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Photodegradation and advanced oxidation of endocrine disruptors in aqueous solutions

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ABSTRACT

Endocrine disruptors, sometimes also referred to as hormonally active agents, are exogenous substances that act like hormones in the endocrine system and disrupt the physiological function of endogenous hormones. Our recent studies concern degradation of some representatives of this class of chemicals: n-butylparaben (BP), 4-*t*-octylphenol (OP), trenbolone (TB) and boldenone (BD). We applied three methods for their elimination from aqueous solution: photolysis by 254 nm irradiation, advanced oxidation process using hydroxyl radicals and photosensitized oxidation using mainly singlet molecular oxygen. The kinetic parameters of those processes were calculated. The most efficient degradation of studied compounds was observed in H_2O_2/UV system.

1. Introduction

Recently, it was found that many compounds from various classes of chemicals may cause negative effects on the endocrine systems of humans and wildlife. They were given a group name ‘endocrine disrupting compounds’ (EDCs). People are exposed to chemicals with estrogenic effects in their everyday life, because they are found in low doses in literally thousands of products (cosmetics and other personal care products, drugs and foodstuffs) [1]. Nowadays many laboratories conduct investigation on new EDCs trying to measure their presence and their concentrations in the environment.

With regard to the widespread use of EDCs they are detected also in surface waters. The concentrations of some EDCs in surface waters are evaluated in the range of ppt and ppb [2]. Even in finished drinking water supplies various EDCs and pharmaceuticals have been detected at ng L^{-1} concentrations [3]. The evidence is mounting that even at these low levels of concentrations EDCs may have an adverse impact on aquatic animals [4,5]. Studies have linked the adverse biological effects of EDCs in animals, giving rise to concerns that low-level exposure might cause similar effects in human beings. EDCs can also be transferred to drinking water due to insufficient removal in conventional sewage treatment plants, creating a hazardous impact on humans [6]. Therefore there is a growing interest in efficient degradation methods in the aqueous environment [7–9]. The broad spectrum of removal or degradation methods used so far, including physical, chemical and biological techniques have been lately reviewed by Liu et al. [10].

In our work we present the studies of some EDCs elimination from the aqueous solutions using three methods: direct photolysis, advanced oxidation in the H_2O_2/UV system and a spontaneous process occurring in natural aqueous reservoirs—photosensitized oxidation. The obtained results allow us to determine kinetic parameters of those processes. We fixed our attention on two phenol derivatives: *n*-butylparaben (*n*-butyl ester of 4-hydroxybenzoic acid), 4-*tert*-octylphenol, and two anabolic steroids: trenbolone (17-β-hydroxyestra-4,9,11-trien-3-one) and boldenone (1-dehydrotestosterone). A short characteristic of the tested chemicals is given in Table 1.

2. Materials and methods

All chemicals were commercial available products: butylparaben (BP) (>99%), 4-*tert*-octylphenol (OP) (≥90%) and boldenone (BD) from Fluka and trenbolone (TB) (≥98%) from Sigma. Two dye sensitizers were used: rose bengal (RB) from Fluka, and aluminum phthalocyanine chloride tetrasulfonic acid (PC) from Frontier Scientific. The concentration range of target compounds were $1.2–20 \times 10^{-5}$ M for BP, $0.7–3.6 \times 10^{-5}$ M for OP, $0.51–10 \times 10^{-5}$ M for TB and $0.48–3.17 \times 10^{-5}$ M for BD.

The experiments of direct photolysis and in H_2O_2/UV system were performed in quartz test tubes of the capacity of about 10 mL placed in a merry-go-round. Reaction solutions were irradiated at 25 °C by two exposure panels placed on both sides of the merry-go-round. The panels were equipped with five low-pressure LP lamps each (Luzchem), emitting mainly at the wavelength 254 nm. Only

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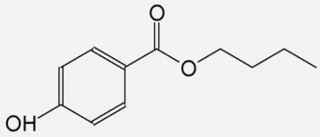
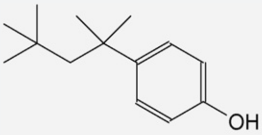
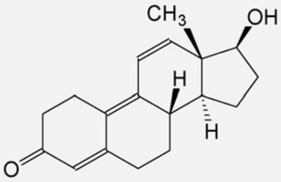
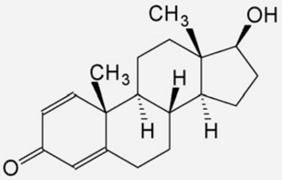
Table 1
Characteristic of EDCs used in the study.

Compound	Molecular structure	ε at 254 nm pH 7	pK_a	log K_{OW}	Uses, concentration in natural water (C_{NW})
n-Butylparaben CAS [94-26-8] $C_{11}H_{14}O_3$		15400	8.24 [11]	3.57 [12] 3.37 [13]	Preservative and antioxidant in cosmetics, drug formulations and some foods [13,14] $C_{NW} \leq 50$ ng dm^{-3} [2]
4-*t*-Octylphenol CAS [140-66-9] $C_{14}H_{22}O$		675	10.39 [15]	5.28 [16] 4.12 [17]	Substrate in the production of phenol formaldehyde resins and nonionic detergents [18,19] $C_{NW} \leq 190$ ng dm^{-3} [20]
Trenbolone CAS [10161-33-8] $C_{18}H_{22}O_2$		6300	N/A	2.65 [21]	Synthetic androgen used in veterinary medicine and as growth promoter for farm animals [22,23] C_{NW}: N/A
Boldenone CAS [846-48-0] $C_{19}H_{26}O_2$		14570	N/A	2.75 [24]	Androgenic anabolic steroid used for growth promotion in animals destined for meat production and in veterinary medicine [25] $C_{NW} \leq 3$–9 ng dm^{-3} [26]

N/A: Not available.

in the case of OP direct photolysis studies were carried out using a medium-pressure lamp (MP) TQ 150 (150 W, Heraeus, Hanau). The MP lamp was placed in a quartz well with cooling jacket. In the photosensitized reactions we used a xenon arc lamp (XBO) (100 W, Osram), simulating solar radiation. The photon flux entering the reaction space was determined in the experiments with uranyl oxalate for LP and MP lamps and Reinecke's actinometer for the XBO lamp. The photosensitized experiments were conducted in homogeneous solutions using a 1.2 L glass reactor with cooling jacket and central glass well for immersion of the lamp. The reactor was equipped with a porous plate to deliver gases and provide agitation of the reaction mixture.

Absorption spectra were recorded using a Unicam spectrophotometer. Reaction progress was traced by HPLC analysis (Waters). A mixture of acetonitrile and acidified water (0.01% H_3PO_4) at the constant flow rate equal to 1 mL min^{-1} was used as an eluent. The quantification limit of chromatographic analysis equaled to 2×10^{-8} M The other details of experiments and analytical methods were described in our earlier work [11,15,27].

3. Results and discussion

3.1. Direct photolysis

For a successful direct photolysis the overlap of lamp emission spectrum and absorption spectrum of a target compound is necessary. The spectra, shown in Fig. 1, indicate that for BP, BD and TB decomposition the use of the LP lamp is advantageous. The OP degradation with LP lamps was slow and the use of MP lamp of higher fluence rate enabled accomplishment of a higher rate of photolysis.

Fig. 2 shows changes of relative concentration BP, TB and BD upon direct photolysis at 254 nm. In our experimental conditions the highest rate of decomposition was observed for boldenone. Its initial concentration was reduced by 50% in only 2 s. The degradation of BP and TB was less efficient–the initial concentration was halved after 7.5 and 26 min of the reaction, respectively.An increase of photon fluence rate caused a rise in decay rate for all studied compounds. An increase of pH of the reaction solution led to lowering of the degradation rate, which can indicate smaller susceptibility

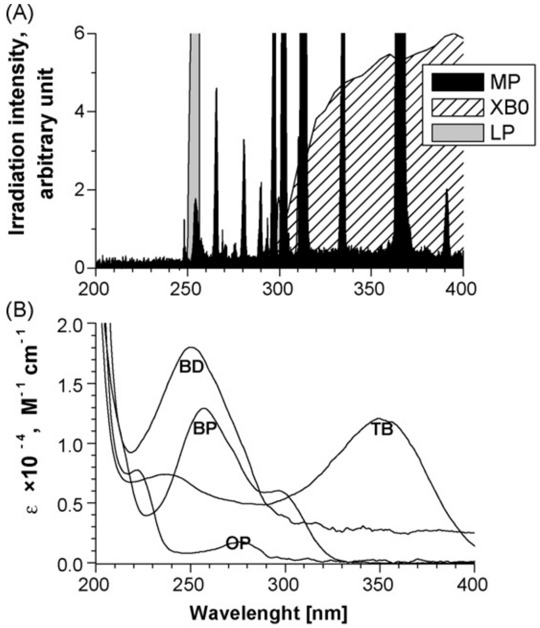


Fig. 1. (A) Emission spectra of the lamps used in experiments and (B) absorption spectra of investigated compounds ($C_{OP} = 3 \times 10^{-5}$ M, $C_{BP} = 8 \times 10^{-5}$ M, $C_{TB} = 5 \times 10^{-5}$ M, $C_{BD} = 1.75 \times 10^{-5}$ M).

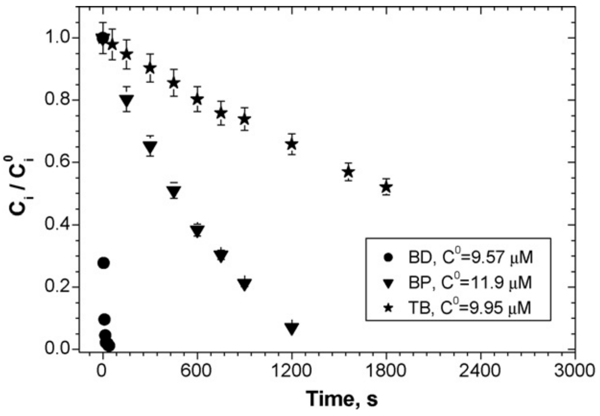


Fig. 2. Changes of relative concentrations of investigated compounds versus irradiation time upon direct photolysis using LP lamps ($E_0 = 1 \times 10^{-5}$ einstein dm^{-3} s^{-1}) in neutral solution.

of BP and OP anions toward photolysis. The decomposition of BD and TB was practically independent of the acidity of reaction solutions.An increase of the initial concentration of target compounds led to an increase of the reaction rate (Fig. 3). Only in the case of BP at a higher content the drop of the decay rate was observed. This phenomenon was caused by concentration quenching of excited BP molecules [28].

For the initial reaction time, when studied molecules are solely absorbing species, the reaction rate can be expressed using the following formula [29]:

$$r_0 = -\frac{dC_i}{dt} = \phi_i E_0 [1 - \exp(-2.3\varepsilon_i b C_i)] \quad (1)$$

where ϕ_i is the quantum yield of target compound decay, E_0 is the volume fluence rate, ε_i is the molar absorption coefficient, b is the optical pathway and C_i is the concentration of target compound.

The above expression was used to estimate an apparent quantum yield of the decay of investigated molecules. The results of calculation are given in Table 2.

3.2. *AOP process in the H_2O_2/UV system*

The performed preliminary experiments allowed us to estimate the extent of direct reaction of chosen chemicals with hydrogen peroxide in the absence of radiation, in the so called “dark reaction” and to establish an optimal hydrogen peroxide concentration. In the first case, results indicated an insignificant role of the direct reaction of studied compounds with H_2O_2. The results of the next series of experiments carried out at various concentrations of hydrogen peroxide indicated that the highest elimination rate was attained at H_2O_2 concentration of about 0.01 M for all investigated chemicals. The photolysis of hydrogen peroxide (1) at this concentration ensured such hydroxyl radicals concentration that the degradation rate was the highest, and simultaneously the scavenging role of H_2O_2 was confined (2).

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \quad (2)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \quad (3)$$

The pH of reaction solution is of utmost importance for the decomposition of studied compounds. A decrease of the reaction rate with rising pH value is mainly caused by formation of an inactive hydroperoxide anion due to H_2O_2 dissociation (pK_a = 11.6) [30]. The HO_2^- not only absorbs light more effectively than H_2O_2 [31], but also acts as an efficient scavenger of OH radicals (4) [32], which leads to the inhibition of the degradation.

$$HO_2^- + {}^{\bullet}OH \rightarrow H_2O + O_2^{\bullet -} \quad (4)$$

The presence of hydrogen peroxide at optimal concentration in the reaction mixture during photolysis leads to a strong increase of the reaction rate. The degradation time for 50% reduction of starting concentration of BP, OP and TB ranged from few minutes to few seconds, depending on target compound and its initial concentration. The OP direct photolysis under 254 nm irradiation was slow and addition of 0.01 M H_2O_2 shortened the reaction time over 100 times. In the case of BP the degradation is about 20 times faster in the presence of H_2O_2 than without hydrogen peroxide. And in the case of TB the half-life time dropped from 120 min in photolysis to 90 s in the H_2O_2/UV system.

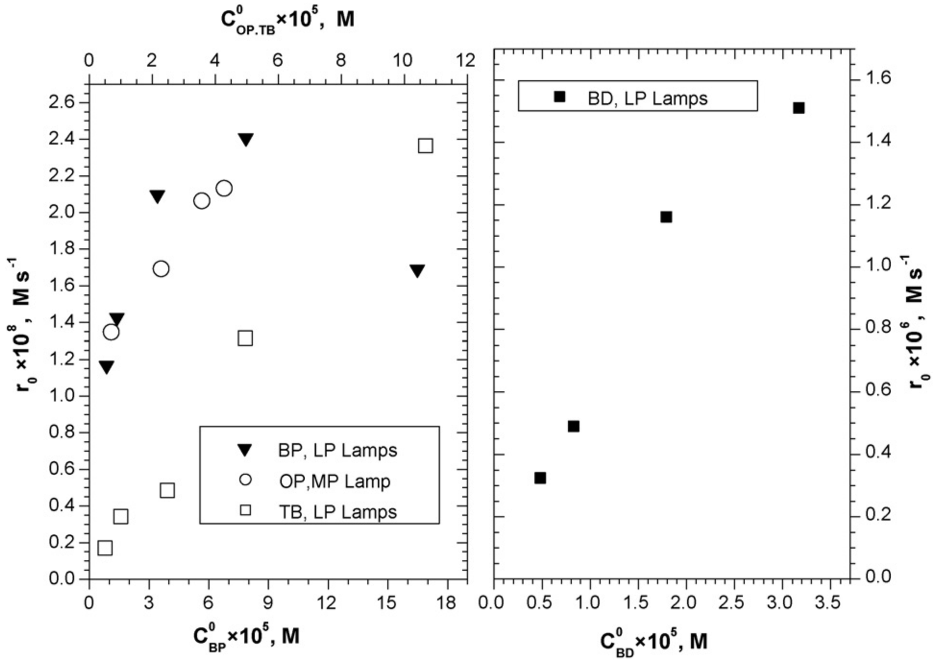


Fig. 3. Degradation rates of studied EDCs during photolysis for various initial concentrations (BD, BP, TB: pH 7; LP lamp $E_0 = 1 \times 10^{-5}$ einstein dm^{-3} s^{-1}; OP: pH 7, MP lamp $E_0 = 1.28 \times 10^{-4}$ einstein dm^{-3} s^{-1}).

Table 2
Collected values of kinetic parameters of studied processes for chosen EDCs.

EDCs	Direct photolysis			H_2O_2/UV	Photosensitized oxidation			
	Quantum yields ϕ			k_{OH}, $M^{-1}\,s^{-1}$	k_r, $M^{-1}\,s^{-1}$		k_t, $M^{-1}\,s^{-1}$	
	LP		MP	LP	XBO			
	pH 7	pH 10	pH 7		pH 7	pH 10.8	pH 7	pH 10.8
BP	$(3.3\pm0.4)\times10^{-3}$	$\sim6\times10^{-4}$	–	$(4.8\pm0.7)\times10^{9}$	$(2.4\pm0.1)\times10^{6}$[a]	$(1.1\pm0.1)\times10^{7}$[a]	$(5.1\pm0.6)\times10^{9}$[a]	$(1.8\pm0.2)\times10^{9}$[a]
OP	$(1.6\pm0.4)\times10^{-2}$	–	$(2.0\pm0.6)\times10^{-2}$	$(4.2\pm1.2)\times10^{9}$	$(3.4\pm0.2)\times10^{4}$[b]		$(1.5\pm0.8)\times10^{9}$[b]	
TB	$(2.9\pm0.2)\times10^{-3}$	$(3.8\pm1.2)\times10^{-3}$	–	$(4.3\pm0.8)\times10^{9}$			–	
BD	$(6.1\pm0.3)\times10^{-1}$	$(6\pm2)\times10^{-1}$	–	–			–	

[a] With RB sensitizer.
[b] With PC sensitizer, pH 9.2 (6% of OP is in a dissociated form).

The dependence of initial reaction rates at pH 7, upon starting concentration of OP and TB was typical—the higher concentration the higher rate. In the case of BP the maximum decay rate was observed at the concentration of about 8×10^{-5} M (Fig. 4).

The decrease of reaction rate at higher BP concentration can be explained by the rising absorption of radiation by BP due to its high absorption coefficient. At the lowest BP concentration (Fig. 4) 60% of incident photons were absorbed by hydrogen peroxide and 40% by BP and at the highest BP concentration it absorbs 93% of photons, while H_2O_2 only 7%. Those changes in photon distribution upon concentration, calculated according to (5) [29], indicate significant mitigation of H_2O_2 photolysis and decrease the rate of hydroxyl radicals reaction with BP.

$$F_H=\frac{\varepsilon_H C_H}{\sum \varepsilon_i C_i} \tag{5}$$

where F_H is the fraction of absorbed photon flux by hydrogen peroxide, C is the molar concentration and ε is the molar absorption coefficient; subscript H applies to H_2O_2.

The determination of rate constants was performed at high hydrogen peroxide concentration and at low pH value of the reaction solution. In these conditions almost all incident radiation was absorbed by H_2O_2 which allowed the photolysis of studied compounds to be neglected. The neutral or slightly acidic reaction mixture prevented the dissociation of hydrogen peroxide and BP or OP. The high hydrogen peroxide concentration not only excluded photolysis but also allowed us to treat its concentration as constant at initial stages of the reaction which in turn, created a basis for applying steady-state assumption for hydroxyl radicals concentration [33]. So, the reaction rate can be described by the pseudo-first order equation:

$$-\frac{dC_i}{dt}=k_{app}C_i \tag{6}$$

where the apparent rate constant is

$$k_{app}=k_{OH}[OH] \tag{7}$$

The results of experiments were plotted in the coordinate system $\ln(C^0/C)$–t, arising from an integrated form of (6). The slope of the obtained rectilinear relation corresponds to the apparent rate constant (Fig. 5).

The determined k_{app} was used to calculate the second-order rate constant of hydroxyl radicals with studied EDCs. The assumption of steady-state concentration of the hydroxyl radicals allows us to consider the following relationship to be true:

$$2\phi_H E_0 F_H(1-10^{-b\sum \varepsilon_i C_i}) = k_3 C_H[OH]+k_4[HO_2{}^-][OH] + k_{OH}C_i[OH] \tag{8}$$

where the left-hand side describes the generation rate of OH radicals with ϕ_H the quantum yield of OH radicals formation, C_H the concentration of H_2O_2, F_H the fraction of photons absorbed by H_2O_2 and the right-hand side describes the sum of reaction rates where OH radicals disappear, i.e. the reaction with H_2O_2 (3) and its anion (4) and the reaction with the studied compound. The formed intermediates react also with hydroxyl radicals but primary intermediates react with OH radicals at the same or very close rate constant as a target compound. So, considering the beginning of the process, at small conversion the steady-state assumption remains valid [34].

Combining Eq. (8) with (7) and after rearrangement we obtain:

$$k_{OH}=\frac{k_{app}(k_3C_H+k_4[HO_2{}^-])}{2\phi_H E_0 F_H(1-10^{-b\sum \varepsilon_i C_i})-k_{app}C_i} \tag{9}$$

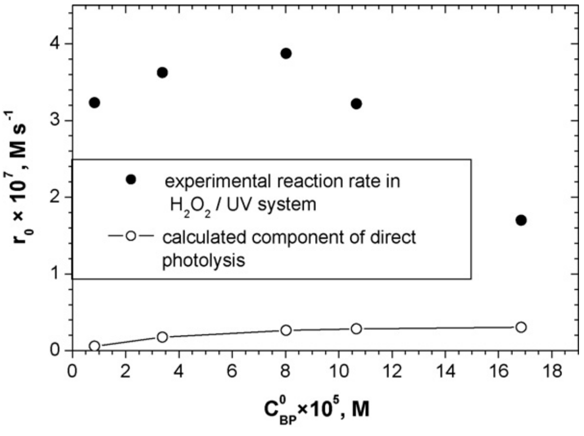


Fig. 4. Dependence of total experimental reaction rate and its calculated component—direct photolysis on the initial BP concentration in the H_2O_2/UV system ($E_0=1\times10^{-5}$ einstein dm^{-3} s^{-1}, pH 7, $C_H=1\times10^{-2}$ M).

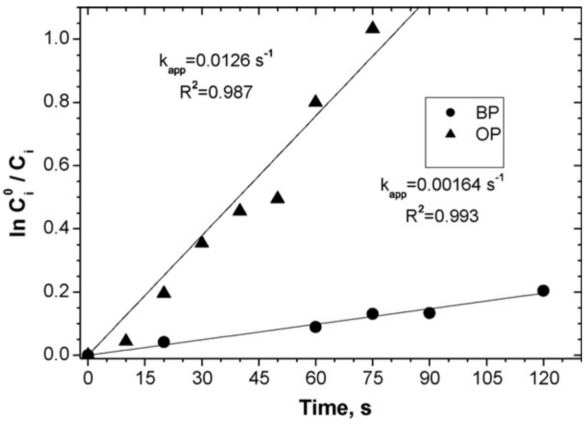


Fig. 5. Determination of apparent rate constants for pseudo-first order reaction of BP and OP degradation in the H_2O_2/UV system.

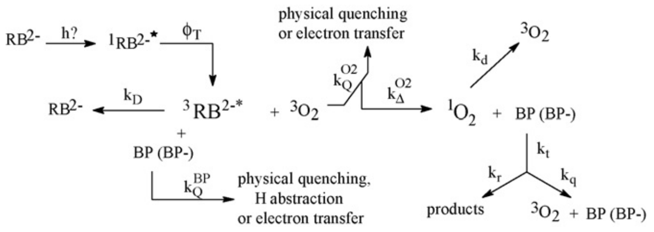


Fig. 6. Scheme of reaction pathways in photosensitized oxidation of BP with RB sensitizer.

Relationship (9) enables calculation of the values of rate constants of OH radicals reaction with studied EDCs using experimental and literature data [32]. The obtained values of k_{OH} are given in Table 2.

3.3. Photosensitized oxidation

Photosensitized oxidation can proceed due to the absorption of UV–vis radiation by an intermediate substance—sensitizer introduced into the reaction mixture. The sensitizer in its excited state can transfer energy or electron to a non-absorbing molecule, mainly to ubiquitous oxygen, generating reactive oxygen species: molecular singlet oxygen $^1O_2$ or/and superoxide radical anion $O_2^{\bullet -}$ which resulted in the decomposition of pollutants. The photosensitized oxidation was examined in the degradation of BP and OP in a homogeneous aqueous solution. The sensitizers RB and PC were used at concentrations 2×10^{-5} M, assuring the highest rate of BP and OP degradation. RB is one of the most popular dyes employed for generation of molecular singlet oxygen due to its water solubility and high value of singlet oxygen quantum yield $\phi_\Delta = 0.76$ [35]. PC has lower ϕ_Δ in the range 0.22–0.42, which depends on the position of sulfonic group in phthalocyanine moiety [36].

The pH of the reaction solution influenced the process rate. The highest decay rates of BP and OP were observed in alkaline solutions for both sensitizers. Assuming constant value of the quantum yield of $^1O_2$ formation in the studied pH range, the changes in reaction rate are surely caused by a growing amount of BP and OP anion at higher pH [37].

The scheme in Fig. 6, as an example for BP and RB sensitizer, shows complexity of the photosensitized oxidation and main reactions leading to the BP decomposition. Besides the reaction with singlet oxygen, BP can decay in radical reactions initiated by superoxide radical anion and in the reaction with excited sensitizer in the triplet state. The kinetic study of photosensitized oxidation requires the determination of the most important pathways of degradation. In order to indicate the dominating pathway of BP degradation, a series of experiments with some additives were performed. The addition of *tert*-butyl alcohol or isopropanol, known hydroxyl radical scavengers, eliminated the reaction with hydroxyl radicals. The presence of superoxide dismutase (SOD) should indicate the presence of superoxide anion radical. And finally, the reaction in the presence of sodium azide, a known molecular singlet oxygen quencher, excluded the reaction with singlet oxygen. The results of performed series of experiments are shown in Fig. 7 for the case of BP with a PC sensitizer and they clearly indicate that BP decay occurred exclusively in the reaction with singlet oxygen. The run of reaction with sodium azide coincides with the reaction which proceeds without the sensitizer, i.e. BP photolysis, while reactions with the hydroxyl radical scavenger and SOD do not change the course of photosensitized oxidation. In the case of OP the reaction with molecular singlet oxygen was also a dominating pathway of its degradation.

Taking into account the obtained results, neglecting direct photolysis of BP and OP at XBO lamp radiation and assuming only physical quenching of the excited RB, the rate of studied compounds decay can be described by the following expression [27]:

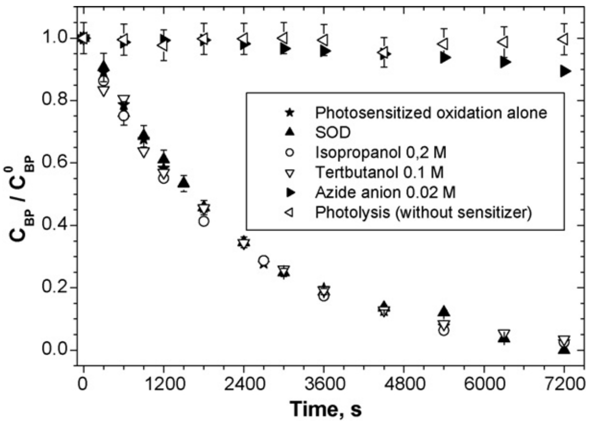


Fig. 7. The influence of additives on photosensitized oxidation of BP with PC sensitizer (pH 10.8).

$$r = -\frac{dC_i}{dt} = \frac{\phi_\Delta E_a C_i k_r}{k_d + k_t C_i} \qquad (10)$$

where $\phi_\Delta = \phi_T(k_\Delta^{O_2}/k_Q^{O_2})$, $k_t = k_r + k_q$ and the denotations are explained in scheme (Fig. 6).

Basing on experimental and literature data [37], the values of rate constant of BP, OP and BP anion with singlet oxygen – k_r, and rate constant of physical quenching of $^1O_2$ by BP and OP – k_q, were estimated using Marquardt's optimization procedure. The values of k_r and k_t are given in Table 2.

3.4. Comparison of the methods

Results of the photolysis studies show efficient degradation of chosen EDCs by 254 nm radiation, however the rate of the process is low. The rate of photolysis of studied compounds at pH 7 can be ordered as follows: BD > BP > TB ≥ OP. This sequence of degradation rates is confirmed by the values of molar absorption coefficients and apparent quantum yields. The molar absorption coefficient of BD and BP are very close but the rate of BD elimination is significantly higher. This is caused by very high quantum efficiency of BD (Table 2). From every ten absorbed photons, six lead to desired result. For TB every thousand of absorbed photons cause elimination of only three molecules.

Interesting is a comparison of the BD and TB photolysis rates. In spite of a very similar chemical structure of both compounds, the molar absorption coefficient of BD is above two times higher than that of TB, while the quantum yield of BD decay is 200 times higher than that of TB.

The disinfection doses usually applied for water treatment are estimated to be about 400 J m^{-2} [38], and for majority of studied compounds are far insufficient for degradation. Only boldenone at the fluence rate 1×10^{-5} einstein dm^{-3} s^{-1} (29 W m^{-2}) is degraded within a few seconds. For BP this value of fluence does not cause practically any compound degradation. At the same fluence rate a 90% BP concentration reduction is achieved after 20 min which overcomes the disinfection dose almost 90 times.

The advanced oxidation processes in the H_2O_2/UV system seem to constitute an efficient and very quick method for EDCs degradation. The calculated rate constants for the reaction of hydroxyl radicals with studied compounds are very high and close to diffusion-controlled limit (Table 2). The k_{OH} values determined for BP and TB are comparable with values quoted for similar compounds [12,39]. In the case of OP the obtained rate constant is very close to literature data [40]. The significant increase of the degra-

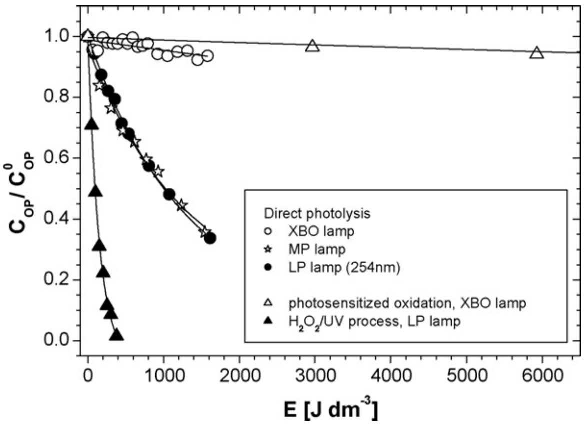


Fig. 8. Changes in the relative concentration of OP as a function of absorbed energy (pH 7, $C_{OP} = 3 \times 10^{-5}$ M).

dation rate in the H_2O_2/UV system, comparing to photolysis, is not achieved gratuitously, the costs of hydrogen peroxide should be taken into account.

In photosensitized oxidation the estimated rate constants of reaction with singlet molecular oxygen are by two or more orders of magnitude lower than k_{OH} values. For OP photooxidation the values of k_r and k_t differ significantly which means that there is strong physical quenching of singlet oxygen on OP molecules. Relatively high values of rate constants indicate that in surface waters some EDCs can undergo spontaneous degradation quite efficiently in the presence of natural sensitizers. The application of photosensitized processes for practical purposes seems very attractive due to possibility of using cheap solar energy and air as a source of oxygen. However, some disadvantages should be overcome, namely photostability of the sensitizer and the necessity of sensitizer separation from treated water. These problems can be solved by using stable sensitizers immobilized onto proper support. These issues are currently investigated by our team.

The evaluation of usability of investigated methods can also be performed from the point of view of energy consumption for chosen EDCs degradation by studied methods. Fig. 8 shows the reduction of OP concentration depending on absorbed radiation energy for various processes.

The absorption of 1000 J dm^{-3} energy emitted by the LP lamps and MP caused nearly the same, about 50% reduction of OP concentration. The photolysis of OP under simulated solar radiation of the XBO lamp, or photosensitized oxidation seems to be an ineffective process, but the unlimited accessibility to solar radiation and oxygen can be useful in certain circumstances.

According to our results of both comparisons, the UV radiation–hydrogen peroxide system is the most beneficial method to degrade the investigated endocrine disrupting chemicals.

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