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Reactors for simultaneous application of UV light and ultrasound on the reaction mixture and their modifications for kinetic studies

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Abstract

This paper describes four photo-sonochemical reactors for simultaneous application of UV light and ultrasonic irradiation on the reaction mixture. Two of them allow a follow-up of the reaction course by UV–vis spectroscopy continuously and are therefore regarded as suitable for kinetic studies.

Keywords: Photo-sonochemical reactor; Quantum yield; Light intensity; Photochemical kinetic

1. Introduction

Ultrasound is the irradiation with a frequency between 20 kHz and 1 GHz. The velocity of ultrasound in the liquid is between 1000 up to 1600 m/s and depends on the quality of the liquid medium [1]. The effect of ultrasound on the chemical reaction is a function of several physical parameters [2–5] such as the shape of the reactor and accessories, which are inserted into the reaction mixture (thermometer, stirrer, etc.). Two types of sonochemical equipments are being used in laboratories. The first type is the ultrasonic cleaning bath, which can be modified by cooling device, timer, etc. The efficiency of ultrasound energy transfer from the ultrasound emitor (piezoelectric crystal) to the reaction medium is maintained to be low in this equipment. In the second type of the reactor, ultrasound is generated by piezoelectric crystal and is transmitted via a horn into the reaction medium. This latter technique provides a relatively better ultrasound energy transfer.

The aim of our study was to design reliable photo-sonochemical reactors and to describe them in details. There was only one published paper [6] describing such reactors before we constructed our first one [7]. Since that time, several papers were published depicting the good photo-sono reactors [8–12]. However, all of these reactors presented some weakness or advantages.

2. Results and discussion

At the beginning of our study we carried out photo-sono reactions in the ultrasonic cleaning bath. The photochemical reactor was designed as a compact item where position of UV light and the cuvette was kept fixed (Fig. 1) [7]. The source of UV light (S) was used 50 W high pressure Hg lamp with a point discharge (Narva HBO 50). The spectral region of the applied UV light can be change by the insertion of the appropriate interference filter (F). UV light was made to pass through the optical cuvette (2–10 cm long) (C). The intensity of light was measured with the help of light-guide (G) and photodiode (D). The temperature was kept constant by a ring shape glass tube inside ultrasonic cleaning bath with circulated cooling water. The cuvette (C) was easily removed from the reactor and transferred into a UV–vis spectrophotometer to monitor the reaction course. After monitoring the spectra, cuvette was placed in the same position of the reactor again. The advantage of the removable cuvette was simplicity of degasification of the reaction mixture. In the case of “silent “experiments, it was possible to stir the reaction mixture in the cuvette by electromagnetic stirrer.

Work with such a reactor is far from being convenient, especially due to the following reasons. It is difficult to find a right

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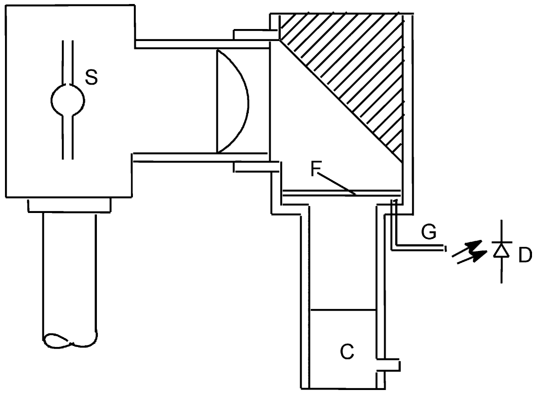

Fig. 1. Photochemical reactor which can be used in ultrasonic cleaning bath.

position of the photochemical reactor in the ultrasonic cleaning bath. The cuvette (or the reaction flask) must be installed in the same place of the cleaning bath for good reproducibility of the results. However, this is not the end of the problems. The ultrasonic cleaning bath was constructed in a way to achieve great amplitude of oscilation with a low input of electrical power. The bath is an active part of the ultrasound generator. A change in the amount of water in the ultrasonic bath or using normal tap-water instead of re-distilled water had a profound effect on the efficiency of ultrasonic irradiation.

To solve the problems mentioned above, we designed two new reactors with the ultrasound generator T (piezoelectric crystal) with working frequency (20 kHz) and (250 W) input powers. The reactor depicted in Fig. 2 had the piezoelectric crystal (T), which was fixed on the bottom glass housing of photochemical reactor by a thin layer of epoxy glue. High-pressure mercury lamp (L) (type RVK 125, Tesla Holesovice, CzR) was used as a source of UV light. The lamp was inserted in immersion finger of the reactor (S) (Simax, $\lambda_{\mathrm{irr}} > 290\,\mathrm{nm}$) and closed with a ground-Teflon stopper (B). The constant temperature of the reaction medium was maintained by circulation of water in the immersion finger. The volume of the reactor was 150 ml and the reaction mixture was stirred by nitrogen flow.

Low-pressure 8 W discharge mercury lamp (L) (Osram) was used as the source of UV light in the reactor as shown in Fig. 3. UV lamp was inserted into the immersion finger (K), which was safeguarded by the Teflon closure (B) on the top of the reactor. This set up facilitated a change in the energy of the UV light used for irradiation. UV lamps with different luminophore ($\lambda_{\max} = 254$, 313 or 366 nm) could also be used. The advantage of such UV lamps is that they produce just a very small amount of heat. The temperature inside the reactor is kept constant by the circulating water in the outer walls of the reactor (P). The volume of the reactor was 60 ml and the reaction was carried out in inert atmosphere. The same reactor could also be used in the "silent" experiments [without horn (T)] and the reaction mixture can be stirred by a magnetic stirrer. Electric power source of UV lamp allowed controlling the output of UV lamp continuously from 0 up to 10 W. The weak point of this reactor was that the layers of luminophore of the lamp were corroded by sonication and could peel off, which might cause the change of intensity and spectral region of UV light.

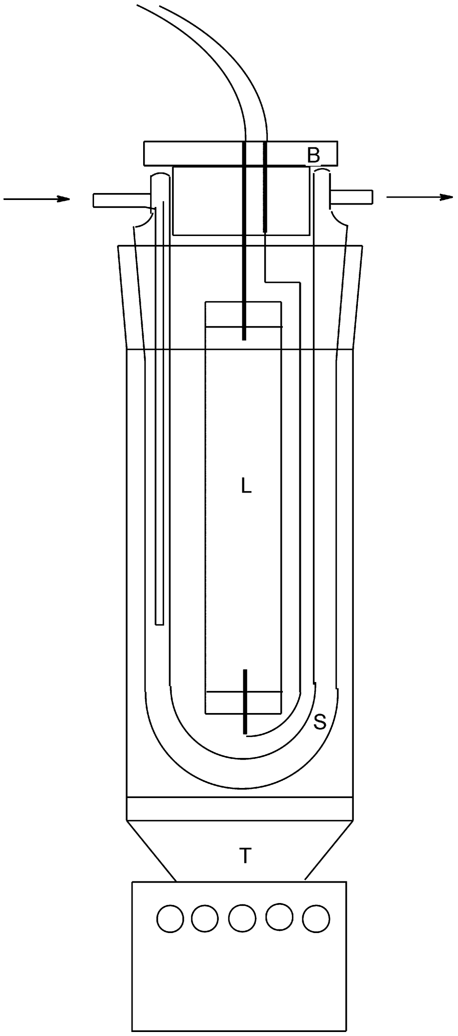

Fig. 2. Photochemical reactor with a piezoelectric transformer (T).

The advantage of reactors depicted in Figs. 2 and 3 is that the position of the ultrasound emitter and reaction flask cannot be changed. This fact has a positive effect on the reproducibility of photo-sonochemical experiments.

The reactors described above did not allow continuously monitoring of the reaction course or to study the kinetics of the reaction. We made a modification of the reactor (Fig. 3) to solve this problem (Fig. 4). Spectrophotometer DU 2000 (Ocean Optics, Inc.) was used to monitor a reaction course. The source of UV light was used for irradiation of the reaction mixture as well as for monitoring of the reaction course. The light from the UV emitter is partially absorbed by the reaction mixture and is transmitted through the outer walls of the reactor where it is monitored by the light-guide S, which is connected with the DU 2000 spectrometer. This spectrometer register transmitted UV light in selected time intervals. Light distribution was not homogeneous in the photochemical reactor. We used a bifurcated wave-guide for monitoring the reaction course in two places. The resulting signal represented the sum of spectra from these two monitoring places. Commercially available light-guides allowed the monitoring of the reaction course in more than two places.

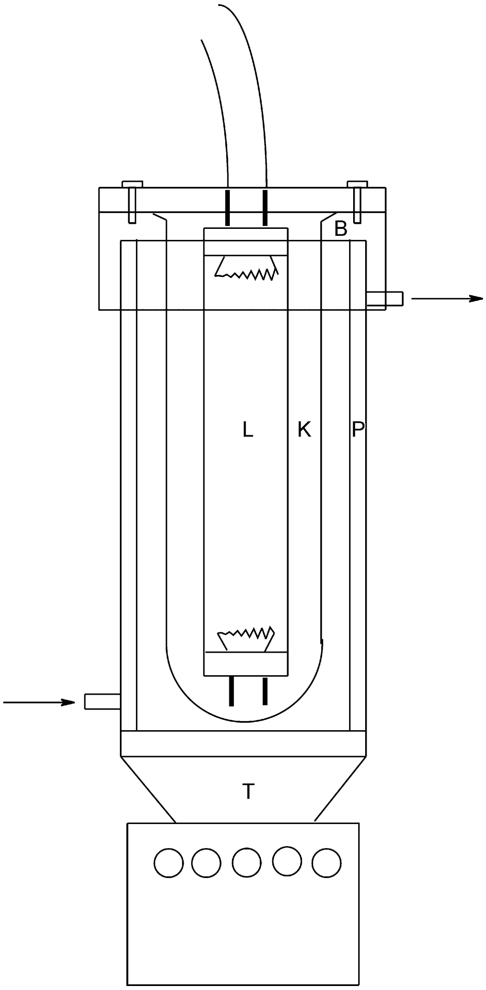

Fig. 3. Photochemical reactor with a piezoelectric transformer (T).

On the other hand, we found out that monitoring in one place is sufficient in the case of a well-stirred reaction mixture. The reactor had to be constructed from such material, which does not hamper the light transmission in the region where the substance absorbs the UV light and a part of emitted light must be transmitted outside of the reactor. This condition can be easily fulfilled by using a more powerful light emitter or by changing the concentration of the photochemically active compound. This system can be used also for measurements of quantum yields of photochemical reactions.

The second type of the reactors allowed continuously irradiation of the reaction mixture with UV light and ultrasound and also continuously measured UV–vis spectra. The reactor in Fig. 5 consists of temperature controlled cuvette block (T). The position of the cuvette block is in the cuvette space of Array spectrometer (HP 8452 A). As the UV light was used 150 W xenon UV lamp (S) (Osram). The light focused on the cuvette (C) by lens (L) in the direction perpendicular to the optical beam of the spectrometer. Spectral region can be changed by using an interference filter (F). As the ultrasound source (US), commercial ultrasound horn-type generator was used (Branson, 40 kHz), which allowed continuous change of ultrasound power. Ultrasound horn (H) is inserted into the cuvette (C) (Fig. 5). It is possible to use either a commercial cuvette or a cuvette of our construction, which is depicted in Fig. 6.

This cuvette was designed especially for photo-sonochemical experiments allowing work in the inert atmosphere. Ultrasound energy is transmitted into the reaction mixture by ultrasonic horn (H), which is immersed into water (B) in glass vessel of a special shape. Cooling of the ultrasonic horn is carried out by circulation of the cooling medium in the cuvette jacket. The reaction mixture (R) is in the lower part of the cuvette having a cylinder shape directly under the tip of US horn. The reaction mixture is illuminated in perpendicular direction by UV light

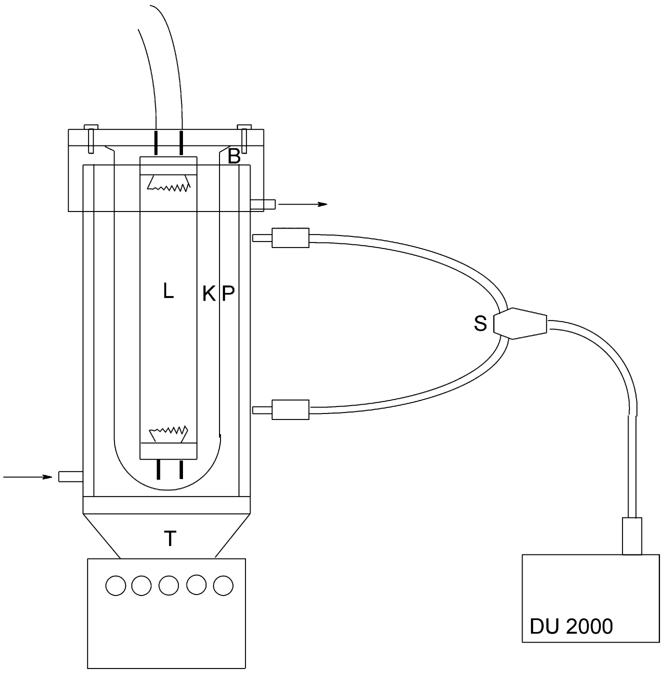

Fig. 4. Modification of a preparative photochemical reactor for kinetic experiments.

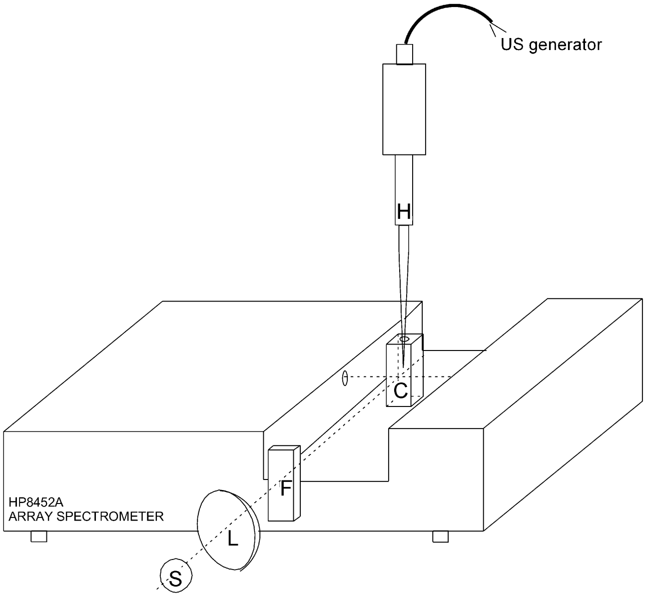

Fig. 5. Photochemical reactor for kinetic study of ultrasound effect on photo-sonochemical reaction.

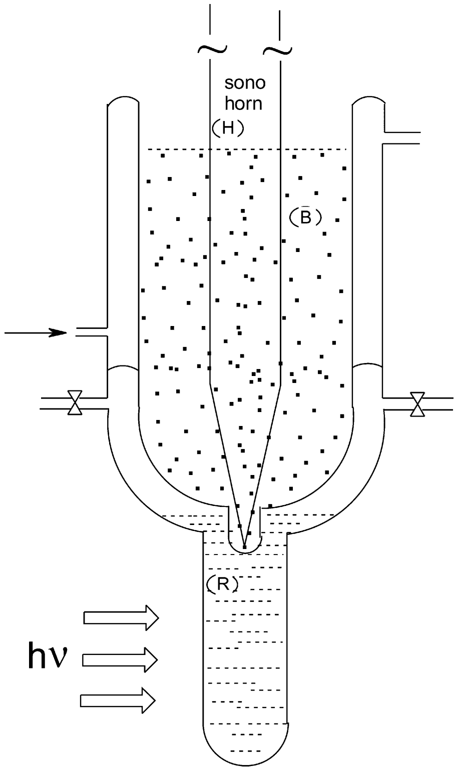

Fig. 6. Cuvette designed for photo-sonochemical experiments.

and monitored at the same time. There are two basic conditions which must be fulfilled at work with this cuvette. The first one is that the mutual position of the light source and the spectrometer must always be the same, which is especially important for measurements of the intensity of UV light. This can be secured by mechanical connection of both parts or by their fixing on an optical bench. We used the optical bench in this case. The second very important condition is to keep the position of the horn constant in the cuvette. The horn of US source was fixed on stand. This arrangement allowed us to fix very precisely the position of the horn in two coordination axis. The position of the horn in the third coordination axis is maintained by fixation of the support with spectrometer. It is imperative to keep these two conditions constant for good reproducibility of the results.

Another crucial condition is that the light intensity must be held constant during photochemical experiments. The change of emission intensity of the lamp as a function of time affected the precision of quantum yields determination. For the reason mentioned above, the intensity of photolytic light passing through the reaction mixture was measured continuously by spectrometer Ocean Optics and at the same time was measured (perpendicular on flow of photolytical light) by spectrum of reaction mixture by spectrometer HP 8452.

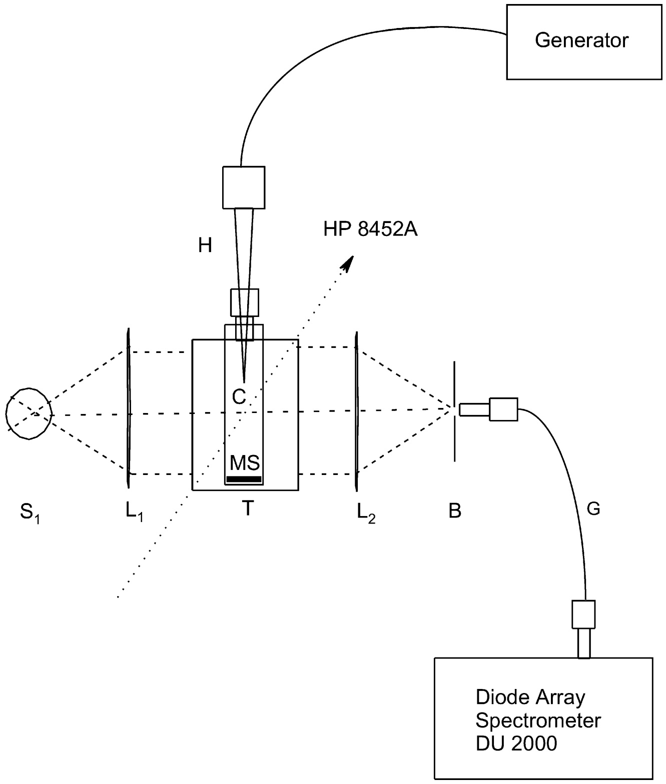

Fig. 7. Arrangement for the measurement of the quantum yields of photo-sonochemical reactions.

Thermostatic block (T) located in the cuvette compartment of the array spectrophotometer HP 8452A is depicted in Fig. 7. This block can be used in sonochemical experiments where the reaction mixture is stirred by sonication as well as by stirring bar (MS) in the silent experiments. Stirring bar (MS) is located under the base of the optical cuvette. The photochemical light (S_1) passing through the lenses (L_1, L_2) and cuvette (C) is focused on the connector of the wave-guide (G) and is directed to the diode array spectrometer DU 2000, which monitors the intensity of transmitted light as a function of wavelength (Fig. 8).

It is possible that the intensity can change during the integration time. Therefore the range of the spectrophotometer (DU 2000) should be restricted for this measurement. Restrictions can be performed by two ways. The first restriction is to select

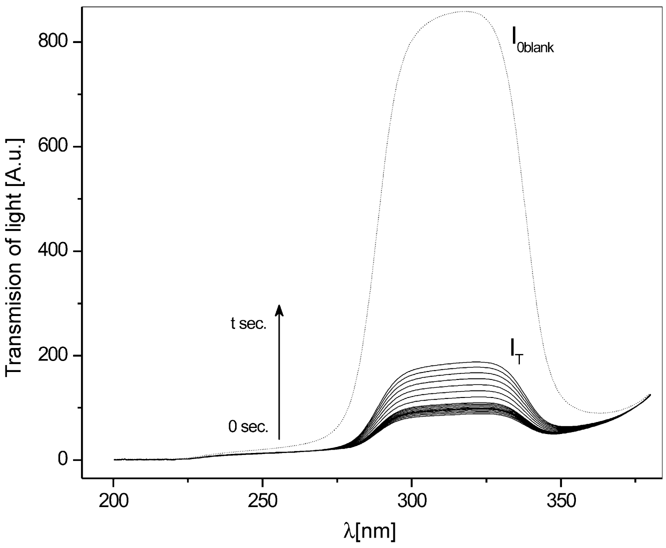

Fig. 8. Change of the intensity of transmission photolytical light (λ_{max} = 313 nm) during photolysis of azobenzene ((- - -) the cuvette with methanol, $I_{0\,blank}$; the cuvette with azobenzene in methanol, I_t).

the proper integration time. When the proper integration time is selected, the measured value is accumulated in the memory of the computer of the spectrometer. The second possible restriction is to set up the intensity of transmitted light passing through the slit (B) (Fig. 7) in a value which cannot overload the measuring system until the end of the reaction. During photochemical experiment, we measured the transmitted (photolytically active) light by spectrometer Ocean Optics as well as the UV–vis spectra (concentration of the substance) of the reaction mixture by spectrophotometer HP 8452A.

The absolute values of light intensity of the lamp (S_1) I_0, intensity of the transmitted light I_T or intensity of absorbed light I_a can be obtained by calibration of the system. Intensity of the absorbed light can be calculated by Eq. (1):

$$I_a = I_0 - I_T \tag{1}$$

Total light absorbed by substance A ($\Delta\Phi_A$) in the reaction mixture, which consists of several other substances ($A+B+\cdots i$), can be expressed by Eq. (2) or (3), where α is the linear absorbance coefficient (m^{-1}) characterizing the substances in the reaction medium:

$$\Delta\Phi_A = \left[\frac{\alpha(A)}{\alpha(A)+\alpha(B)+\cdots\alpha(i)}\right] SI_0 \times \left[1 - e^{-[\alpha(A)+\alpha(B)+\cdots\alpha(i)]l}\right], \tag{2}$$

respectively,

$$\Delta\Phi_A = \left[\frac{\alpha(A)}{\alpha(A)+\alpha(B)+\cdots\alpha(i)}\right] SI_a \tag{3}$$

The values of denominator in Eq. (3) are obtained by measuring the spectra of the reaction mixture by spectrophotometer HP in the equal spectral range as light used for photolysis. The value of the numerator (A) can be obtained either from UV–vis spectrum of the substance (A) especially if the reaction products do not absorb UV–vis light in the same region as substance (A) or by another analytical method for example GC, LC chromatography. I_a is the intensity of absorbed light by all components of reaction mixture in the same spectral range as emission spectrum of UV source used for photolysis. The total light flux absorbed by substance A can be used for quantum yields calculation. This system even allows measuring quantum yields when the polychromatic light is used.

Described reactors have been used in photo-sonochemical experiments described in our papers [13–20].

3. Conclusion

Several new reactors were described for simultaneous irradiations of the reaction mixture by UV light and ultrasound. A special cuvette was designed for photo-sonochemical experiments with high precision and good reproducibility of the experiments. Modifications of photochemical reactors were also described allowing to study kinetics either of photochemical or photo-sonochemical reactions. With this intent, described instruments were used in our photo-sonochemical studies [13–20].

Acknowledgements

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