

TiO₂ photocatalytic oxidation of monochloroacetic acid and pyridine: influence of ozone

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Abstract

The influence of ozone on the photocatalytic oxidation of monochloroacetic acid and pyridine with TiO₂ (0.5 g/l) at pH 3 (H₂SO₄) was investigated. Illumination was performed in a batch reactor (400 ml), with UV-lamp (360–420 nm; 7×10^{-6} Einstein s⁻¹) with continuous introduction of oxygen or ozone containing oxygen. The photocatalytic ozonation of monochloroacetic acid and pyridine which does not react with ozone alone under given conditions leads to 6 and 24 times higher degradation rates than without TiO₂ and 4 and 18 times higher rates than without ozone. Moreover the photocatalytic ozonation shows the lowest specific energy consumption (kW h/g DOC-reduction) of the different processes under the experimental conditions. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

In heterogeneous photocatalysis the photocatalyst a solid semiconductor and reactants exist in different phases. During illumination by light of appropriate wavelength electrons are promoted from the valence band to the conduction band. Some electron–hole-pairs recombine immediately, some migrate to the surface of the semiconductor where redox reactions can occur. The redox potentials of electron–hole-pairs and relevant redox pairs are illustrated in Fig. 1.

In TiO₂-photocatalytic oxidation processes oxygen is widely used as an additional oxidizing agent. The disadvantage is the slow electron transfer from TiO₂ to O₂ [1]. Ozone, with its high redox potential $E^0 = 2.07$ V and its electrophilic properties, is used for disinfection and oxidation of organic and inorganic compounds in waste water treatment [2,3]. Ozone should be a potential oxidant for photocatalytic oxidation processes. But until now only a few results on this topic are published by Sierka and Hendricks [4], Ohtani et al. [5], Paillard et al. [6], Allemane et al. [7], Koji [8], Noguchi et al. [9], Preis et al. [10] and Prados et al. [11]. Most authors apply UV-B-light (254 nm) as a radiation source. Not only the photocatalyst TiO₂ but also ozone itself can absorb light in this range. Therefore it is often not possible to distinguish between photocatalytic

reactions initiated by the solid photocatalyst and photolytic reactions by ozone. In this work, a 360 nm cut-off filter is used to avoid photolytical ozone reactions.

2. Experimental

A 0.4 l batch-reactor of glass (Duran®), temperature controlled (20°C) with stirrer was used. The reactor walls were covered by a reflecting layer. Illumination was performed by a UV-lamp (UVAHAND 250, Hönle, Planegg) through the bottom of the reactor. Between lamp and reactor a 360 nm cut-off filter (Ø49 mm) was installed (WG 360, Schott, Mainz). The photon rate ($7(\pm 1) \times 10^{-6}$ Einstein s⁻¹) into the reactor was determined with ferrioxalate-actinometry. Pure oxygen or ozone containing oxygen (20 l/h) was continually bubbled into the solutions. Ozone was produced from pure oxygen using a Fischer ozone generator (dose rate 400 mg/h). As photocatalyst, commercially available TiO₂ (P25, Degussa) (0.5 g/l) was used. Initial concentrations of monochloroacetic acid and pyridine were 1 mmol/l. Before starting illumination, pH was adjusted to pH 3.0 (H₂SO₄). The suspension was filtrated to separate the photocatalyst and to stop the photocatalytic reaction. Quantitative determination was performed by isotachopheresis (monochloroacetic acid and organic acids as oxidation products), high performance liquid chromatography (HPLC, pyridine) and ion chromatography (nitrate, chloride,

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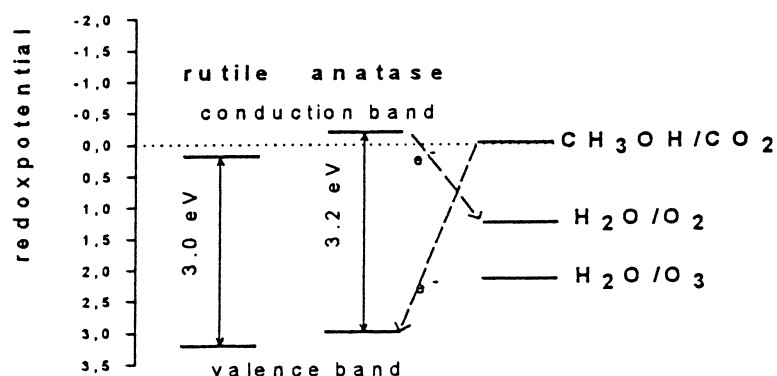


Fig. 1. Level of redox potentials of TiO_2 electron-hole-pairs and of relevant organic redox species in solution (pH 0).

ammonium). The ozone in solution was determined by the indigo-method [12].

In order to obtain the differences between processes initiated by oxygen and by ozone, the organic model compounds were illuminated under following conditions:

1. TiO_2/O_2 . The titanium dioxide is suspended in an aqueous solution of the substrate (pyridine or monochloroacetic acid). The gas flow consists of ozone-free, pure oxygen.
2. $\text{H}_2\text{O}/\text{O}_3$. The solution is free of titanium dioxide. The supplied gas contains oxygen and 20 mg/l ozone. The illumination should have no effect on the reactions because there is no absorbing species present.
3. TiO_2/O_3 . The titanium dioxide is suspended in an aqueous solution of the substrate (pyridine or monochloroacetic acid). The supplied gas contains oxygen and 20 mg/l ozone.

The combination TiO_2/O_3 is called the “photocatalytic ozonation”. The other combinations were investigated to check possible parallel reactions during photocatalytic ozonation. During these reactions oxygen can make photocatalytic oxidation reactions and the ozone in solution possibly can react with the organic compounds.

3. Results

3.1. Photocatalytic ozonation of monochloroacetic acid

In Fig. 2 the photocatalytic ozonation of monochloroacetic acid compared to the ozonation and photocatalytic oxidation is shown.

The concentration curves were approximately linear. Therefore degradation rates were determined by regressing the experimental data (Table 1). The degradation rate of photocatalytic ozonation is about 24 times higher than the degradation by ozonation under same conditions without TiO_2 and 4 times higher compared to the elimination by TiO_2/O_2 treatment.

The degradation rate of TiO_2/O_3 process is about 3.6 times higher than the sum of the degradation rate of TiO_2/O_2 and

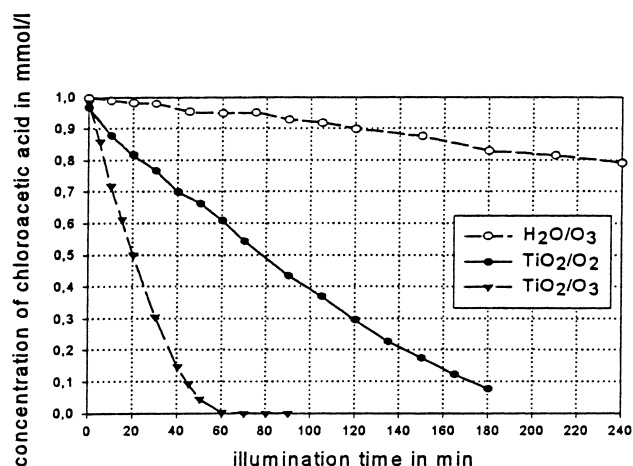


Fig. 2. Photolysis of monochloroacetic acid; $\lambda > 360$ nm; pH 3, elimination in dependence on different conditions; $\text{TiO}_2 = 0.5$ g/l; ozone dose rate 400 mg/h.

$\text{H}_2\text{O}/\text{O}_3$. This means that even if we postulate that both processes TiO_2/O_2 and $\text{H}_2\text{O}/\text{O}_3$ occur during photocatalytic ozonation there should be additional reactions leading to the faster degradation rates. The reason should be the additional illumination in the presence of ozone because the elimination rates of chloroacetic acid measured by using the combination O_3/TiO_2 without light and by illumination with a 435 nm cut-off filter are comparable to the rate found with $\text{H}_2\text{O}/\text{O}_3$.

Therefore the photocatalytic ozonation is a photoreaction which needs all the three components: titanium dioxide, ozone and UV > 360 nm. Probably the photocatalytic oxygen-reaction and the direct ozone oxidation of the monochloroacetic acid happen also during illumination.

Table 1
Photolysis of monochloroacetic acid, $\lambda > 360$ nm degradation rates in dependence on different conditions

	TiO_2/O_2	$\text{H}_2\text{O}/\text{O}_3$	TiO_2/O_3
Degradation rate in mmol/(lmin)	0.0049 ± 0.0002	0.00088 ± 0.00006	0.021 ± 0.001

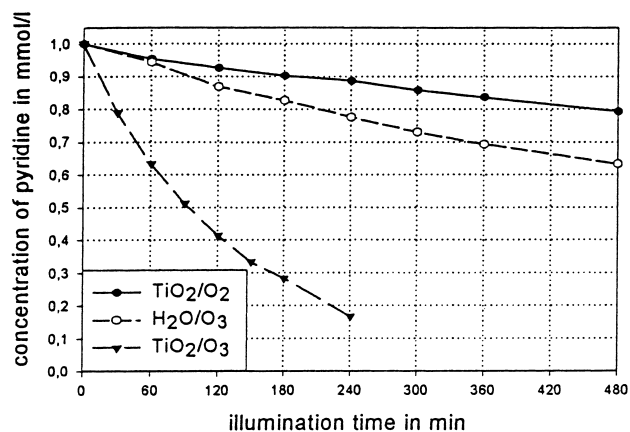


Fig. 3. Photolysis of pyridine, $\lambda > 360$ nm; pH 3, elimination in dependence on different conditions; TiO₂ = 0.5 g/l; ozone dose rate 400 mg/h.

But a further contribution to the degradation of the monochloroacetic acid should be initiated by the reaction of the ozone with the illuminated titanium dioxide.

Investigations concerning the oxidation products showed that parallel to the degradation of the monochloroacetic acid, the corresponding concentration of chloride was generated during all the three oxidation processes. The concentration of dissolved organic carbon (DOC) in the samples was about the same as the calculated DOC of the remaining monochloroacetic acid. The sum of chlorine (calculated from monochloroacetic acid and chloride concentrations) lies between 85 and 105% of the initial concentration during all the experiments. Concerning the analytical accuracy, all the organic chlorine was found as chloride after 100% elimination of the initial compound.

3.2. Photocatalytic ozonation of pyridine

In Fig. 3 the photocatalytic ozonation of pyridine compared to the ozonation and photocatalytic oxidation is shown. Assuming pseudo-first-order decomposition, the rate constants were determined by regressing the experimental data (Table 2).

Comparing the data of Table 2, like in the case of monochloroacetic acid, it could be shown that the degradation rate of pyridine in the photocatalytic ozonation process is about 5 times higher than the sum of the degradation rates of pyridine in the TiO₂/O₂ and H₂O/O₃ process.

The photocatalytic ozonation of pyridine decreases the DOC of the solution parallel to the elimination of pyridine (Fig. 4). As organic oxidation products oxalic acid and

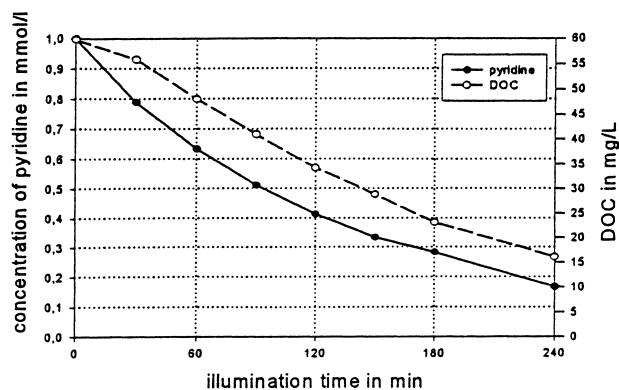


Fig. 4. Photocatalytic ozonation of pyridine; $\lambda > 360$ nm; pH 3; TiO₂ = 0.5 g/l; ozone dose rate 400 mg/h; decrease of pyridine and DOC in dependence on illumination time.

oxalic acid monoamide (oxamic acid) could be quantitatively measured. The yields of the two oxidation products lie between 0.05 and 0.1 mmol/l. These products together with pyridine cover 85% of the measured DOC. The small amount of oxidation products shows that the photocatalytic ozonation leads besides the initial oxidation of pyridine in competition reactions to the mineralization of primary intermediates. This is also shown in the nitrogen balance where 90% of the pyridine nitrogen is covered by ammonia, nitrate, and small amounts of oxamic acid and pyridine.

3.3. Mechanistic studies

To get more information about the photocatalytic ozonation processes, the ozone decay by illumination in aqueous solution and in TiO₂ suspension in the absence of organic compounds was measured. The solutions (pH 3) were saturated with ozone. After stopping the gas supply illumination was started. In Fig. 5 the ozone decay in both cases is shown.

From the data in Fig. 5 the decay rate of ozone in illuminated water was calculated. The value in pure water 0.03 mg/(l min) lies in the same range as in water without illumination 0.04 mg/(l min). Also TiO₂ in the dark did not enhance the ozone decay. But in illuminated suspensions the ozone decay was higher by a factor of 50 (1.6 mg/(l min)). It is obvious that the decay is accelerated by the application of titanium dioxide and appropriate light. The reaction depends on the light intensity. If the light intensity is decreased to $\frac{1}{50}$ by applying a grey-glass filter (NG9, Schott, Mainz) the ozone decay is also decreased (Fig. 5). These results show that a real photocatalytic reaction occurs in the suspension, not the radiation alone but the combination of radiation and photocatalyst initiates a decay reaction of ozone. But with this it is not possible to decide if ozone reacts directly on the surface of TiO₂ or in a second step via oxygen, because in the suspensions the concentration of oxygen (1.2 mmol/l) is about 9 times higher than that of ozone (0.13 mmol/l). Therefore it is possible that the electron transfer mechanism from titanium dioxide to the ozone molecule is not a direct

Table 2
Photolysis of pyridine, $\lambda > 360$ nm, degradation rates in dependence on different conditions

	TiO ₂ /O ₂	H ₂ O/O ₃	TiO ₂ /O ₃
Time constant (l/min)	0.00047±0.00002	0.0011±0.0002	0.0075±0.0008

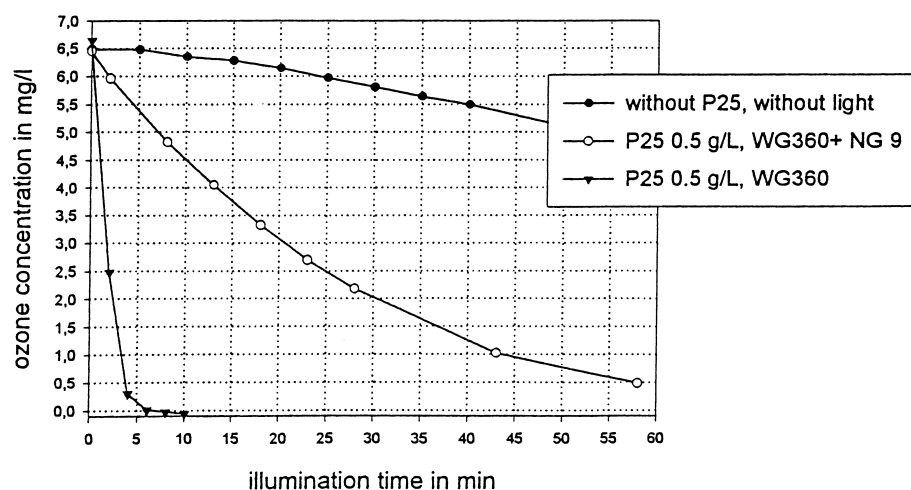


Fig. 5. Photolysis (360 nm cut-off filter) of ozone containing water and TiO₂ suspension (0.5 g/l) at pH 3; decay of ozone in dependence on illumination time.

transfer. Probably the oxygen molecule first reacts with the photoelectron and in the following reaction steps the electron is transferred to the ozone molecule.

In order to investigate this assumption the degradation reactions of pyridine and monochloroacetic acid were performed once with pure oxygen as supply gas and once with synthetic air (21% oxygen). The ozone concentration in both experiments was 20 mg/l. Because of the reduced oxygen concentration in synthetic air, the oxygen concentration in the suspension should be only one fifth of the oxygen concentration when using pure oxygen as supply gas. The influence of the higher oxygen concentration on the decrease of chloroacetic acid and pyridine is shown in Fig. 6.

With the 5 times higher oxygen concentration, the rate of decrease of pyridine and chloroacetic acid is 50–60% higher. This result indicates that oxygen should have an influence on the photocatalytic ozonation. Besides other reaction paths, for example direct ozone attack, or direct electron transfer from TiO₂ to the ozone molecule, a further reaction path is proposed:

Charge separation:



Charge transfer of positive charge:



Electron transfer and further reactions:

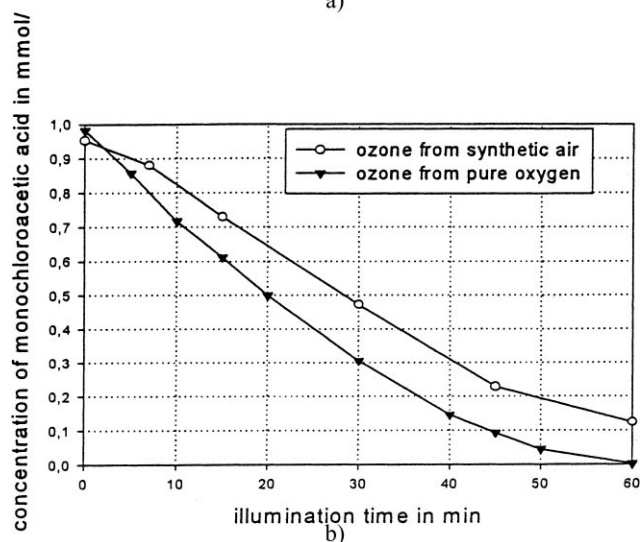
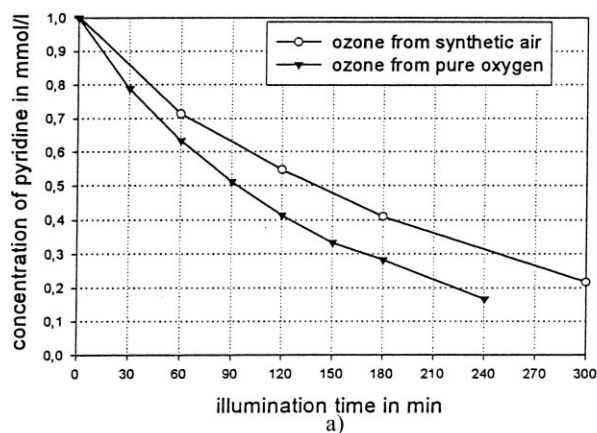


Fig. 6. Influence of the oxygen concentration on photocatalytic ozonation; synthetic air 21% O₂, pure oxygen: 99.99% O₂, ozone concentration: 20 mg/l in both experiments; decrease of pyridine (a) and monochloroacetic acid (b).

Oxidation of the organic compound R:



or



In reactions (4)–(7) the ozone decay according to the mechanism of Weiss with the extension of Buhler et al. [13] is described. The difference between photocatalytic ozone decay and ozone decay in aqueous solution is the initiation of the reaction. The starting radical is formed photochemically by an electron transfer from titanium dioxide to oxygen and not, like in the Weiss-mechanism, by the reaction of OH^- -ion with ozone. In both cases primarily $\text{O}_2^{\bullet-}$ is formed. $\text{O}_2^{\bullet-}$ reacts with ozone forming the ozonide ion (5) with a rate constant of $1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [13]. After protonation OH-radicals are formed ((6) and (7)). The formation of OH radicals in acidic solutions via direct electron transfer from the catalyst to the ozone molecule or via $\text{O}_2^{\bullet-}$ explains the degradation of organic compounds by photocatalytic ozonation which react very slowly with the ozone molecule or with HO_2 , one of the primary oxidizing species in photocatalytic processes.

3.4. Efficiency of photocatalytic ozonation

To show the difference between photocatalytic oxidation and photocatalytic ozonation the quantum efficiency of the two processes is compared. The quantum efficiency is defined as initial rate of degradation of organic compound divided by the applied photons (Table 3).

In the case of monochloroacetic acid and pyridine the quantum efficiency of photocatalytic ozonation is 4, 18 times higher than that of photocatalytic oxidation.

Sun and Bolton [14] calculated the quantum yield for the oxygen process to be 0.04 referred to the generation of OH-radicals. But the quantum efficiency is always much lower than the quantum yield because of the difference between applied and absorbed photons. It is also to be considered that in these experiments the photonic efficiency was calculated for the initial molecule disappearance and not for the generation of OH-radicals.

In view of a technical process it is necessary to consider the energy consumption of the photocatalytic ozonation compared to the two other processes. Photocatalytic ozonation needs additional electrical energy for the ozone generator. Therefore energy consumption of the three processes

Table 3
Photocatalytic ozonation of monochloroacetic acid and pyridine, quotient of degradation rate and applied photon

	TiO_2/O_2	TiO_2/O_3
Monochloric acetic acid	0.009 ± 0.001	0.038 ± 0.007
Pyridine	0.0008 ± 0.0002	0.014 ± 0.002

Table 4
Energy consumption of the UV-lamp and the ozone generator

UV-lamp	0.046 kW h in 60 min
Ozone generator	0.018 kW h in 60 min or 0.045 kW h/g ozone

Table 5
Photocatalytic ozonation of monochloroacetic acid and pyridine; specific energy consumption (kW h/g DOC-reduction)

	TiO_2/O_2 (kW h/g DOC-reduction)	$\text{H}_2\text{O}/\text{O}_3$ (kW h/g DOC-reduction)	TiO_2/O_3 (kW h/g DOC-reduction)
Monochloroacetic acid	19	110	5.4
Pyridine	120	73	11

was compared according to consumption of electrical power (kW h) of the laboratory device under the experimental conditions. Energy consuming components are given in Table 4.

In view of energy consumption the DOC decrease, in dependence on energy applied, of the three processes were compared (Table 5). It is obvious that the photocatalytic ozonation has a lower specific energy consumption compared to the photocatalytic oxygen-process and to the ozonation without photocatalyst. The value is only 5 and 15% of the value of the ozonation and only 9 or 28% of the value of the photocatalytic oxygen-process (Table 5).

4. Conclusions

The results show that the photocatalytic oxidation in the presence of ozone is a process which is qualitatively and quantitatively different from the well-known photocatalytic oxidation with oxygen and the ozonation without photocatalyst. The reason for the higher oxidation rate is probably a photocatalytic induced decay of ozone, initiated by the combination of titanium dioxide and UV-A-radiation. A comparison of the consumption of electric energy during the experiments revealed that, considering the total mineralisation of the compounds, the photocatalytic ozonation shows a much lower specific energy consumption than the other processes.

In this study organic compounds were used which are hardly oxidized by ozone at pH 3. Especially this kind of organic compounds showed acceleration of degradation rate in photocatalytic ozonation. Therefore the photocatalytic ozonation could be an alternative way to the common oxidizing processes for oxidation and elimination of refractory organic compounds under specific conditions.

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