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Photosensitized oxidation of citronellol in microreactors

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Abstract

The present study describes the examination of a photochemical model reaction in two different reactor types: a batchreactor and a microreactor. In order to evaluate both reactors' efficiency, they had been compared in terms of their respective space–time yield and photonic efficiency. In this model reaction we performed the oxidation of citronellol by singlet oxygen generated with the aid of a photosensitizer. As sources of radiation, light emitting diodes (LED) were used for the first time.

Keywords: Microreactor; Photoreaction; Singlet oxygen; Citronellol; LED; Ru-complex

1. Introduction

In recent years, microreaction technology has become an independent field of research. Here, their small dimensions and the resulting advantages are still the centre of interest. Some of the most interesting advantages of microreactors are laminar flow, short molecular diffusion distances, large specific interfacial areas and excellent heat transfer characteristics [1]. Due to these features, microreaction technology has found access to many sections of chemical process engineering. Reaction parameters like pressure, temperature, residence time and flow rate are much easier to control in reactions with small volumes than in conventional reactors. By this, the hazard potential of highly exothermal or explosive reactions is clearly decreased [2]. Even reactions with toxic substances or those carried out under high pressures are easier to realize [3].

Compared with previous studies on microreaction technology, there are only a few examples of photochemical applications in microreactors [4–7]. The few examples in the literature include the photochemical coupling of benzophenone to benzopinacol [4] and the photochemical chlorination of alkylaromatics [5]. Another study presents aspects of the photooxygenation of 4-chlorphenol in a photomicroreactor by means of TiO_2 as the photocatalyst [6]. A photosensitized reaction with the aim to effect the singlet oxygen mediated oxidation of α-terpinene to ascardiole with high yields was also accomplished in a microreactor [7]. Apart from the listed advantages, irradiation of the reaction medium with light of a specific wavelength is still a key problem for selective photochemical reactions [7] in complex geometrical structures such as microreactors.

This study focuses on the investigation of a dye-sensitized reaction in a photomicroreactor. We choose the photosensitized oxidation of citronellol by singlet oxygen as a model reaction. In contrast to the commercial process we used a ruthenium polypyridyl complex as the photosensitizer which displays higher photostability and quantum yields of singlet oxygen formation compared with rose bengale, the conventional sensitizer. Further we will introduce a minimised light source, because the efficient irradiation in a microreactor will determine the photochemical efficiency dramatically. Due to these prerequisites set by the reactor and the reaction we choose nearly monochromatic light emitting diodes (LED) as an irradiation source. They are sufficiently small in size and low in cost and their wavelength can be adapted to the dye employed. In this way, detrimental photochemical isomerisation reactions can be minimised while optimising the necessary energy input. A comparison of the microreactor with a conventional reaction setup according to the laboratory scale was used to determine the specific influence of the reaction vessel on the process and result of the reaction.

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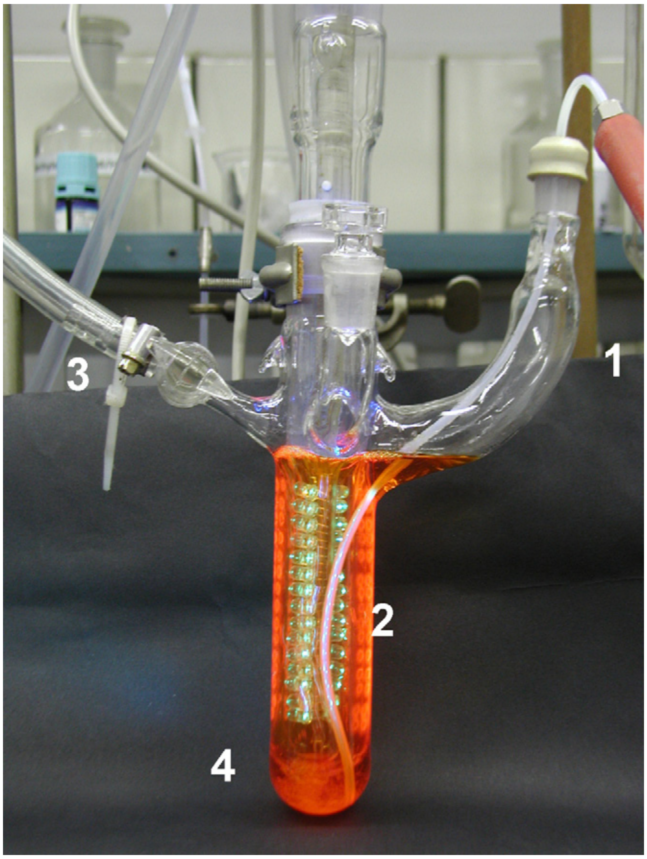


Fig. 1. Schlenk-reactor: 1, air supply; 2, LED light source; 3, exhaust valve; 4, stirrer.

2. Materials and methods

2.1. Reactors

For the following investigations we used two different types of reactors. The first one is a modified Schlenk-tube (Fig. 1) with different ports. On the first port, the reactor carries a reflux cooler. As Fig. 1 shows, the second port is used to saturate the solution with compressed air. The light source is placed in the middle of this reactor. It is separated from the reaction solution by a glass-sleeve.

Table 1
Technical data of both reactor types

	Schlenk-reactor	LTF-microreactor
Volume	40 ml	0.27 ml
Illuminated area	15.19 cm^2	6.87 cm^2
Illuminated volume	7.46 ml	0.27 ml

The second reactor is an HT-residence glass (Borofloat) microreactor (Little Things Factory GmbH, Ilmenau, Germany). This HT-residence tool consists of half-round meandering channels with a width of 1 mm, in which the reaction medium will be illuminated. The reaction medium is held available in a cooled double-wall storage container with an additional reflux cooler. In this container, the saturation of the reaction medium with compressed air is realized. The light source is embedded in a special holster in order to get an equal illumination (Fig. 2). Fig. 2 depicts the experimental setup for the microreactor experiments.

Table 1 lists the technical data for both reactors. Fluidic connections were made by 1/8 in PEEK tubing and flangeless fittings (Upchurch Scientific). The reactant flow was driven by a peristaltic pump (Ismatec IPC#4, tubing 0.51 mm Tygon F-4040-A).

2.2. Reaction, conditions and analysis

In order to characterize and compare both reactors, we used the oxidation of citronellol via singlet oxygen. This reaction is easy to handle and has a technical background. The photochemical oxidation of (*S*)-(−)-β-citronellol (Merck) is used to produce (−)-rose oxide as an elemental substance in the perfume industry [8]. We only investigated the first reaction step to characterize our reactors: the direct oxidation of citronellol via singlet oxygen ($^1O_2$) (Scheme 1). This first step is the real photoreaction in which (*S*)-(−)-β-citronellol is oxidized with $^1O_2$ and via an ene-reaction to give both peroxides 2 and 3.

Singlet oxygen is formed from triplet oxygen ($^3O_2$) by means of a photosensitizer and light, due to a spin allowed triplet–triplet

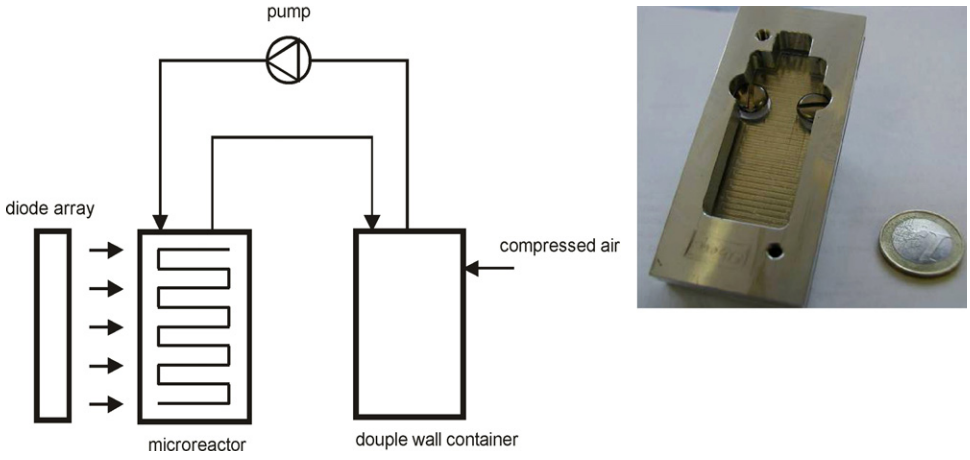
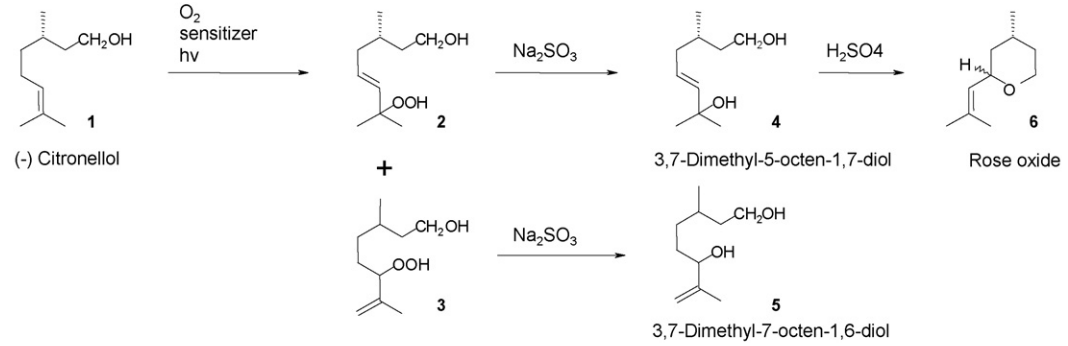


Fig. 2. Experimental setup microreactor and microreactor with retainer for the diode array.



Scheme 1. Formation of rose oxide by oxidation of citronellol with singlet oxygen.

energy transfer. Photoactive compounds populating a long-lived triplet excited state ($^3PS^*$) are known for their ability to produce singlet oxygen. Beside the formation of singlet oxygen, triplet oxygen can be transferred by a triplet excited state of a photosensitizer into other highly reactive species like superoxide anion ($O_2^{\bullet-}$). A light induced energy transfer leads to singlet oxygen, while the negative charged superoxide anion radical results from a photoelectron transfer. The two species can be interconverted to each other. But a photo-induced electron transfer from $^3PS^*$ to $^3O_2$ to give $O_2^{\bullet-}$ formation depends on an electron donor to regenerate the photooxidized photosensitizer. In principle the superoxide anion can also react with citronellol to a radical cation to give rose oxide [17]. Under the reaction conditions used in this study such a reaction mechanism is not possible.

Many substances are known for their ability to produce singlet oxygen. Porphyrins [9], some ruthenium complexes [10], but also many dyes like rose bengale or methylene blue are able to generate $^1O_2$. The commercial process uses rose bengale for the formation of singlet oxygen [8]. For our investigations, we decided to use Ru(^{t}bpy)$_3$Cl$_2$ (tris(4,4′-*tert*-butyl-2,2′-dipyridyl)-ruthenium(II)-dichloride) [15] for the singlet oxygen production. In contrast to rose bengale, the ruthenium complex has a much higher stability towards oxidation by $^1O_2$ and a higher quantum yield for singlet oxygen production [11].

For the quantitative analysis of the reaction process, especially the photooxygenation of citronellol and the formation of the peroxide products, we preferred high pressure liquid chromatography (HPLC) instead of gas-chromatography (GC) which is generally used for terpene analysis [12]. A quantification of the samples with GC proved to be very complicated due to the complex purification procedures necessary. Another advantage of using HPLC is the fact that the peroxides are detectible in spite of their known instability [13]. For this reason we isolated the hydroperoxides **2**, **3** as reference substances for the HPLC analysis. Chromatograms were collected with a standard reversed-phase column (Dionex C18 RP 4.6 mm × 250 mm), and the eluent was a mixture of 70% acetonitrile (Merck, LiChrosolv) and 30% 0.1 M phosphoric acid (VEB Laborchemie, Apolda). The flow rate was 1 ml/min, and the detection wavelength was 215 nm. The experiments have been quantified by means of the peak area of citronellol. In addition some samples were reduced to the diols **4** and **5** and analyzed by GC.

In order to confirm our analytical measurements, we isolated the first step products: the 1,6- and the 1,7-citronellolhydroperoxide (products **2**, **3**, Scheme 1). After the reaction of 5.45×10^{-3} mol citronellol and 5.45×10^{-5} Ru(^{t}bpy)$_3$Cl$_2$ in 40 ml ethanol which took 5.5 h, ethanol was evaporated under reduced pressure, and the crude reaction mixture was dissolved in diethyl ether in order to separate the photosensitizer from peroxides and citronellol. For the same reason, the ether extract was washed several times with water. For purifying the peroxides, the organic phase was evaporated under reduced pressure and added to the top of a silica gel column. The eluent was a mixture of ether/petrol ether 1:2. After eluting the citronellol and by-products, both hydroperoxides were washed off the column with pure ether. The mixture of the hydroperoxides was characterized by ^{1}H and ^{13}C NMR. For both substances all signals could be assigned and correspond to the literature values [12] (characteristic signals: (*E*)-7-hydroperoxy-3,7-dimethyloct-5-en-1-ol (**2**): ^{1}H NMR (400 MHz, CDCl$_3$), $\delta = 1.32$ (6H, s, 2Me–C7), 5.59 (1H, ddd, H5), 5.61 (1H,d, H6); ^{13}C NMR (50 MHz, MeOD), $\delta = 19.8$ (Me–C3), 29.4 (2Me–C7), 29.7 (C3), 39.1 (C2), 39.5 (C4), 60.9 (C1), 76.3 (C7), 130.1 (C5), 135.0 (C6) and 6-hydroperoxy-3,7-dimethyloct-7-en-1-ol (**3**): ^{1}H NMR (400 MHz, CDCl$_3$), $\delta = 1.72$ (3H, s, Me–C7), 4.05 (1H, t, H6), 4.84 (1H, d, H8a), 4.91 (1H, d, H8b); ^{13}C NMR (50 MHz, MeOD), $\delta = 17.2/17.09$ (Me–C7), 19.4/19.5 (Me–C3), 28.0/28.1 (C3), 32.6 (C5), 32.8 (C4), 39.4 (C2), 60.9 (C1), 77.0/77.6 (C6), 114.05 (C8), 143.0 (C7)). The ratio of the hydroperoxides was determined from the characteristic ^{1}H NMR data. The amounts of **2** and **3** were measured by integrating the C5, C6 proton, and the two C7-methyl group NMR signals, respectively. A typical experiment yielded approximately 60% of **2** and 40% of **3**.

2.3. Light sources

For illumination, we used two different types of light sources. Both of them are based on LED-technology. They were specially built for each reactor in order to achieve the best performance. The main light sources are light emitting diodes (LED; Kingbright; $\lambda = 468$ nm type L-7113PBC-BLUE) which are commercially available. For the Schlenk-reactor we used an LED-stick

Table 2
Technical data of the diodes

Type:	LED T-1 3/4 (5 mm) SOLID STATE LAMP L-7113PBC-BLUE (InGaN)
Maximum intensity	2000 mcd
Radiation angle	20°
λ	468 nm
λ_Δ (full width at half maximum)	26 nm

consisting of 2 × 15 LEDs in a row with a length of 8.5 cm. The technical data of the LED are displayed in Table 2.

The light source we used for the microreactor was a diode array consisting of 4 × 10 diodes. It is specially designed for use in combination with the LTF-microreactor. Both light sources are variable in their light intensity. The light intensity was measured with an electrical power meter (InternationalLight; NIST Traceable RADIO-METER PHOTOMETER; IL1400A) with a UV-stabilized silicon photodiode detector (InternationalLight; SEL033).

2.4. General procedures

A 40 ml of an ethanol solution with (−)-β-citronellol (Merck) and Ru(^{t}bpy)$_3$Cl$_2$ in various concentrations were flushed for 20 min with compressed air (flow rate: 5.08 l/h) in a Schlenk-reactor. The reaction solution was stirred and illuminated for 5–8 h with a light intensity of 6.5 mW cm^{-2}. Samples were taken half-hourly to hourly. We used an XBO 450 W Xe-lamp (light intensity 12–16 mW cm^{-2}) for the comparison of rose bengale with the ruthenium photosensitizer. These reactions were carried out analogous to the ruthenium experiments. It also proved that it is possible to use the established HPLC method for the rose bengale experiments.

In case of the LTF-microreactor, 10 ml of a prepared (−)-β-citronellol/ethanol (0.1 mol/l) solution with Ru(^{t}bpy)$_3$Cl$_2$ (0.001 mol/l) were filled in a double-walled container with a reflux cooler and flushed with compressed air for 20 min (flow rate: 0.393 l/h). Then, the solution was continuously pumped through the microreactor in a loop where the illumination took place for about 60–70 h. The light intensity varied from 1 to 7.98 mW cm^{-2}. Samples were taken twice a day.

3. Results and discussion

3.1. Influence on the reaction conditions

In a first step, the reaction parameters like dye ratio, light intensity or the influence of the educt concentration in the Schlenk-reactor were examined in order to determine the ideal conditions for both experiments. The dye–citronellol ratio plays an important role for the course of the reaction, since the dye concentration will determine the concentration of singlet oxygen. In comparison to the commercial photosensitizers (rose bengale), ruthenium is very expensive which is only partially compensated by the increased photostability. Because of this aspect we tried to decrease the ratio photosensitizer/citronellol (RPC, Ratio Photosensitizer citronellol). Fig. 3 shows the reaction rate of different ratios of ruthenium/citronellol as a function of the photooxygenation of citronellol and time. The higher the photosensitizer ratio, the faster is the photooxygenation of citronellol. However, there is still a significant photooxygenation of citronellol at a RPC of 1:10,000.

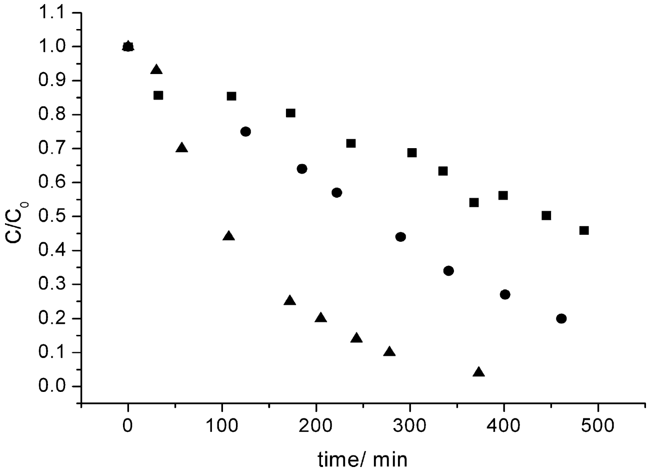


Fig. 3. Photooxygenation of citronellol in different photosensitizer ratios: (▲) 1:100; (●) 1:1000; (■) 1:10,000; $C_{\text{citronellol}} = 0.15$ mol/l; $T = 48$ °C.

During our investigations, another point of interest was the comparison of our photosensitizer Ru(^{t}bpy)$_3$Cl$_2$ with the commercially available photosensitizer rose bengale which is also used in the commercial process. Fig. 4 shows the photooxygenation of citronellol with both photosensitizers by using an XBO 450 W Xe-lamp emitting light between 50 and 1600 nm. The total light intensity for our experiment was 12–16 mW cm^{-2}.

We choose a Xe-lamp for this comparison, because the absorption behaviour of both dyes is completely different, Fig. 5. The quantum yield Φ_Δ of the photosensitized generation of singlet oxygen is 0.68 for rose bengale (in ethanol) and 0.83 for Ru(bpy)$_3$Cl$_2$ (in methanol) (structurally related to the used Ru(^{t}bpy)$_3$Cl$_2$ [16]. After a reaction time of 400 min the citronellol concentration of the ruthenium-sensitized photooxygenation

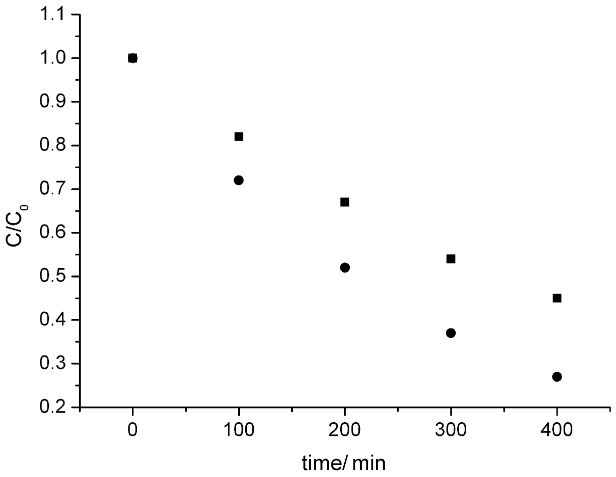


Fig. 4. Photooxygenation of citronellol by different photosensitizers: (■) Ru(^{t}bpy)$_3$Cl$_2$; (●) rose bengale; ratio citronellol/dye 1:100; start concentration 0.1 mol/l.

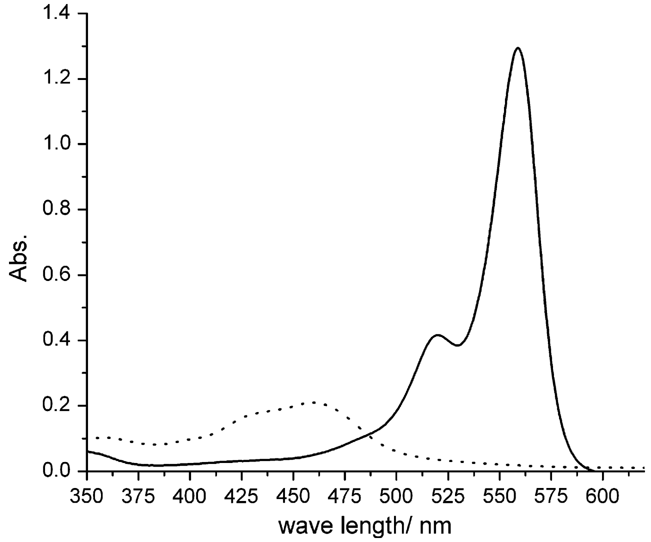


Fig. 5. Absorption spectra of Ru(^{t}bpy)$_3$Cl$_2$ (0.1 mmol/l ethanol) (dashed line) vs. rose bengale (0.01 mmol/l ethanol).

was two times higher than that of the rose bengale-sensitized reaction. The conversion rates for citronellol show that rose bengale is about twice as efficient as the ruthenium complex Fig. 4.

3.2. *Comparison of the Schlenk-reactor and the LTF-microreactor: photonic efficiency and space–time yields*

The main aspect in our work is the comparison of both reactor types. For this comparison it is very convenient to compare photonic efficiency and space–time yields for the Schlenk-reactor and the microreactor. For the characterization of conventional photocatalytic processes it is important to determine the quantum yields. However, the measurement of quantum yields is very difficult in technical setups of the kind we employed for our investigations. In our case, it is more useful to perform the characterization by means of the photonic efficiency ξ [14]. It derives from the relation between the reaction rate d[R]/dt and the incident monochromatic light or the absorbed photon quantity, respectively. If monochromatic light is used for illumination, ξ is defined as follows:

$$\xi = \frac{\mathrm{d}[R]/\mathrm{d}t}{I_0} \tag{1}$$

In our experiment, the emission wavelength was 468 nm and can be regarded as nearly monochromatic. The photon flux (I_{ph}) for the LED-stick was 3.665×10^{-7} mol/s ($I_0 = 6.15\,\mathrm{mW\,cm^{-2}}$), and 8.38×10^{-8} mol/s ($I_0 = 3.0\,\mathrm{mW\,cm^{-2}}$) for the diode array. For the Schlenk-reactor, the radiated area was determined at 15.14 cm^2 (with regard to the radiation angle of the LED), and for the LTF-microreactor at 6.78 cm^2. Concerning the reaction rate, the initial reaction rates were chosen. Regarding the radiated volume of the LTF-microreactor, its total volume of 270 μl was estimated because it can be assumed that the reaction takes place in the whole volume of the channels which are 0.5 mm deep.

Table 3
Photonic efficiency for the different reactor types

	ξ
Schlenk-reactor	0.022
LTF-microreactor	0.048

Concerning the radiated volume in the Schlenk-reactor, only the actually radiated reaction volume was assumed, supposing that the intermixing of the reaction solution is not ideal and that the reaction of the singlet oxide only takes place in the illuminated region. The accuracy in determining the photonic efficiency value depends on the exactness of information about the photon quantum absorbed in the reaction solution. In case of the Schlenk-reactor, the amount of absorbed photons ($3.0\,\mathrm{mW\,cm^{-2}}$) could be ascertained regarding the difference of the measured light intensities before and after passing the reaction solution. As to be seen in Table 3, the photonic efficiency could be determined from the initial reaction rates with regard to the presumptions made.

Another general possibility to compare both reactors is by means of space–time yields (STY). Space–time yields are directly influenced by the reactors' geometry and able to characterize both reactor types. STYs are referring to the amount (n) of converted citronellol (Ru/citronellol 1:1000) during the illumination and are represented by:

$$\mathrm{STY} = \frac{n}{V_{\mathrm{R}}^{t}} \tag{2}$$

where V_{R} is the reactor volume and t is the time.

Fig. 6 shows the space–time yields at different times within the course of the experiments carried out in the Schlenk-reactor. The highest STY has been detected for a concentration of 0.13 M citronellol. The volume of the Schlenk-reactor was 40 ml, and the volume of LTF-microreactor 0.27 ml. In direct comparison between the microreactor and the Schlenk-reactor it is obvious that after 20 min reaction time the STY is about one order of magnitude higher in a microreactor than in a Schlenk-reactor (Fig. 7).

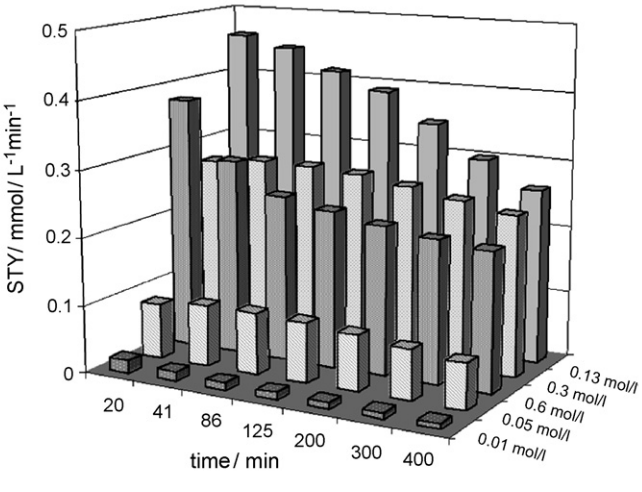


Fig. 6. Space–time yield for the reaction of citronellol with ^{1}O$_2$ in the Schlenk-reactor. The Ru:citronellol ratio for these different experiments was 1:1000. The z-axis shows the different start concentration on citronellol.

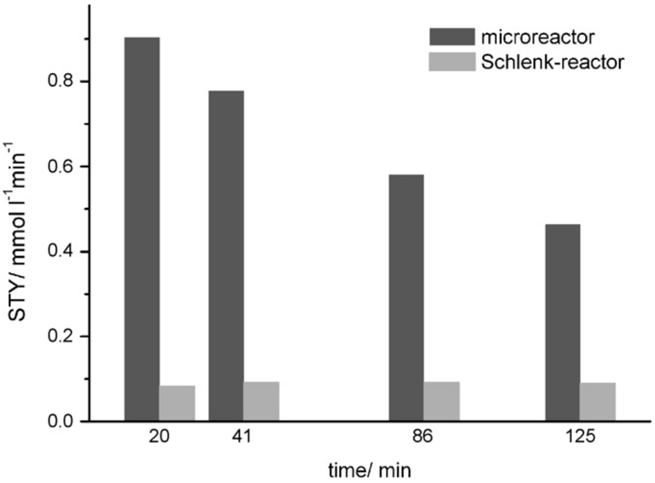


Fig. 7. Space–time yields of the microreactor (start concentration 0.06 mol/l) vs. Schlenk-reactor (start concentration 0.05 mol/l).

4. Conclusion

In the present study, the photosensitized citronellol-oxidation chosen as a model reaction could successfully be transferred into a microreactor. With this, a number of difficult and challenging technical questions concerning the experimental setup could be solved. By means of foregoing experiments carried out in a Schlenk-reactor, an optimization of the conditions of the chosen model reaction could be achieved. Above all, the HPLC could be established as a standard method for product analysis, which represents a great improvement compared to product analysis by means of GC–MS. Due to the highly complex reaction mechanism as well as the many and often insufficient determinable kinetic data, up to now a complete kinetic characterization of the model reaction could not ensue. The employment of LED's as light source combined with the chosen photosensitizer exemplifies the high potential of this irradiation source within chemical technology for light driven processes. A slight advantage of the LTF-microreactor over the Schlenk-reactor resulted from the calculations concerning the space–time-turnovers and the photonic efficiencies. Future investigations will focus more on mechanistic questions, i.e. how the reactor types influence the ratio of both products.

Acknowledgments

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