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Titanium dioxide mediated photocatalytic degradation of 1,2-diethyl phthalate

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Abstract

The photocatalyzed degradation of 1,2-diethyl phthalate (DEP) in aqueous suspensions of titanium dioxide has been investigated under a variety of conditions employing a pH-stat technique. The degradation was studied by monitoring the change in substrate concentration employing HPLC analysis and by the decrease in the total organic carbon (TOC) content as a function of irradiation time. The depletion of DEP and TOC was studied under different conditions such as pH, catalyst concentration, substrate concentration, different types of TiO_2 as the photocatalyst and in the presence of several electron acceptors (H_2O_2, $KBrO_3$ and $(NH_4)_2S_2O_8$) in addition to molecular oxygen. Highest degradation rates were observed with Degussa P25 being the photocatalyst at pH 6, while with Sachtleben Hombikat UV 100 smaller decomposition rates were obtained. The degradation of DEP was found to be only slightly enhanced by the addition of electron acceptors, whereas the mineralization is markedly improved in the presence of bromate ions. The degradation products were analyzed by GC–MS technique and probable pathways for the formation of products are proposed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Titanium dioxide; 1,2-Diethyl phthalate; Total organic carbon; Photocatalysis; Photocatalytic degradation pathway

1. Introduction

Phthalate esters are used in virtually every major product category including construction, automotive, household products, package and medicine products. They represent a large family of chemicals, which are widely used as plastisizers primarily in the production of polyvinyl chloride (PVC) resins [1]. The short-chained esters (dimethyl and diethyl phthalate esters) are typically used in cellulose ester-based plastics, such as cellulose acetate or butyrate, respectively [2]. As these products become waste and are exposed to photochemical, thermal and microbial degradation, the phthalate esters are leached out by water thus turning into ubiquitous water pollutant [3]. Some of the phthalate esters, especially the long chained esters, have been recognized as cancer suspect agents and are, therefore, considered as priority pollutant [4]. In addition, phthalate esters are found to accumulate in the environment and to be toxic to a variety of aquatic organisms, which are at the base natural food chain in both marine and fresh water environments [5–9]. Numerous studies have demonstrated the biodegradability of several phthalate esters from soil, synthetic or real waste waters by activated sludge treatment [10–12], by biodegradation from natural sources of microorganisms [13–15] or by pure bacteria cultures and strains isolated from these habitats [16–21]. However, only very few studies related to the use of semiconductors such as titanium dioxide in the photocatalytic degradation of phthalate esters [4,22]. Since phthalate esters are becoming a class of concerning water pollutants and they are still accumulating in the environment though they can be biological degraded within 1–100 days [2], there is a strong need to look for alternative and faster treatment processes for such pollutants. Therefore, we have undertaken a detailed kinetic study on the photodegradation of 1,2-diethyl phthalate (DEP) sensitized by titanium dioxide in aqueous suspensions examining various reaction parameters, e.g. reaction pH, pollutant and substrate concentration, type of photocatalyst and addition of several electron acceptors.

2. Experimental methods

2.1. Reagents

All chemicals were of reagent grade and used without further purification. The water employed in this study was purified by a Milli-Q/RO system (Millipore) resulting in a

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resistivity of >18 MΩ cm. P25 from Degussa and Hombikat UV 100 from Sachtleben Chemie were used as photocatalysts in this study. P25 consists of 75% anatase and 25% rutile with a specific BET surface area of $50\,\mathrm{m^2\,g^{-1}}$ and a primary particle size of 20 nm [23,24]. Hombikat UV 100 consists of 100% pure anatase with a specific BET surface area of $250\,\mathrm{m^2\,g^{-1}}$ and a primary particle size of 5 nm [25].

2.2. Procedures

Stock solutions of DEP containing the desired concentrations were prepared in water. The photochemical reactor was made of Duran® glass with a plain quartz window (through which the parallel light beam is entering) equipped with a magnetic stirring bar, a water-circulating jacket and five openings for electrodes and gas supplies. For the irradiation experiments 250 ml of the desired solution were filled into the reactor. The required amount of photocatalyst was added and the solution was stirred for at least 30 min in the dark to allow equilibration of the system. To ensure a constant pH value throughout the experiment making the addition of any buffer solution unnecessary a pH-stat technique was employed. Details concerning this technique have been reported elsewhere [26]. To guarantee a constant O_2 concentration, the suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a high-pressure mercury lamp (Osram HBO 500 W). IR-radiation and short-wavelength UV-radiation were eliminated by a 10-cm water filter. A 320-nm cut-off filter was used to avoid any direct excitation of DEP. Samples (10 ml) were collected before and in regular intervals during the irradiation. They were centrifuged with a Heraeus Sepatech Labufuge GL before analyses. An actinometry was performed using Aberchrome 540 [27] in order to determine the total incident light intensity in the wavelength region between 310 and 370 nm, i.e. the UV-A — a part of the solar spectrum, which can be absorbed by TiO_2. This technique allows the determination of the incident photon flux entering a photoreactor of a specific geometry at the inner front window, thus, avoiding the necessity of corrections for any influences of light reflections taking into account the reactor geometry. The light intensity throughout all experiments in this study was found to be around $110\,\mu\mathrm{mol\ photons\ l^{-1}\,min^{-1}}$. The photonic efficiency ζ was calculated as the ratio of the photocatalytic degradation rate and the incident light intensity [28]. Its validity for a better comparison of photocatalytic systems has been experimentally verified in several papers recently published [29,30]. For each experiment, the degradation rate of the model pollutant was calculated from the initial slope obtained by linear regression from a plot of the natural logarithm of the DEP concentration as a function of the irradiation time, i.e. first-order degradation kinetics. For the total mineralization (measured in terms of total organic carbon (TOC) content of the sample), the rate was determined from the initial slope obtained by linear regression of the TOC-concentration versus time profiles, i.e. zeroth order degradation kinetics. TOC degradation rates were calculated in terms of (μM "C_1-units" $\mathrm{min^{-1}}$). Unfortunately, by this procedure, one often obtains higher degradation rates for the TOC removal than for the decomposition of the respective model compound itself, which of course is impossible from the logical point of view. However, considering that the TOC-content consists of undegraded substrate and intermediates containing the same, less or in the case of dimerization reactions even a higher number of carbon atoms, a TOC degradation rate in terms of (μM "molecules" $\mathrm{min^{-1}}$) would result in a significant lower rate than the one for the removal of the model compounds. Since the composition of the model compound and the intermediates changes with irradiation time, the only practical way of calculating degradation rates for the TOC removal appears to be to follow the procedure described above. The photonic efficiencies were, therefore, calculated using the following equations:

$$\zeta_{\mathrm{substrate}}\,(\%) = \frac{\mathrm{d}c_{\mathrm{substrate}}/\mathrm{d}t}{\mathrm{d}I/\mathrm{d}t} \times 100 \tag{1}$$

$$\zeta_{\mathrm{TOC}}\,(\%) = \frac{\mathrm{dppm}/\mathrm{d}t}{\mathrm{d}I/\mathrm{d}t} \times \frac{100}{M_{\mathrm{C}}} \tag{2}$$

where $M_{\mathrm{C}} = 12\,\mathrm{g\,mol^{-1}}$, $\mathrm{d}I/\mathrm{d}t$ is the light intensity, $\mathrm{d}c/\mathrm{d}t$ or $\mathrm{dppm}/\mathrm{d}t$ the degradation rate.

Control experiments were carried out in the dark as well as in the absence of TiO_2 photocatalyst. There was no observable loss of parent compound in both cases.

2.3. Analyses

The concentration of DEP was measured by HPLC using a Dionex 4500i chromatograph equipped with a reversed phase column LiChrospher RP-18, 5 μm particle size (Merck). All substances were detected employing a UV-detector at 277 nm. The eluent consisted of a binary mixture of water and methanol (60:40 v/v), the flow rate was $1\,\mathrm{ml\,min^{-1}}$. Concentrations of DEP were calculated by calibration curves obtained from HPLC measurements of the respective compound at different concentrations. TOC was measured with a Shimadzu TOC 500 analyzer directly injecting the aqueous solutions after centrifugation. For the characterization of intermediate products, aqueous solutions of DEP (0.5 mM) containing TiO_2 (P25, $1\,\mathrm{g\,l^{-1}}$) were irradiated and samples were collected at different time intervals. The irradiated mixture was centrifuged and extracted with methylene chloride, which was subsequently dried over sodium sulfate and analyzed by GC–MS. For GC–MS analysis, a Shimadzu GC and MS was used (GCMS-QP 5050) equipped with a 25-m CP SIL 19 CB ($d = 0.25$ mm) capillary column, operating temperature-programmed (40°C for 2 min, 200°C for 30 min), at the rate of $10°\mathrm{C\,min^{-1}}$ in a split mode (injected volume; 1 μl) with helium as a carrier gas. The molecular ion and major mass spectrometric fragmentation peaks along with their relative intensities for the different products are given as follows.

Compound **4**: 240 (M^+, 1.17), 238 (64.93), 193 (–OC_2H_5, 63.75), 165 (–CO, 85.33), 120 (–OC_2H_5, 100), 92 (–$COOC_2H_5$, 73.52), 81 (34.11), 63 (68.56), 53 (41.58).

Compound **6**: 194 (M^+, 2), 193 (18), 165 (–C_2H_5, 100), 121 (–CO_2, 9.25), 92 (7.86), 81 (10.61), 63 (10.14).

Compound **7**: 149 (100), 133 (–O, 4.34), 105 (–CO, 6.43), 77 (–CO, 6.97), 65 (14.66), 50 (16).

3. Results

3.1. pH-effect

The influence of the pH on the DEP degradation kinetics and the mineralization rate was determined in a range between pH 3 and 11 employing a pH-stat technique to ensure constant pH throughout the entire irradiation. The obtained photonic efficiencies for the decomposition of DEP as well as for the TOC depletion are presented as a function of the reaction pH in Fig. 1. It is obvious that the efficiency for both, DEP and TOC removal is increasing from pH 3 to 6 while for higher pH values ζ is decreasing again. Thus, highest photonic efficiencies for the DEP degradation itself as well as for the total DEP mineralization are observed at pH 6, close to the zero point of charge of the photocatalyst. It was not possible to obtain photonic efficiencies for pH 11 because it has been found that the model compound decomposes under these conditions via alkaline-induced ester hydrolysis. For all investigated pH values, the depletion of the model compound followed first-order kinetics whereas the total mineralization could be described by zeroth order kinetics.

3.2. Photocatalyst concentration

The influence of the photocatalyst concentration on the degradation kinetics of DEP has been investigated using different concentrations of Degussa P25 varying from 0.5 to 5 g l^{-1} for DEP (Fig. 2). It can be seen that the addition of photocatalyst is markedly improving the degradation of the model pollutants itself as well as its mineralization in comparison to direct photolysis, i.e. 0 g l^{-1} photocatalyst concentration. A TiO_2-concentration of 1 g l^{-1} appears to be the best condition considering the degradation of DEP as well as mineralization whereas in the presence of lower photocatalyst loading smaller and in the case of higher ones almost identical photonic efficiencies were observed. Again, the degradation of DEP followed first-order while the mineralization followed zeroth order kinetics.

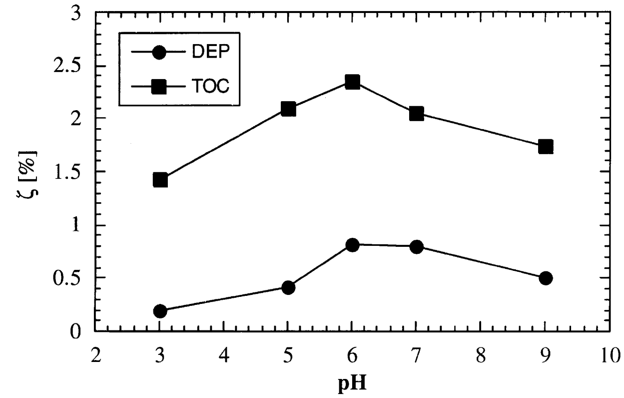


Fig. 1. Influence of the pH on the photonic efficiency of the photocatalytic degradation of DEP and the mineralization. Experimental conditions — 0.25 mM DEP, 5 g l^{-1} Hombikat UV 100, $V = 250$ ml, constant O_2-purging, $t = 6$ h, light intensity: 110 μM min^{-1}.

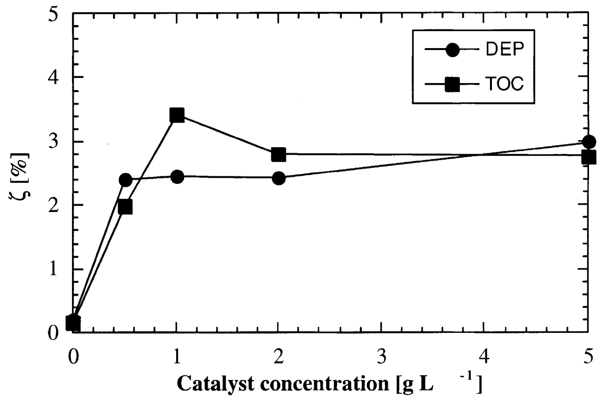


Fig. 2. Influence of the catalyst concentration on the photonic efficiency of the photocatalytic degradation of DEP and the mineralization. Experimental conditions — 0.25 mM DEP, pH 6, photocatalyst: Degussa P25, $V = 250$ ml, constant O_2-purging, $t = 6$ h, light intensity: 110 μM min^{-1}.

3.3. Substrate concentration and type of photocatalyst

The influence of the substrate concentration on the degradation kinetics of DEP where investigated for two commercially available titanium dioxide powders: Degussa P25 (1 g l^{-1}) and Sachtleben Hombikat UV 100 (5 g l^{-1}). The dependence of the photonic efficiency of the DEP and TOC degradation on the initial DEP concentration is shown in Fig. 3 for both employed photocatalysts. The photonic efficiency increases as the initial concentration of DEP is raised up to 0.25 mM for both, TOC and DEP degradation, followed by a plateau region for higher pollutant concentrations. While both materials qualitatively exhibit a similar behavior when studying the influence of substrate concentration on the photonic efficiency, generally higher rates (for the removal of the model compound as well as for the mineralization) were obtained when Degussa P25 was used as a photocatalyst.

3.4. Electron acceptors

The effect of electron acceptors in addition to molecular oxygen (hydrogen peroxide, potassium bromate and ammonium persulfate) on the degradation kinetics of DEP

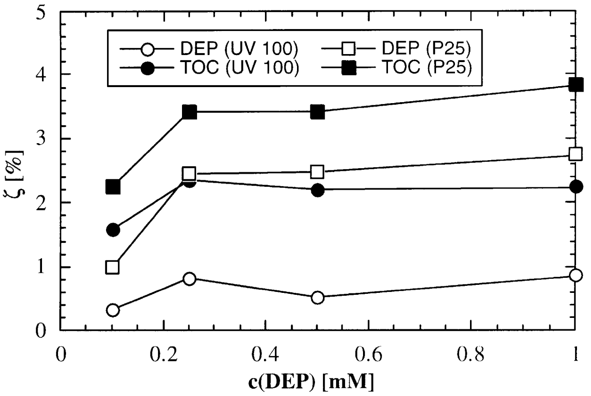


Fig. 3. Influence of the substrate concentration on the photonic efficiency of the photocatalytic degradation of DEP and the mineralization. Experimental conditions — 0.25 mM DEP, pH 6, photocatalysts: Degussa P25 ($1\,g\,l^{-1}$) and Sachtleben Hombikat UV 100 ($5\,g\,l^{-1}$), $V = 250$ ml, constant O_2-purging, $t = 6$ h, light intensity: $110\,\mu M\,min^{-1}$.

Table 1
Photonic efficiencies for the photocatalytic degradation of DEP in the presence of various electron acceptors

Additive	Photonic efficiency (%)	
	DEP	TOC
–	2.46	3.41
H_2O_2	2.82	3.72
$KBrO_3$	2.63	5.60
$(NH_4)_2S_2O_8$	2.67	3.23

has been investigated for optimized conditions, i.e. pH 6 and $1\,g\,l^{-1}$ Degussa P25. The obtained photonic efficiencies are summarized in Table 1. For DEP the addition of electron acceptors is only slightly enhancing the decomposition of the model pollutant itself while the mineralization is markedly improved only in the presence of bromate ions.

3.5. Intermediate products

An attempt was made to identify the intermediate products formed in the photocatalytic degradation DEP in aqueous suspensions of titanium dioxide through GC–MS analysis. The GC–MS analysis of DEP at 195 min irradiated mixture showed the formation of three photoproducts (**4**, **7** and **6**) appearing at retention times (t_R) 15.4, 16.8 and 26.8 min, respectively. The products were identified based on their molecular ion and mass spectrometric fragmentation peaks.

4. Discussion

One of the most important parameter in heterogeneous photocatalysis is the reaction pH, since it influences the surface charge properties of the photocatalyst and, therefore, the adsorption behavior of pollutants [31,32]. In heterogeneous photocatalysis, the adsorption of a pollutant molecule is a prerequisite for its efficient degradation and consequently a change in pH can lead to a change of the degradation rate and the amounts and concentrations of intermediates as it has been recently reported for the photocatalytic degradation of 4-chlorophenol [33] or for several isomers of chloro-hydroxy benzoic acids [34]. For TiO_2 Degussa P25, the zero point of charge (pH_{zpc}) is at pH 6.5. Hence, at more acidic pH values, the particle surface is positively charged, while at pH values above 6.5, it is negatively charged [35]. It is a result of this study, that the degradation rates and, therefore, the photonic efficiencies for the photocatalytic degradation of DEP are strongly influenced by the reaction pH. Highest photonic efficiencies were observed at pH 6, close to the zero point of charge of the photocatalyst. Thus, the adsorption of a relatively unpolar pollutant, such as DEP, on the photocatalyst's surface is apparently increasing under these conditions and consequently its degradation as well as the mineralization rate is enhanced.

The results on the photodegradation of the model compounds using two different kinds of TiO_2 photocatalysts indicate that the latter's bulk and surface properties, i.e. BET-surface, impurities, lattice mismatches or density of hydroxyl groups on the catalyst's surface, are apparently responsible for the photocatalytic activity, since they will affect the adsorption behavior of a pollutant or intermediate molecule and the lifetime and recombination rate of electron–hole pairs. Martin et al. [36] have recently shown that Degussa P25 owes his high photoreactivity to a slow recombination between electron and holes whereas Sachtleben Hombikat UV 100 (named S21 in the paper of Martin et al.) has a high photoreactivity due to fast interfacial electron-transfer rate. Since Degussa P25 was found to be the more active photocatalyst, it is obvious that the rate limiting step cannot be the interfacial electron-transfer reaction but rather the lifetime of electron–hole pairs. Assuming that adsorption–desorption of substrate and reaction intermediates is relatively slow in comparison to the recombination rate of electron–hole pairs, one should expect higher degradation rates when a photocatalyst such as Degussa P25 is used which guarantees longer lifetimes of the photogenerated electron–hole pairs. Thus, higher concentrations of electrons and holes are available for suitable reactants to initiate the photocatalytic reaction.

It is commonly accepted that hydroxyl and superoxide radicals are the primary oxidizing species in photocatalytic oxidation process [37,38]. They are formed by a reaction of electron–hole pairs, generated by the absorption of light with a wavelength $\lambda < 400$ nm, with surface adsorbed oxygen and water (Eqs. (3)–(5)).

$$TiO_2 + h\nu \rightarrow e^-_{CB} + h^+_{VB} \tag{3}$$

$$O_2 + e^-_{CB} \rightarrow O_2^{\bullet -} \tag{4}$$

$$H_2O + h^+_{VB} \rightarrow OH^{\bullet} + H^+ \tag{5}$$

The hydroxyl and superoxide radicals are now able to react with an organic substrate resulting in the degradation of the compound. The efficiency of latter reaction will depend upon the oxygen concentration, which determines the efficiency with which the conduction band electrons are scavenged and the electron–hole pair recombination is prevented. Since the electron transfer reaction is very often the rate limiting step in heterogeneous photocatalysis, alternative electron acceptors such as hydrogen peroxide, bromate and persulfate ions have been studied to improve this reaction and consequently to reduce electron–hole pair recombination. Additionally, hydroxyl or other strongly oxidizing radicals are generated by the reaction of these electron acceptors with electrons according to the following reactions (Eqs. (6)–(10)) which may, in turn, enhance the photocatalytic degradation of pollutants.

$$H_2O_2 + e^-_{CB} \rightarrow OH^\bullet + OH^- \quad (6)$$

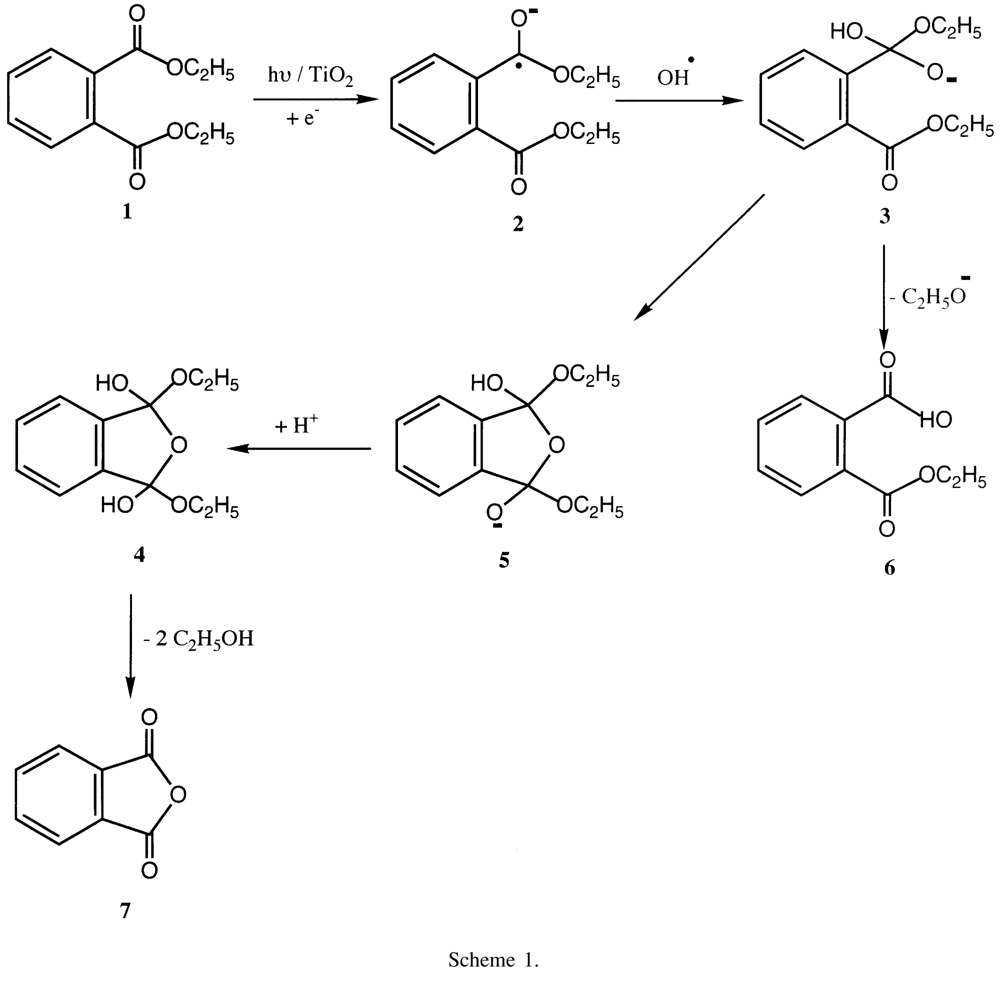
$$S_2O_8{}^{2-} + e^-_{CB} \rightarrow SO_4{}^{2-} + SO_4{}^{\bullet-} \quad (7)$$

$$SO_4{}^{\bullet-} + H_2O \rightarrow SO_4{}^{2-} + OH^\bullet + H^+ \quad (8)$$

$$BrO_3{}^- + 2H + e^-_{CB} \rightarrow BrO_2{}^\bullet + H_2O \quad (9)$$

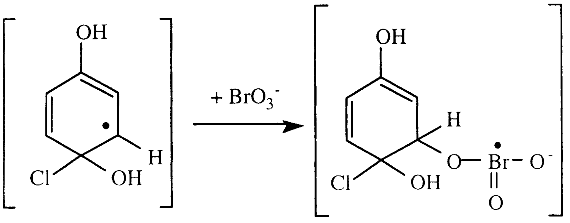
$$BrO_3{}^- + 6H^+ + 6e^-_{CB} \rightarrow [BrO_2{}^-, HOBr] \rightarrow Br^- + 3H_2O \quad (10)$$

By the addition of hydrogen peroxide or persulfate ions, only a slight increase in the degradation rates of the model compound DEP was observed. Thus, the improved formation of hydroxyl radicals via reaction (6) or by the reaction sequences (7) and (8) apparently only plays a minor role for the degradation kinetics of DEP and one could conclude that H_2O_2 and $S_2O_8{}^{2-}$ are no better electron acceptors than molecular oxygen. The addition of bromate ions is at least markedly enhancing the mineralization rate in the case of DEP. These results indicate that bromate ions are a more effective electron acceptors than all the other ones employed in this study. Furthermore, a change in the reaction mechanism can be postulated, since the reduction of bromate ions by electrons leads not directly to the formation of hydroxyl radicals, but to the formation of various very reactive radicals or oxidizing reagents, e.g. $BrO_2{}^\bullet$ and HOBr. Furthermore, bromate ions by themselves can act as oxidizing agents. Lindner has recently proposed a mechanism for the photocatalytic degradation of 4-chlorophenol in the presence of bromate ions (Eqs. (11) and (12)) considering the direct oxidation of the substrate by bromate

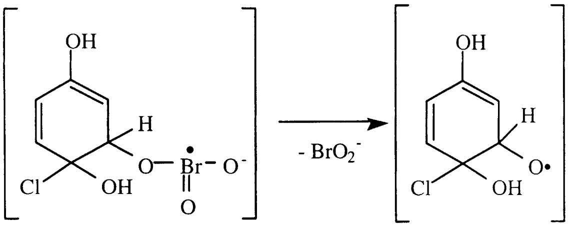


Scheme 1.

ions [39].



(11)



(12)

A similar mechanism might be operative in the case of the model compound studied in this work.

The photocatalyzed degradation of DEP has been found to yield three intermediate products. A plausible mechanism for the formation of different products involving electron transfer reactions and reactions with hydroxyl radicals formed in the photocatalytic system is proposed in Scheme 1. The model compound **1** upon the transfer of an electron can form the radical anion **2**, which may undergo addition of a hydroxyl radical forming the anionic species **3**, which upon loss of an ethoxy group can lead to the formation of the observed product **6**. The species **3** upon cyclization followed by abstraction of a proton will give rise to **4**, which on subsequent removal of two molecules of ethanol will lead to the formation of **7**, as shown in Scheme 1.

5. Conclusion

The result of this study clearly demonstrate the importance of choosing the optimum degradation parameters (pH, kind of catalyst, catalyst concentration, etc.) to obtain a high degradation rate of the model pollutant itself combined with a high mineralization rate, in our opinion one of the most important parameters in photocatalytic oxidation processes. The best condition depends strongly on the kind of pollutant. Especially, the reaction pH is markedly influencing the overall efficiency of the process. Addition of electron acceptors can enhance at least the overall mineralization reducing the amount and concentrations of intermediates. The analysis of the intermediate products formed during the photodegradation process could be an useful source of information on the degradation pathways.

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