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The electrodeless discharge lamp: a prospective tool for photochemistry
Part 5: Fill material-dependent emission characteristics

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Dedicated to Professor Milan Potáček on the occasion of his 60th birthday.

Abstract

This work expands our previous research on an original photochemical reactor consisting of the electrodeless discharge lamp (EDL) inside a reaction mixture that generates ultraviolet radiation in the microwave (MW) field. The effects of temperature MW output power of the reactor, and EDL envelope material, were already published [P. Müller, P. Klán, V. Církva, J. Photochem. Photobiol. A: Chem. 158 (2003) 1]. Now we report on the emission characteristics (250–650 nm) of various EDLs containing different fill materials (Hg, HgI_2, Cd, I_2, KI, P, Se, and S). While distinct line emission peaks were found for mercury, cadmium and phosphorus fills, iodine, selenium and sulfur-containing EDLs emitted continuous bands. Sulfur-containing EDLs are proposed for phototransformations that are of environmental interest due to the emission flux comparable to solar terrestrial radiation. It is concluded that the right choice of EDL envelope fill material can be very useful in planning an efficient course of photochemical process without necessity of filtering off the undesirable part of the UV radiation by other tools, such as glass or solution filters or monochromators. Quantum efficiency measurements of the Norrish type II reaction were accomplished to compare usefulness of the EDLs in photochemical applications. Sulfur and phosphorus-containing EDLs were found as the most efficient sources of UV radiation.

Keywords: Photochemistry; Microwave; Electrodeless discharge lamp; Emission; Spectra

1. Introduction

Photochemistry in the microwave (MW) field [1] provides an opportunity to combine chemical activation by two distinctive kinds of electromagnetic radiation. While low-energy MW radiation ($E = 0.4$–$40\,\mathrm{J\,mol^{-1}}$ at $\nu = 1$–$100\,\mathrm{GHz}$) is usually responsible for dielectric heating causing the thermal chemical activation [2,3], UV/vis radiation ($E = 600$–$170\,\mathrm{kJ\,mol^{-1}}$ at $\lambda = 200$–$700\,\mathrm{nm}$) initiates the excited-state reactions. In the past 5 years, we have successfully utilized electrodeless discharge lamps (EDLs), which are able to generate UV radiation when placed into the MW field, in the microwave-assisted photochemistry studies [4–7]. The photochemical reactor consisting of an EDL inside the reaction mixture was proposed for the first time by Den Besten and Tracy [8], and later applied by Cirkva and Hajek [9]. Since a knowledge of spectral characteristics of EDLs is clearly essential for planning the photochemical experiment, the effects of the envelope material, MW output power, temperature and reaction conditions were recently investigated [10]. In the present study, we wish to describe how spectral characteristics of EDLs change when a standard mercury filling is replaced by a different material: HgI_2, Cd, I_2, KI, P, Se, and S. Quantum efficiency measurements of the Norrish type II reaction were accomplished to compare

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usefulness of some of the EDLs for photochemical applications.

2. Experimental section

2.1. Equipment

The spectral measurements were accomplished in a modified MW oven Whirlpool M401 (900 W), operating at 2450 MHz frequency as described elsewhere [10,11], 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. 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 [5,6]. Valerophenone irradiation experiments were carried out in a MW instrument Synthewave 402 (Prolabo, equipped with an IR pyrometer (validated using a fiber-optic thermometer Nortech ReFlex [6]), 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 [5]. In the experiments with EDLs, every liquid was immediately boiling since the lamps produce a considerable amount of IR radiation [11].

Electrodeless discharge lamps (EDLs) [10,11] were manufactured in the Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic [12]. The lamps were made of a 12 mm quartz (4 ml) or 20 mm Pyrex (9 ml) envelope tubing (of approximately 1 mm thick glass) of ca. 40 mm length, containing the corresponding filling, and sealed under 0.7 kPa argon atmosphere. Pyrex absorbs most of the UV radiation below 290 nm (Fig. 1).

Gas chromatography was accomplished on a Shimadzu GC-2010 apparatus. The UV–vis spectra of all chemicals were measured on a Shimadzu UV-1601 spectrophotometer and the envelope optical properties were measured on a Helios γ UV/vis spectrometer (Thermo Electron Scientific Instruments, USA).

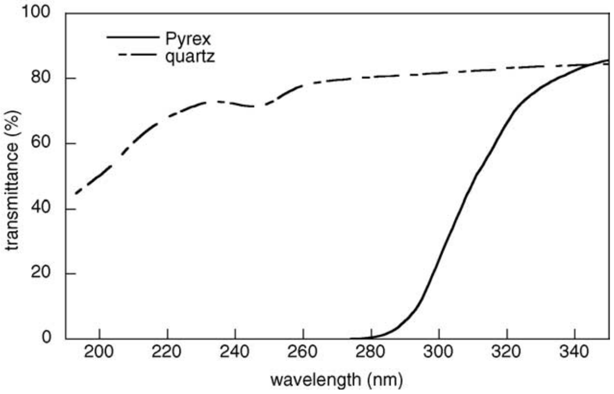

Fig. 1. Transmittance of quartz and Pyrex envelopes.

2.2. Chemicals

Valerophenone (>99%) and *n*-decane (>99%) were purchased from Sigma Aldrich Co. All chemicals were used as received. The quality of the solvent was checked by the UV–vis spectrophotometry and GC. The solvent absorbance values (versus air) were negligible throughout the tested range of wavelengths.

2.3. Spectral measurements

A typical experimental system consisted of a quartz vessel containing *n*-decane (boiling point 174 °C) and EDL, equipped with a reflux condenser, and placed to a microwave oven. The lamp inner temperature was, however, expected to be somewhat higher than that of the solvent as the cooling was not 100% efficient. 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 output power was controlled in the Synthewave 402 MW instrument, in which the MW power (30–300 W) can be adjusted continuously.

2.4. Quantum efficiency measurements

The *n*-decane solutions of valerophenone (0.001 M) were irradiated from EDL in a Synthewave S 402 reactor at 300 W output and a modified MW oven Whirlpool M401 (900 W) for 2–5 min. The only photoproduct followed for all reactants in Norrish type II studies was acetophenone, commonly used in the quantum efficiency measurements [6]. Cyclobutanols were co-formed in ∼10% and a minor photoproduct (<2% yield, assuming the same GC response factor as valerophenone) was also detected. Identification of acetophenone was based on ^{1}H NMR, ^{13}C NMR, and on GC comparisons with the authentic sample (Aldrich) [13]. Photoreaction conversions in all experiments were kept below 20% to avoid the photoproduct interference. Each sample was analyzed three times; in case that the values differed by more than 6% the measurement was repeated. The reproducibility, based on triple measurements, was ±12%.

3. Results and discussion

The electrodeless discharge lamp (EDL) is a glass tube filled with an inert gas under a lower pressure and with an excitable substance [1]. A high frequency electromagnetic field (radiofrequency or MW: 300–3000 MHz) can trigger gas discharge causing the emission of electromagnetic radiation. 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 an electromagnetic radiation with the spectral characteristics according to the composition of the fill. There are a number of operating parameters [1], which have been recognized as influencing the electrodeless discharge lamp performance, such as temperature [10], nature and pressure of the fill gas, choice of the fill material, dimensions and quality of the lamp envelope [10], the nature and characteristics of the MW energy coupling device, and the frequency and intensity of the MW energy.

The fill material is certainly the most important variable and this work describes emission spectral profiles of the EDLs containing the following compounds: HgI_2, Cd, I_2, KI, P, S, and Se, compared to the standard Hg fill. EDLs used had the same size and pressure of the fill gas and temperature was kept at 174 °C (boiling *n*-decane) in all measurements.

3.1. Mercury and cadmium EDLs

EDLs so far applied in photochemistry were based on mercury filling [4–7,11], emitting distinct sharp bands of relative intensities resembling the spectra of the conventional medium-pressure lamps (Fig. 2). The short wavelengths (especially the 254 nm peak) were found to be suppressed by increasing temperature as well as by using a Pyrex envelope [10]. In comparison, the use of a chemically very active mercury iodide had the advantage of providing an easy starting discharge: the HgI_2-EDL in a Pyrex envelope was a source of mercury emission lines (313, 365, 405, 436, 546, 577, 579 nm) and excited HgI^* molecules [14–16], which emit visible light as a small continuum band with maximum about 440 nm (Fig. 3).

Replacement of mercury filling by cadmium is known to change the spectral characteristics and provides new emission bands (229, 327, 347, 361 nm) [17]. Such a Cd low-pressure lamp with a metal antenna (a molybdenum foil) was recently developed by Florian and Knapp [18]. Fig. 4 shows a combined Hg/Cd-EDL emission to display both Hg (254, 297, 313, 365, 405, 436, 546, 577, 579 nm) and Cd (327, 347, 361, 468, 480, 508, 644 nm) bands. The 229 nm band of the cadmium emission was suppressed by increasing temperature. It has been observed that no inter-element (Cd–Hg) interferences occur in this lamp. A small amount of mercury (as vapors) was added to aid in starting a discharge due the lower volatility of cadmium. Simple Cd-EDLs without the antenna were found not very useful for photochemical experiments due to their low ability to be initiated and maintain a steady emission intensity. A Hg/Cd filling combination excluded those difficulties. The relative band intensities can be adjusted by the amount of the elements in the lamp.

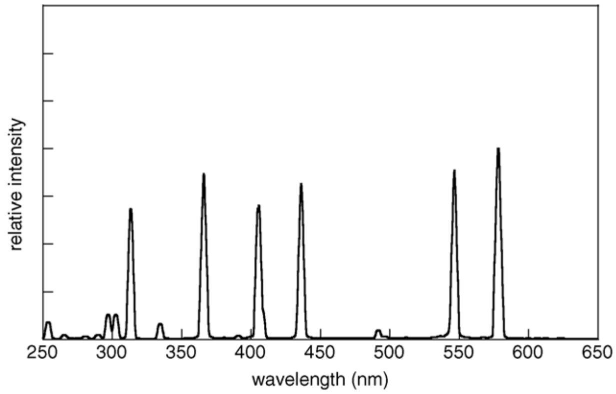

Fig. 2. The emission spectrum of Hg-EDL in *n*-decane (quartz envelope; 0.7 kPa argon atmosphere; 10 mg of mercury).

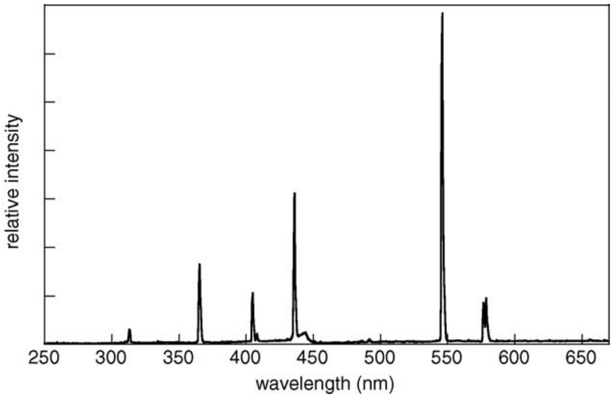

Fig. 3. The emission spectrum of HgI_2-EDL in *n*-decane (Pyrex envelope; 0.7 kPa argon atmosphere; 5 mg of mercury(II) iodide).

3.2. Iodine and potassium iodide EDLs

Figs. 5a and b show the spectra of quartz and Pyrex-EDLs filled with iodine vapors, nicely illustrating a filter effect of the Pyrex glass. Excited iodine forms excimers that are utilized to generate spontaneous emission of high efficiency (342 nm band) as bound-free transitions [19–21]. Due to comparatively broad bands in its spectrum, especially in the region of 280–360 nm, I_2-EDL seems to be relatively universal and applicable to a majority of reactions requiring the pho-

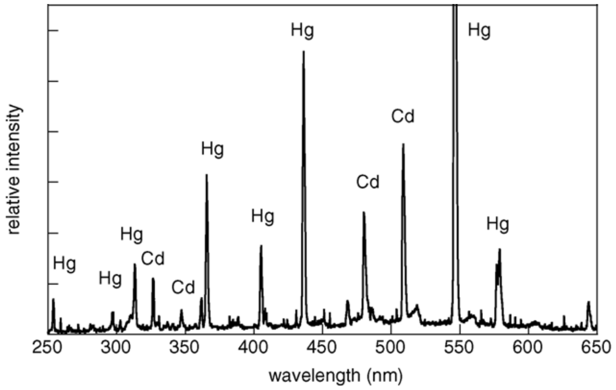

Fig. 4. The emission spectrum of Cd/Hg-EDL in *n*-decane (quartz envelope; 0.7 kPa argon atmosphere; 5 mg of cadmium; Hg vapors).

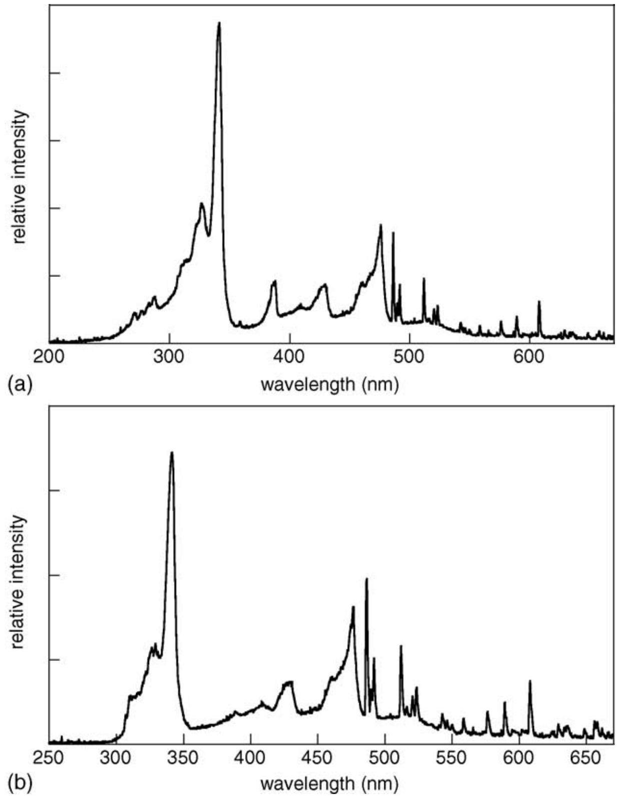

Fig. 5. The emission spectrum of I_2-EDL ((a) quartz; (b) Pyrex) in *n*-decane (0.7 kPa argon atmosphere; iodine vapors).

tochemical initiation. However, I_2-EDLs could not be easily ignited and they also proved to be very unstable. By contrast, lamps filled with potassium iodide (KI-EDLs) proved to be substantially more stable and having the spectral characteristics very similar to those of I_2-EDLs (Fig. 6). Water (486 and 656 nm) and sodium D-line (589 nm) were identified as impurities in this spectrum, probably due to devitrification and etching of the glass wall.

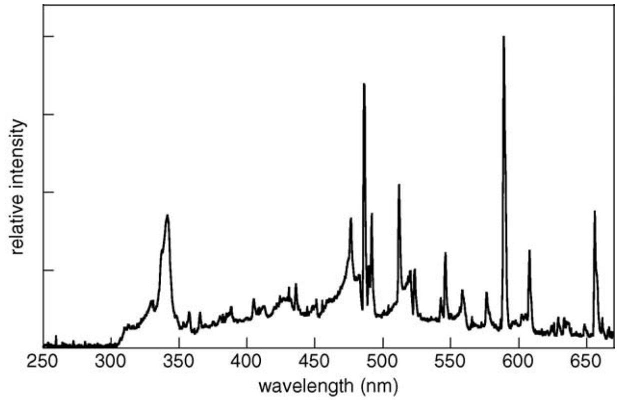

Fig. 6. The emission spectrum of KI-EDL in *n*-decane (Pyrex envelope; 0.7 kPa argon atmosphere; 4 mg of KI).

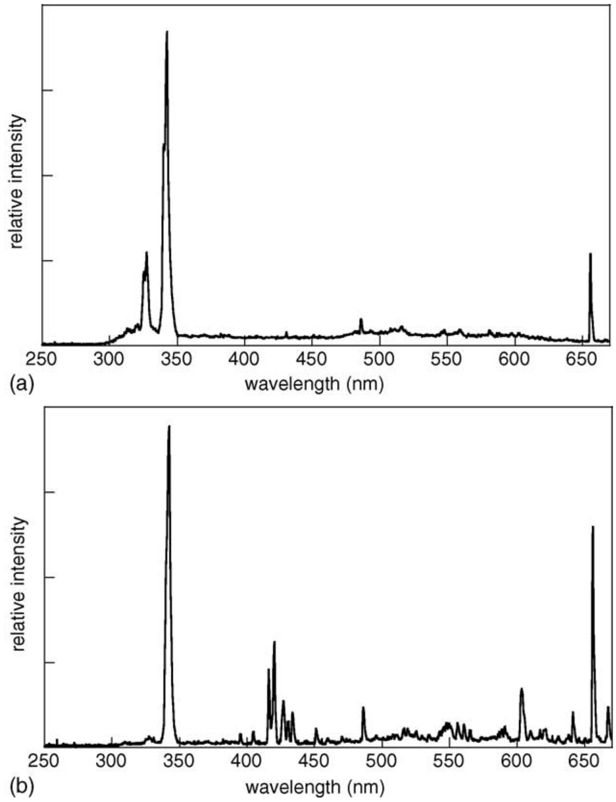

Fig. 7. The emission spectra of P-EDLs in *n*-decane (Pyrex envelope; 0.7 kPa argon atmosphere): (a) 1 mg of P; (b) 10 mg of P.

3.3. *Phosphorus EDLs*

Figs. 7a and b depict the spectra of Pyrex EDLs filled with different amounts of phosphorus (1 and 10 mg, respectively). Spectra of both lamps contained distinct emission bands in the region between 341 and 343 nm [22]. The phosphorus component (as diatomic P_2) emits in the violet to UV region of the spectrum. The 325 and 327 nm bands were found only in the spectrum of the lamp filled with a lower amount of the element. On the other hand, the lamp containing 10 mg of P had a more diverse emission spectrum in the vis region. A relative diminishment of peaks at shorter wavelengths in line with an increasing amount of the filling material (thus in line with an increasing partial pressure) fully corresponds to the general trend (e.g., differences between emission spectra of high-pressure and low-pressure discharge lamps) [10]. Water (486 and 656 nm bands) was identified as an impurity in the spectrum due to etching of the Pyrex wall. EDLs filled with phosphorus proved to be very stable even at temperature as high as the boiling point of *n*-decane (174 °C).

3.4. *Selenium and sulfur EDLs*

EDLs filled with selenium (Fig. 8) were found to be relatively stable but their emission spectra contained rather insignificant bands in the UV region at the expense of radiation

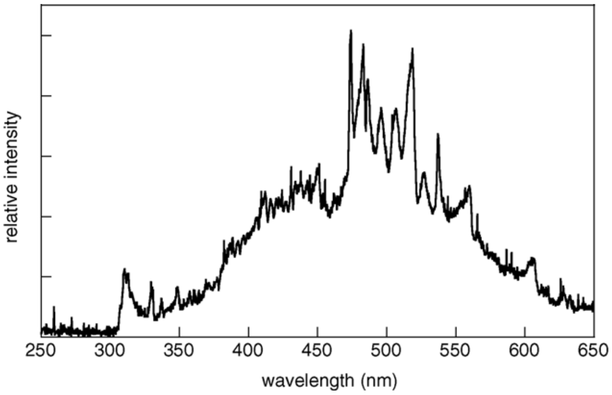

Fig. 8. The emission spectrum of Se-EDL in *n*-decane (Pyrex envelope; 0.7 kPa argon atmosphere; 2 mg of Se).

in the visible region. Thus, their low intensities somewhat limit the application of Se-EDLs in photochemical experiments.

In contrast to Se-EDLs, EDLs filled with sulfur seemed to be predetermined for use in numerous photoreactions. The discovery that a sulfur plasma produced high quality efficient light was announced in 1992 [23]. However, the intense S_2–Ar UV emission was observed already in 1980 [24] and was utilized as a molecular radiator in discharges for possible laser applications [25]. Molecular sulfur is currently in use as a high-power, high-pressure discharge medium for the generation of visible light [26–29]. These MW-powered discharges emit primarily UV–vis light due to the self-absorption of the UV radiation from the S_2 molecules [30]. Sulfur is chemically benign to the glass envelope. The electrodeless sulfur lamps tend to have their peak light output around the blue-green region (400–550 nm) of the spectrum [31]. The spectral shift is dependent on the amount of sulfur [32], i.e. the spectral band is about 490 nm at 1.3 mg cm^{-3} of S, while about 515 nm at 2.5 mg cm^{-3} of S. The decrease of signal and the spectral red shift in line with an increasing amount of fill-material are attributed to the increasing pressure, giving self-reversal and line-broadening. Similar dependent characteristics were observed for electrodeless lamps including selenium or tellurium [33,34] when the spectral red shift is enhanced with the molecular mass.

Here, the emission spectra of S-EDLs containing a low amount of sulfur (1 mg; Fig. 9a) were practically continuous and covered a broad range of wavelengths in the UV–vis region (310–550 nm). When the filling amount was increased (12 mg), the visible part of the spectrum became more important at the expense of the UV radiation (Fig. 9b). This emission spectrum is similar to that of Se-EDL.

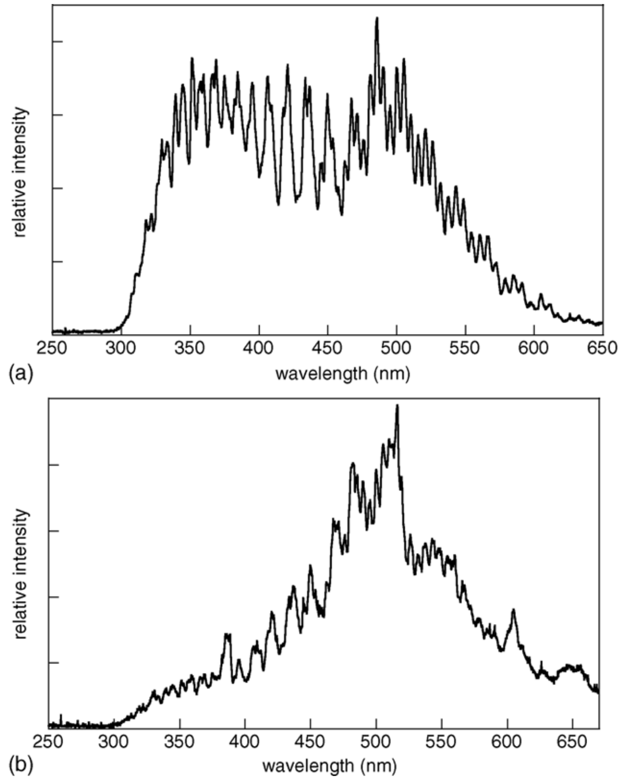

Fig. 9. The emission spectra of S-EDLs (Pyrex envelope; 0.7 kPa argon atmosphere): (a) 1 mg of S; (b) 12 mg of S.

We propose that sulfur-containing EDLs, after optimizing the amount of sulfur in the lamp and the temperature of the ambient reaction system, could be used for phototransformations that are of environmental interest as depicted by the comparison with a typical solar spectral actinic flux (Fig. 10). Photodestruction of anthropogenic pollutants in aqueous media or photocatalysis by titanium dioxide reactions could serve as application examples.

3.5. Quantum efficiency measurements

The effect of the fill on the EDL emission intensity was investigated using the Norrish type II reaction actinometry system (Table 1). Excited valerophenone with hydro-

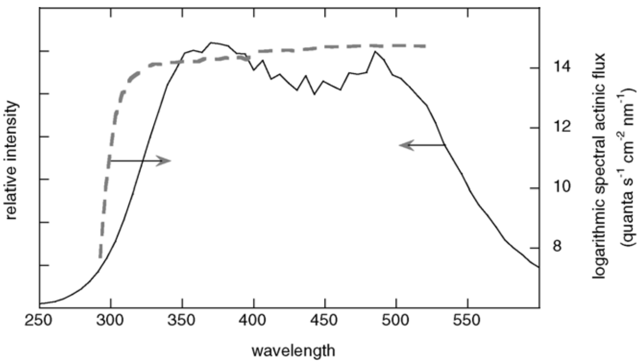

Fig. 10. The smoothed emission spectrum of S-EDL in *n*-decane (—; Pyrex envelope; 0.7 kPa argon atmosphere; 1 mg of S) compared with the calculated solar spectral actinic flux at the Earth's surface for cloud-free skies and at solar 45° zenith angle 5 (- - -) [35].

Table 1
Valerophenone ($c = 10^{-3}$ mol l^{-1}) conversion rates for various EDLs in a domestic MW oven and in the Synthewave apparatus relative to those of Hg-EDL[a]

Filling material	Relative conversion rates (min^{-1})	
	Domestic MW oven	Synthewave S 402
Sulfur (1 mg)	6.5	6.3
Selenium (2 mg)	0.5	1.1
Phosphorus (2 mg)	4.3	2.6
Mercury (1 mg)	1.0	1.0

[a] Measured in *n*-decane; EDLs of the same size: Pyrex envelope; 0.7 kPa argon atmosphere.

gen on γ-carbon reacts on its alkyl chain via the triplet state to produce triplet 1,4-biradicals, which intersystem cross to the short-lived singlet biradical that can cleave (to acetophenone), cyclize, or disproportionate back to the starting ketone [36]. Efficiency of the acetophenone formation served for comparing the emission intensities of four EDLs containing sulfur, selenium, phosphorus, or mercury. Valerophenone absorbs efficiently up to 366 nm ($\varepsilon_{313} = 55.2$ and $\varepsilon_{366} = 4.0$ l mol^{-1} cm^{-1} in benzene), where all EDLs exhibited strong emission. The experiments were accomplished both in the modified domestic MW oven and in a monomode Synthewave S 402 apparatus. The irradiation periods ranged from 3 to 5 min and the maximum overall VP conversions did not exceed 20% to avoid the photoproduct interference.

All tested EDLs demonstrated a better stability and higher emission efficiency when powered by focused microwaves (Synthewave 402). This phenomenon was most pronounced in the case of Se-EDL. In contrast, the performance of phosphorus EDL was almost the same in both MW devices, probably due to high emission stability even when powered by unfocused microwaves in the modified domestic MW oven. The highest conversion rate in both domestic MW oven and the Synthewave 402 instrument was reached with the S-EDL, which proved to be somewhat unstable in a domestic MW. Thus, a source of homogenous MW field is highly recommended for possible photochemical applications.

In conclusion, spectral characteristics of EDLs are definitely of general interest for microwave-assisted photochemical experiments. The right choice of EDL envelope fill material can be very useful in planning an efficient course of a photochemical process without the necessity of filtering off the undesirable part of the UV radiation by other tools, such as glass or solution filters or monochromators. The distribution of radiation was markedly different in all line emission spectra of mercury-, cadmium or phosphorus-containing EDLs and in continuous spectra of iodine, selenium and sulfur-containing EDLs. The most efficient UV lamp, S-EDL, was suggested to be an excellent choice for environmental applications, where a source of solar-like radiation is needed.

Acknowledgements

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