 300–3000 MHz) can trigger gas discharge causing the emission of electromagnetic radiation. This phenomenon has been studied for many years and was already well understood in the 1960s [23]. EDL is usually characterized by a higher emission intensity than that of the hollow cathode lamps, a lower contamination due to the absence of the electrodes, and a longer lifetime [6]. EDLs operate due to free electrons in the fill that are accelerated by the MW field energy. They collide with the gas atoms and ionize them to release more electrons (the "avalanche" effect). The energetic electrons collide with the heavy-atom particles present in the plasma, thus exciting them from the ground state to higher energy levels. The excitation energy is then released as the electromagnetic radiation with the spectral characteristics according to the composition of the fill. There are a number of operating parameters [6], which have been recognized as influencing the electrodeless discharge lamp performance, such as temperature, nature and pressure of the fill gas, choice of the fill material, dimensions of the lamp envelope, the nature and characteristics of the MW energy coupling device, and the frequency and intensity of the MW energy.

The effect of temperature on EDL is closely associated with the fill gas pressure. At room temperature ($T \approx 300$ K) the gas mixture in the lamp has a pressure of approximately 2.6 kPa (0.026 atm), while in an operation mode the temperature of the plasma is most likely between 700 and 1400 K, and the pressure about 1 MPa (10 atm) [24]. The plasma includes strong non-equilibrium states due to high-energy particles. The plasma pressure influences the characteristics

of the radiation; it affects the mean free path of the particles and their collisional cross-sections. Pressure thus affects the number of collisions per unit of time. Lower-state atoms, which are outside the plasma but still within the lamp volume, have a lower temperature than the emitting atoms within the plasma. Therefore, their absorption line profile is narrower than the emission line profile from the plasma [24]. The spatial distribution and relative concentrations of emitting and absorbing atoms critically depend on the partial pressure of the element within the discharge volume: the higher the partial pressure of the element, the more lower-state atoms exist outside the emitting plasma. Therefore, more self-absorbed and -reversed atomic lines result from the simultaneous presence of emitting atoms and lower-state atoms.

The effect of temperature on radiance from EDLs was already investigated [24–26]. It was found that the optimum operating temperature for the mercury fill is $42\,^{\circ}C$ (for 253.7 nm line, 6^1S_0–6^3P_1). The output is reduced when the temperature is beyond optimum. Operation at high power or high temperatures can increase the intensity but, at the same time, reduce the lifetime and also lead to a broadening of the atomic line profile due to self-absorption and -reversal effects. The temperature dependence of emission intensities from mercury atoms at steady state for lines 365, 405, 436, 546 and 579 nm was also investigated [27]. The increase of the line emission intensities above $37\,^{\circ}C$ is explained by a decrease of the activation energy of mercury atoms or ions and by reduction of the number of bonds of a mercury atom in plasma. The influence of the lamp cooling by air stream, that can cause a lamp emission instability, was also examined [28]. If the vapor pressure in EDL is too high, the discharge may be limited or even extinguished completely [29].

3.1. Effects of temperature

In this work, the temperature-dependent emission spectra of Hg-EDL were determined in various UV-transparent hydrocarbons with boiling points of 35–174 $^{\circ}C$ (n-pentane, 35 $^{\circ}C$; n-hexane, 69 $^{\circ}C$; n-heptane, 98 $^{\circ}C$; n-decane, 174 $^{\circ}C$), which guaranteed a constant cooling down of the lamp temperature. The lamp temperature was, however, expected to be somewhat higher than that of the solvent. The relative emission peak intensity changes in n-pentane and n-decane are shown in Fig. 2. It is demonstrated that the relative intensity of the 254 nm band is highly dominant at a lower temperature in n-pentane while this band is negligible in n-decane, at the same time the 313 nm band becomes a principal wavelength in the UV region, which is well consistent with the above-described facts. The change of the solvent in a photochemical experiment would therefore dramatically influence the course of the reaction. Figs. 3 and 4 show a series of *relative* peak intensities (normalized on the 254 nm peak) at temperatures from 35 to 174 $^{\circ}C$ for two differently sized quartz EDLs. The spectra of both lamps present similar dependencies. Generally, the short
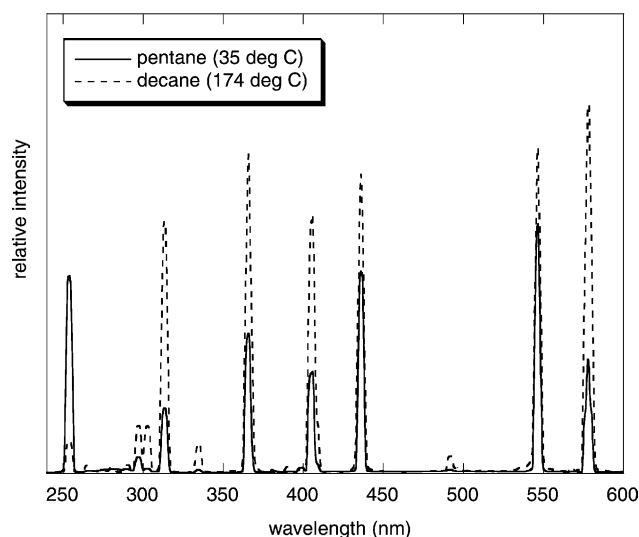

Fig. 2. Emission spectra of EDL in n-pentane and n-decane.

wavelengths (especially the 254 nm peak) are suppressed with increasing temperature.

3.2. Effects of the MW output power

The effect of the MW reactor output power was already investigated in our preliminary paper describing its influence on the Norrish type II reaction efficiency [12]. It was found that the reaction conversion increased with increasing MW power, which boosted the UV irradiance. Fig. 5 shows the emission spectra of a quartz Hg-EDL at two different output power values (30 and 300 W). Relative peak intensities were the same and their dependencies on the power are shown in Fig. 6. All values increased linearly at small power values and then leveled off. This means that the emission
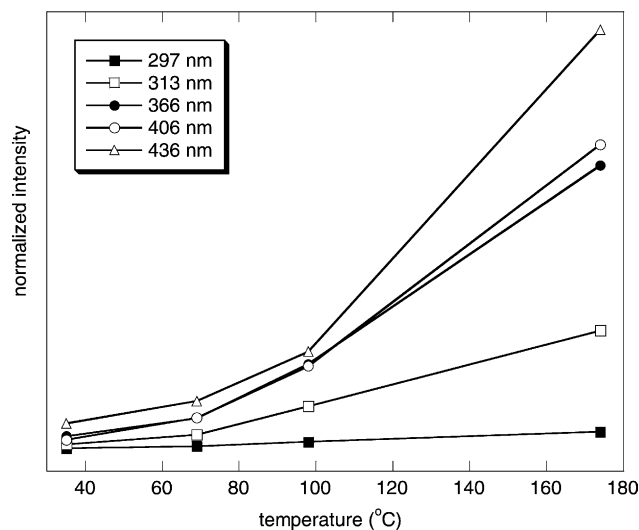

Fig. 3. Temperature dependence of the normalized emission bands in a 9 mm × 13 mm EDL.
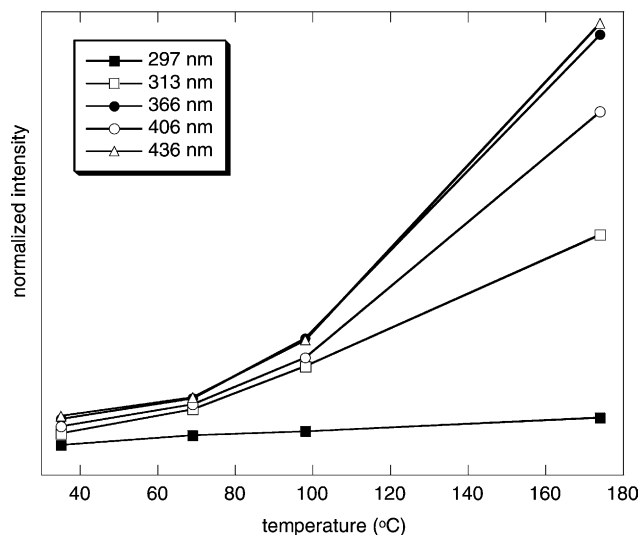
Fig. 4. Temperature dependence of the normalized emission bands in a 14 mm × 37 mm EDL.

Fig. 6. Output power dependence of the emission bands (a quartz EDL; Synthewave 402).

efficiency of the lamp has been saturated at ∼200 W power and EDL was not able to accept more MW energy (that was then dissipated to the environment). For routine experiments with EDLs, such an optimization of the power/emission efficiency ratio is highly recommended. The output power of a commercially available MW oven can be lowered by a cooling water in the tube inside the cavity [13], however, it had only minor effect on the lamp emission efficiency in our experiments.

A solvent, which absorbs MW radiation, reduced the intensities of all emission bands since it reduces the amount of MW energy that powers the lamp. The EDL spectrum in methanol (bp = 65 °C) is compared to that in hexane (bp = 69 °C) in Fig. 7. The actual temperature of
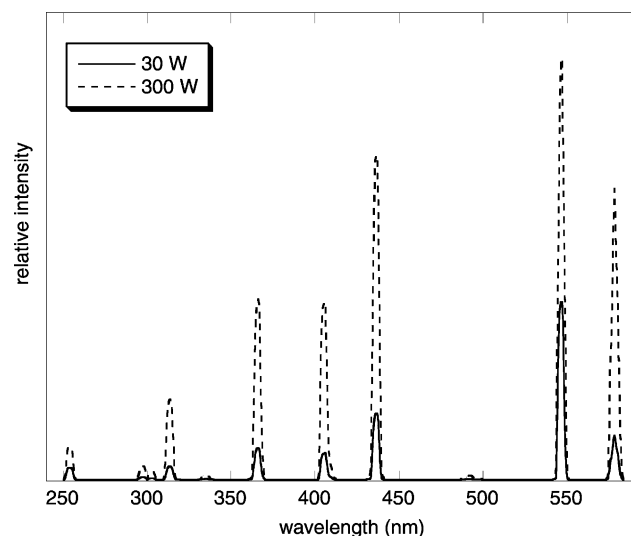
methanol could be little higher due to the superheating effect [17].

3.3. Effects of the EDL envelope material and solvents

Comparative conventional irradiation experiments with either quartz or Pyrex Hg-EDLs were already presented in our previous work [12]. The conversion of valerophenone in the Norrish type II reaction was lowered when a Pyrex Hg-EDL was used, which was explained by filtering off the part of the UV radiation. Fig. 8 shows a comparison of the emission spectra of quartz and as Pyrex Hg-EDLs. The Pyrex glass completely removed the 254 and 297 nm bands, however, the intensity of the remaining bands was the same. This

Fig. 5. Emission spectra of a quartz EDL at the 30 and 300 W output power (Synthewave 402).
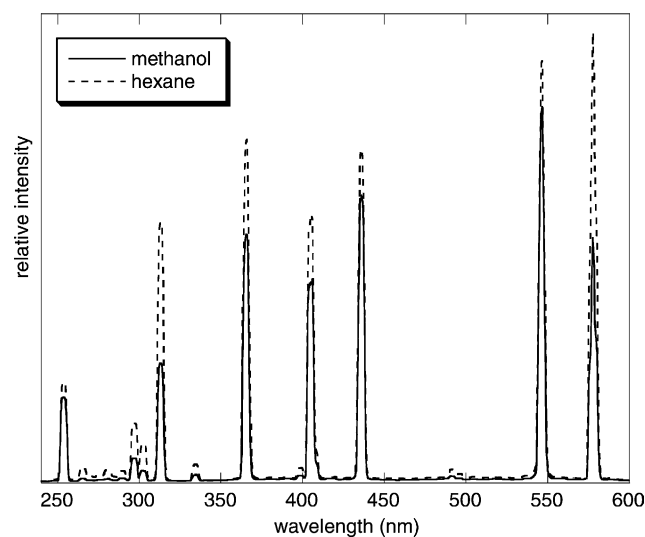

Fig. 7. Comparison of the emission spectra of a quartz EDL in *n*-hexane and methanol.
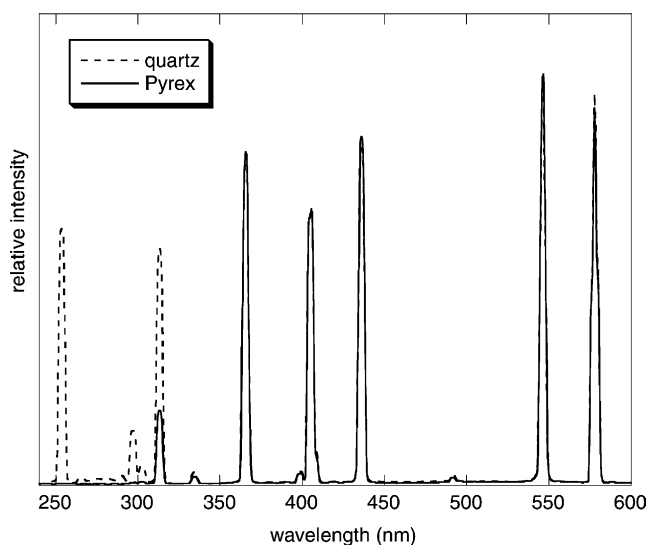
Fig. 8. A comparison of the emission spectra of quartz and Pyrex EDLs in *n*-hexane.

well explains the efficiency loss observed in photochemical experiments. The solvent can be also used as an internal UV filter. Benzene, for example, significantly suppressed the wavelengths below 280 nm (Fig. 9). Therefore, *n*-hexane or other non-polar solvents, that are transparent over 220 nm, are ideal in case a short-wavelength irradiation is required.

In conclusion, the aim of this paper was to show that the spectrum of the electrodeless discharge lamps can be easily modified by choosing a proper temperature, the EDL envelope glass material, or a solvent used in a photochemical reaction. In addition, the EDL emission intensity could be adjusted by changing the MW output power. Since the application of EDLs in photochemistry is very simple and
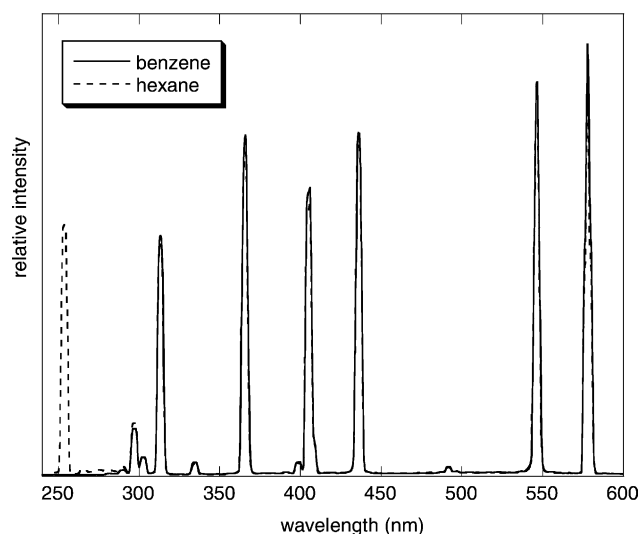
accessible to a broad spectrum of chemists, it could find its way into a conventional chemical laboratory. Studies of EDLs that contain other filling materials than mercury are currently under investigation.

Acknowledgements

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Fig. 9. A comparison of the emission spectra of a quartz EDL in *n*-hexane and benzene.