

Oxygen Exclusion from the Organic Solvents Using Ultrasound and Comparison with Other Common Techniques Used in Photochemical Experiments

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Received 27 April 2004

We compared three different methods for exclusion of oxygen from organic solvents. Removal of oxygen was determined by quenching of anthracene fluorescence in acetone, propan-2-ol, chloroform, heptane, and benzene. The best degassing method was found to be freeze-pump-thaw method and bubbling of nitrogen through the solution. The least effective was ultrasound method. The best degassing by ultrasound was observed in acetone and propan-2-ol.

Oxygen is known as an effective quencher of the triplet excited states. For this reason it is necessary to carry out the photochemical reactions without oxygen in the solution. Oxygen can be removed from solution by bubbling of reaction mixture with inert gas. The vacuum technique at 0.0133 Pa (3 or 4 freeze-pump-thaw cycles) and the application of ultrasound are the other ways, which would exclude oxygen from the reaction mixture. Last 15 years the attention was paid to the study of influence of ultrasound on the classical chemical reactions. There is no doubt that ultrasound affects the chemical reactions in cavitation mode [1, 2]. There are two types of cavitation: transient and stable [3]. Just transient cavitation causes the degassing of solutions. Cavitation process is affected by the different factors like solvent properties, reaction temperature, irradiation frequency, irradiation power, and the presence of dissolved gases [4, 5]. Except of cavitation, the processes in the liquid media could be affected by acoustic flow, resulting in stationary sinuous flow which is produced by application of ultrasound energy on nonhomogeneous solid–liquid systems [6].

Homogeneous photochemical reactions are suitable model for studying the influence of ultrasound. Concentration of excited species depends on their distance from the source of light. Cavitation and acoustic flow can change this concentration gradient in the photochemical reactor. If the concentration of the excited species becomes independent of the distance, the re-

action rates should be the same at any point in the solution [7, 8].

The main goal of this work was to examine the influence of different factors on the ultrasonic degassing of the reaction mixture and to compare this method with other frequently used methods.

EXPERIMENTAL

Anthracene (Merck, > 99 %) was recrystallized twice from ethanol. Acetone, benzene, chloroform, heptane, and propan-2-ol (Lichrosolv grade, Merck) were used without further purification. All fluorescence emission spectra were recorded at 25 °C using HITACHI F-2000 fluorescence spectrophotometer at excitation wavelength 350 nm. Excitation slit was set to 20 nm and emission slit to 10 nm.

Some experiments were carried out in sonochemical reactor – transducer S₁ (Fig. 1). It is a sandwich piezoelectric transducer (57 mm diameter, 20 kHz, 16 W cm⁻²) attached by an epoxy resin to the bottom of a water-cooled photochemical reactor. The another used equipment was ultrasonic microtip horn – transducer S₂ (40 kHz), 3 mm in diameter, fitted to a Branson Sonifier 250 and three ultrasound intensities at power settings P₁ ((2.0 ± 0.3) W cm⁻²), P₂ ((3.7 ± 0.5) W cm⁻²), and P₃ ((5.7 ± 0.5) W cm⁻²) were employed.

The LP VS-35B high-vacuum diffusion pump was used at 0.133 Pa.

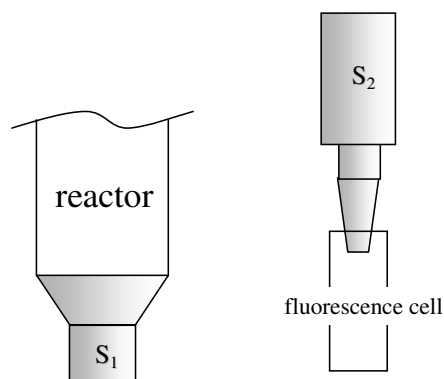


Fig. 1. Sonochemical reactor with transducer S_1 and titanium rod transducer S_2 .

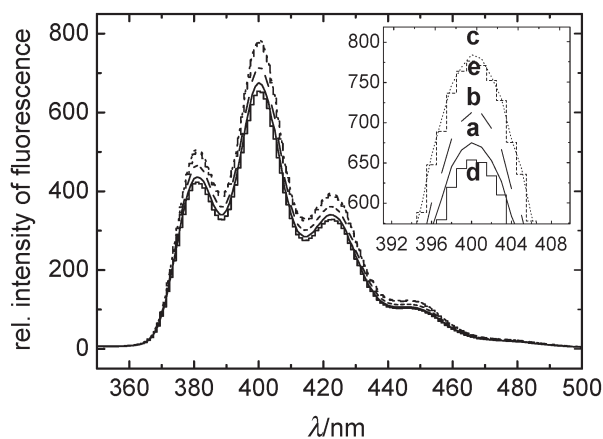


Fig. 2. The change of fluorescence intensity of anthracene in acetone ($c \approx 10^{-4}$ mol dm $^{-3}$) caused by modulation of oxygen presence in sonicated solution with argon atmosphere (transducer S_2 , power P_2): a) before sonication, b) after 5 s of sonication, c) after 125 s of sonication (first limit point), d) after saturation with air (60 s), e) after 125 s of sonication (second limit point).

Sonication

Transducer S_1

Solutions of anthracene ($c \approx 10^{-4}$ mol dm $^{-3}$) in acetone or propan-2-ol were sonicated in the certain time periods. The part of solution was placed into fluorescence cuvette with septum cap and was kept under the argon atmosphere. Fluorescence spectra were recorded in the certain time intervals until the limit state was reached.

Transducer S_2

The same experiment was carried out in fluorescence cuvette with septum cap and with titanium rod immersed into the solution. Additional solvents were used.

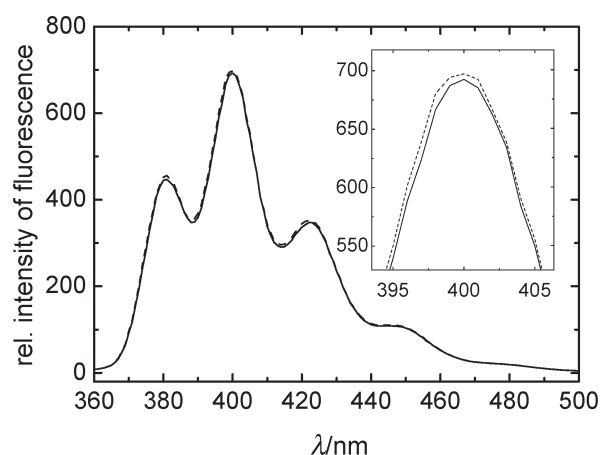


Fig. 3. The change of fluorescence intensity of anthracene in acetone ($c \approx 10^{-4}$ mol dm $^{-3}$) caused by modulation of oxygen presence in sonicated solution (125 s) without argon atmosphere (transducer S_2 , power P_2): — before ultrasound application, - - - after ultrasound application.

RESULTS AND DISCUSSION

Three different methods of solution degassing were compared in this study. Measuring the oxygen solubility in organic solvents involves special experimental technique [9]. For the monitoring of oxygen presence we used anthracene as a fluorescence marker. Fluorescence intensity of anthracene depends on the presence of oxygen in solution, which can be determined from the Stern—Volmer equation for the fluorescence quenching [10]

$$\frac{1}{K_{O_2}} \left(\frac{\Phi_f^0}{\Phi_f} - 1 \right) = [O_{2\text{solution}}]$$

where Φ_f^0 and Φ_f are the quantum yields of the fluorescence marker without and with oxygen and K_{O_2} is the Stern—Volmer constant for oxygen quenching.

Two different equipments for ultrasound application were also used (Fig. 1). Sonotransducers S_1 and S_2 are described in the literature [11—13].

Fig. 2 depicts the fluorescence spectra of anthracene in acetone with argon atmosphere before and after ultrasound application.

Sonication of solution caused decreasing of the concentration of oxygen with simultaneous increasing of fluorescence intensity of anthracene. We observed the reversibility of this process after saturation of “125 s sonicated solution” with air. After saturation of solution with air we applied ultrasound again. The inert atmosphere over sonicated solution (no bubbling) is necessary during or after sonication. Redissolving of air occurs if there is no argon over the sonicated solution. Without argon atmosphere there is no change of fluorescence intensity of anthracene after sonication (125 s) (Fig. 3).

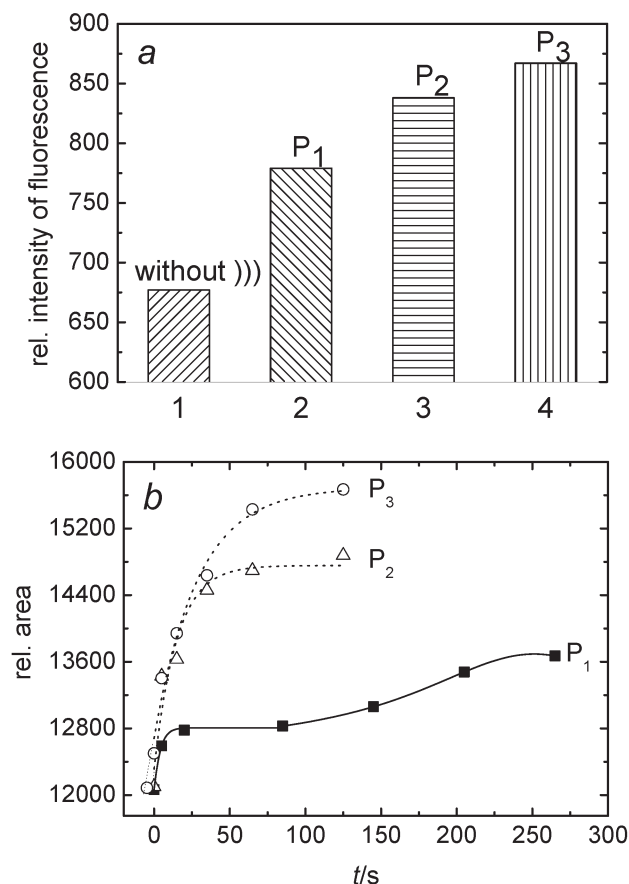


Fig. 4. a) The changes of limit intensities of anthracene fluorescence in acetone ($c \approx 10^{-4} \text{ mol dm}^{-3}$) caused by modulation of oxygen presence in sonicated solution with argon atmosphere using different power of ultrasound (transducer S₂): 1) without ultrasound, 2) power P₁, 3) at power P₂, 4) at power P₃. b) Time dependence of degassing by ultrasound at power P₁ (■), P₂ (△), and P₃ (○).

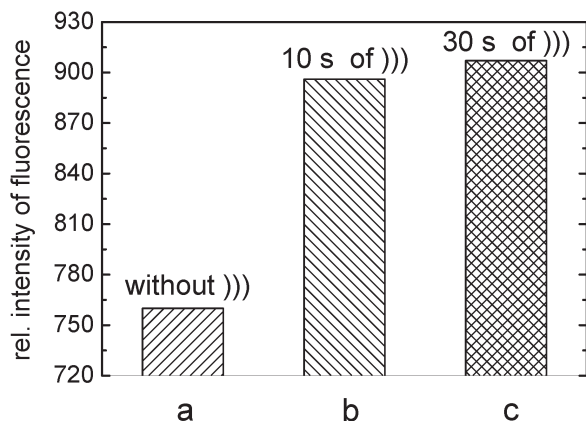


Fig. 5. The change of fluorescence intensity of anthracene in acetone ($c \approx 10^{-4} \text{ mol dm}^{-3}$) caused by modulation of oxygen presence in sonicated solution with argon atmosphere (transducer S₁): a) before ultrasound application, b) after 10 s of sonication, c) after 30 s of sonication (limit value).

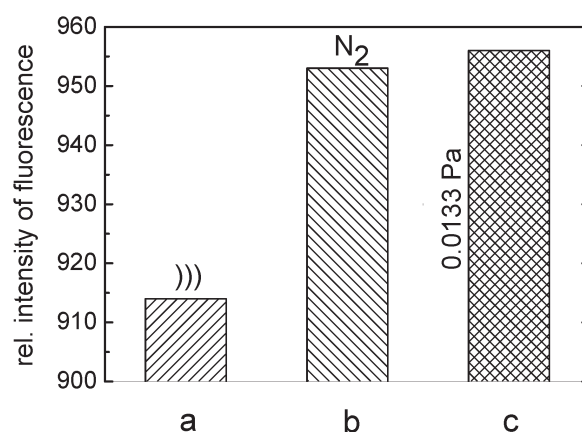


Fig. 6. The changes of limit intensities of anthracene fluorescence in acetone ($c \approx 10^{-4} \text{ mol dm}^{-3}$) caused by decreasing of oxygen concentration in solution with argon atmosphere (transducer S₁): a) with ultrasound, b) bubbling by nitrogen, c) freeze-pump-thaw cycle method.

The rate of oxygen exclusion from the solution increased with increasing of the ultrasound power. About 12 min at ultrasound power P₁ or 2 min at power P₃ is needed to achieve limit concentration of oxygen by sonication of acetone solution (Fig. 4); the fluorescence spectra of anthracene were integrated in the range of wavelength 390–415 nm and are expressed as areas in column.

We obtained similar results if the experiment was carried out in sonochemical reactor with transducer S₁. In this case the limit concentration of oxygen reached the lowest value (Fig. 5).

The concentration of oxygen depends on the physical properties of solvents that modify the propagation of ultrasound waves. Except of acetone, we studied the influence of ultrasound on the concentration of oxygen in benzene, chloroform, heptane, and propan-2-ol. We found out no effect of ultrasound on degassing anthracene solution in benzene, chloroform, and heptane. Degassing effect of ultrasound in propan-2-ol was similar to that in acetone. Freeze-pump-thaw cycle method and degassing of solutions by nitrogen were more efficient than ultrasound. Differences of limit intensities of anthracene fluorescence are depicted in Fig. 6.

We also tried re-degassing experiment with solution of anthracene in acetone using transducer S₁. In this case we degassed the solution with ultrasound to the limit concentration of oxygen. The limit was reached after 15 s of sonication (Fig. 7). Consequently the degassed solution was bubbled with oxygen to the starting point. Secondly, the solution was sonicated again to the limit intensities of anthracene fluorescence. This limit was reached again after the 15 s of sonication following by 120 s of sonication.

The properties of cavitation bubbles (*e.g.* size, lifetime, temperature, pressure) depend on the ultra-

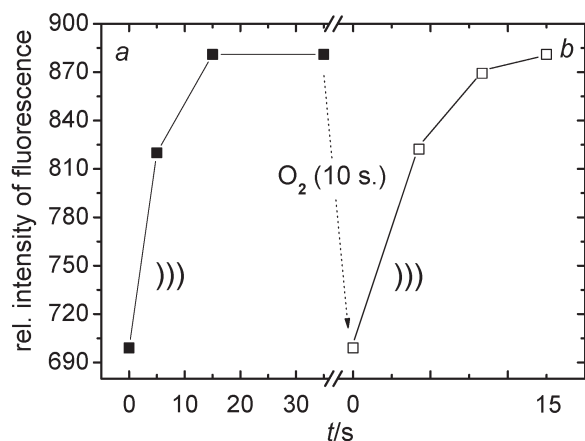


Fig. 7. *a*) Solution of anthracene in acetone ($c \approx 10^{-4}$ mol dm^{-3}) sonicated until the limit point was reached (transducer S_1). *b*) Solution of anthracene in acetone ($c \approx 10^{-4}$ mol dm^{-3}) after sonication consequently bubbled with oxygen (10 s) and again sonicated to the limit. Fluorescence spectra were integrated from 390 nm to 415 nm.

sound frequency. Final concentration of oxygen in sonicated solution is affected by competitive processes associated with properties of cavities and with processes, which affect the rate of oxygen dissolution. Complete exclusion of oxygen from the sonicated solution is not possible, if the solubility of oxygen which occurs in cavity interior is able to compete with the rate of cavity decay or with the collapse of cavities. Our results are in agreement with this hypothesis. On the basis of the present knowledge of cavitation process, we can suppose that ultrasound higher intensity can reach better degassing of solutions. The changes of intensity of anthracene fluorescence in the degassing

experiments were not so marked. Even though the anthracene generally shows intense fluorescence in the solution, its sensitivity to oxygen as a quencher of fluorescence is probably small.

Ultrasound is not so convenient method for the exclusion of oxygen from the organic solvents as the other methods mentioned above.

Acknowledgements. This work was supported by research grants VEGA 1/0089/03, 1/0516/0 and VT project.

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