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A comparative study for the synergistic effect of ozone on the γ-irradiated and photocatalytic reaction of 4-chlorobenzaldehyde

Işil Akmehmet Balcioglu [a,*], Nicola Getoff [b], Miray Bekbölet [a]

[a] *Boğazici University, Environmental Science Institute, 80815 Bebek, Istanbul, Turkey*
[b] *Institut für Thoeretische Chemie und Strahlenchemie der Universitat Wien, Althanstraβe 14, Ebene 5, A-1090 Vienna, Austria*

Abstract

The synergistic effect of ozone on both, the TiO_2-mediated photocatalytic and γ-rays induced degradation of 1×10^{-3} mol dm^{-3} 4-chlorobenzaldehyde (4-ClBzAl) was studied as a function of absorbed energy. The formation of formaldehyde (HCHO), H^+ and Cl^- ions as well as of carboxylic acid was used to follow the degradation processes. The highest efficiency for the substrate degradation was achieved by the simultaneous action of ozone and photocatalysis on 4-ClBzAl in aqueous solution. On the other hand, the degradation yield of the substrate by ozonation is three times higher compared to the degradation yield observed by γ-rays in the presence of ozone. This yield is however, higher than that obtained by γ-radiolysis in the presence of air. Benzoic, 4-chlorobenzoic, fumaric, glyoxylic, mucconic, and oxalic acids were formed as common final reaction products in each degradation process. © 2000 Published by Elsevier Science S.A.

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1. Introduction

Hydroxyl radicals OH$^\bullet$ are the most reactive oxidants for the treatment of refractory pollutants in water and wastewater [1–8]. These radicals are rather non-selective and, therefore, they can react with most organic and inorganic solutes 10^6–10^9 times faster than the better known oxidizing agents (ozone, hydrogen peroxide, etc.) [9]. There are several processes of generating OH$^\bullet$; e.g. by radiolysis and photolysis of water, UV/ H_2O_2, Fe^{2+}/H_2O_2, O_3/OH^-, O_3/H_2O_2, TiO_2/H_2O_2 [2,4,6–8] which are known as advanced oxidation processes (AOPs) [5]. By far the simplest method for in situ generation of OH$^\bullet$ is the action of ionizing radiation on water, because it works without any addition of chemical agents. The ionization and excitation of water molecules by high-energy radiation are known to result in the formation of reducing species like solvated electron (e$^-_{aq}$) and hydrogen atoms (H) as well as OH$^\bullet$ which are of interest for pollutant decomposition. Since the total amount of the reducing species in air-free solutions is even somewhat higher yield than that of OH$^\bullet$, they often induce undesirable side reactions and may reduce the economy of an irradiation process considerably [10]. The addition of air and/or ozone to the water before or during irradiation converts H atoms and e$^-_{aq}$ into peroxyl radicals [2–4,10–13].

In contrast to the treatment with high-energy radiation, the destruction of organic impurities in water is possible with near-UV light-illuminated suspensions of titanium dioxide (TiO_2) which has been the subject of numerous reports [3–5].

The purpose of the present study is to investigate the synergistic effect of ozone on both the photocatalytic and γ-radiated decomposition of 4-chlorobenzaldehyde (4-ClBzAl) solution that was used as model compound. The degradation products of each process were determined by HPLC analysis.

2. Experimental

2.1. Methods and material

Photocatalytic reactions were carried out in a special 4π-quartz irradiation vessel [14,15]. A 100-ml reaction mixture with or without ozone and TiO_2 was irradiated with a low-pressure Hg-lamp (Osram HNS 10W) with a Vycor-filter incorporated for removal of the 185-nm line. The UV light intensity was determined by using monochloroacetic acid actinometer measuring the Cl$^-$-yield [16]. Taking Q(Cl$^-$)=0.36 at 32°C [17], the UV-intensity at 254 nm was determined as $I_0 = 9.3 \times 10^{15} h\nu$ ml^{-1} min^{-1}.

* Corresponding author.

Ozone was produced with an electrolytic laboratory type generator (Fischer 500 model). High purity oxygen (Griesheim, Vienna, Austria) was used for the generator feed gas. Each ozonation run was conducted at a gas flow rate of $1.07\,dm^3\,min^{-1}$. Ozone input concentration was determined iodometrically as $6\times10^{-4}\,mol\,dm^{-3}$.

A ^{60}Co-γ source (Gammacell 220, Nordion International, Canada) equipped with lead absorbers for reducing the dose rate was used for γ-radiation experiments. The dose rate was $4.8\,krad\,min^{-1}$, which was determined by means of modified Fricke-dosimeter [18] using G-value [1] $G(Fe^{3+})=15.6$. The experiments were carried out in a Pyrex reaction vessel in which air or ozone is continuously introduced from the reactor bottom through 100-ml solution.

2.2. Preparation of the solutions

The 4-CLBzAl was supplied by Fluka and further purified by sublimation. TiO_2 (Merck) used in photocatalytic experiments was rutile type. All other chemicals were reagent grade and used without further purification. Triply distilled water was used for the preparation of all solutions.

2.3. Product analysis

The total degradation of 4-ClBzAl was followed both spectrophotometrically (Perkin–Elmer λ 16) and by HPLC analysis. In addition to this Cl^- ion, formaldehyde and formation of total acids were determined. The cleaved chlorine as Cl^- ions was determined by the mercury (II) thiocyanate method [16] and the formation of formaldehyde was followed by the method of Nash [19]. The pH measurements of the solutions were performed by using an Orion model 420 pH-meter. A Hewlett–Packard 1050 HPLC, equipped with a multiple wavelength UV detector (210, 259 nm) and an EC detector, was used for the identification of reaction products. Aminex ion exclusion HPX-87 H column (300 mm×7.8 mm, eluent: 1% H_3PO_4) and Spherisorb ODS 2 column (125 mm×4 mm, eluents H_2O/MeOH=40/60 by volume) were used to analyze the small acids and the other reaction products, respectively.

3. Results and discussion

In order to achieve sufficient sensitivity for the determination of reaction products, $10^{-3}\,mol\,dm^{-3}$ 4-ClBzAl and $6\times10^{-4}\,mol\,dm^{-3}$ O_3 were used as initial concentration in all experiments conducted with ^{60}Co-γ irradiation, TiO_2 mediated photocatalytic reaction, and a combination of both methods with O_3. The decomposition of 4-ClBzAl by application of various oxidizing processes is presented in Fig. 1 as a function of reaction time.
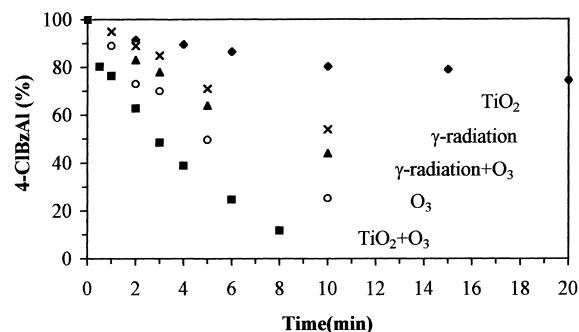

Fig. 1. Degradation of $1\times10^{-3}\,mol\,dm^{-3}$ 4-ClBzAl under the influence of various oxidation processes. Temperature=32°C, pH_i =6.1, $[O_3]_i=6\times10^{-4}\,mol\,dm^{-3}$, $TiO_2=1\,mg\,ml^{-1}$.

Table 1
Degradation efficiency of $1\times10^{-3}\,M$ 4-ClBzAl by different oxidation processes

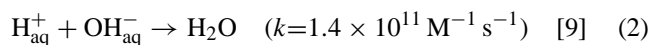| Type of process	G_i	k (min^{-1})	Type of process	Q_i	k (min^{-1})
γ-Radiation	6.45	0.064	UV/TiO_2	2.68	0.012
$O_3+\gamma$-Radiation	19.60	0.080	O_3+UV/TiO_2	16.06	0.252
O_3	–	0.173			

Degradation of 4-ClBzAl followed a pseudo-first-order kinetics in all applied processes. By the simultaneous application of ozone and photocatalytic processes, the highest yield was obtained and $1\times10^{-3}\,mol\,dm^{-3}$ 4-ClBzAl was completely degraded in 10 min. Although the beneficial effect of ozone addition on both, the photocatalytic and γ-radiation, processes was observed for the degradation of 4-ClBzAl, a higher degradation yield was achieved by ozone alone when compared to $O_3+\gamma$-radiation. The efficiencies of applied processes are compared in Table 1 in terms of pseudo-first-order reaction rate constants (k), initial radiation (G_i) and quantum yields (Q_i) [2]. The initial values for G and Q are calculated for substance degradation and products formation before secondary reactions take place. The data in Table 1 indicated that, in the presence of O_3, a considerable effect, particularly on Q_i and G_i, was obtained. UV radiation in the absence of TiO_2 was found to cause very slow degradation of 4-ClBzAl with an initial quantum yield value of 0.64. It was also found that only 1% of used amount of 4-ClBzAl adsorbed on TiO_2 surface in the absence of light.

First, it should be mentioned that water radiolysis produces a number of primary products which are shown with their radiation yield values (G-value) at pH $\sim$7 in Eq. (1):

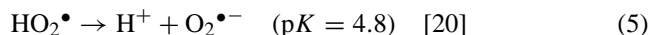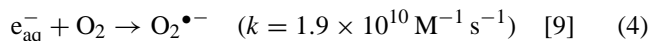$$H_2O \rightarrow e_{aq}^-,\ H^\bullet,\ OH^\bullet,\ H_2,\ H_2O_2,\ H_{aq}^+,\ OH_{aq}^+ \qquad (1)$$
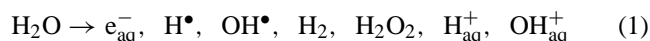
(G-value) (2.7) (0.6) (2.8) (0.45) (0.7) (3.2) (0.5)

$$H_{aq}^+ + OH_{aq}^- \rightarrow H_2O \quad (k=1.4\times10^{11}\,M^{-1}\,s^{-1}) \quad [9] \quad (2)$$

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[1] G-value is the number of molecules reacting per 100 eV of absorbed energy.

[2] Q-value is the number of molecules changed per quantum ($h\gamma$) absobed energy.

In the presence of air, H-atoms and e_{aq}^- are scavenged by oxygen, forming peroxyl radicals ($HO_2^\bullet$, $O_2^{\bullet-}$)

$$H^\bullet + O_2 \rightarrow HO_2^\bullet \quad (k = 2.1 \times 10^{10}\,M^{-1}\,s^{-1}) \quad [9] \quad (3)$$

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet-} \quad (k = 1.9 \times 10^{10}\,M^{-1}\,s^{-1}) \quad [9] \quad (4)$$

$$HO_2^\bullet \rightarrow H^+ + O_2^{\bullet-} \quad (pK = 4.8) \quad [20] \quad (5)$$
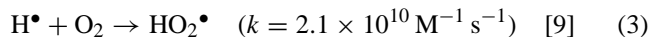
In the simultaneous application of O_3 and γ-radiation, O_3 will be attacked by the primary species of water radiolysis, resulting into a number of very reactive transients [4].

In the ozonation process, the following primary reaction steps are playing an important role:

$$(6)$$
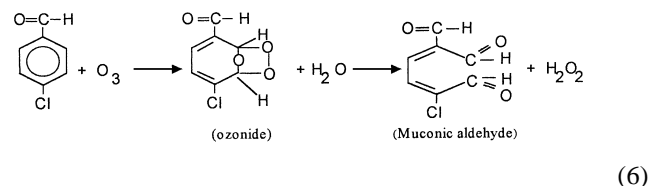
The resulting muconic aldehyde is further decomposed to formaldehyde, carboxylic acids and other substances.

The reason of lower reaction efficiency of $O_3 + \gamma$-radiation process than that obtained by the ozonation process could be explained by the fact that a certain part of the primary products of water radiolysis react with O_3 while the rest is consumed by the substrate. However, in the ozonated radiation process, $HO_2^\bullet/O_2^{\bullet-}$ as well as the OH radicals act as carriers for the chain reaction of ozone degradation [21–25]. This effect may increase the degradation of 4-ClBzAl in ozonated radiation compared to γ-radiation.

Although photocatalytic degradation of 4-ClBzAl was a comparably slow process, the highest yield was obtained by the simultaneous application of ozonation and photocatalytic processes. In UV-illuminated TiO_2 suspensions, electrons and positive holes are formed within the particles. Some of these migrate to the surface of the particle, where oxidation and reduction reactions may occur at rates controlled by interfacial phenomena. Solutes do not have access to all of the initially formed photo-excited species and most will decay to the ground state with the liberation of heat, but without initiating a chemical reaction. The radicals in γ-radiated aqueous solutions do not undergo recombination
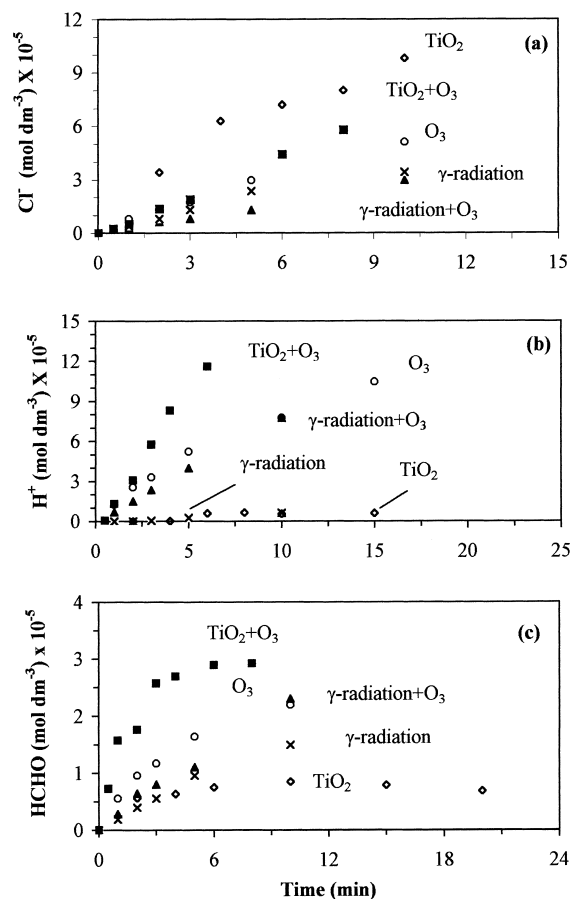

Fig. 2. Cl^-, H^+ ions and formaldehyde formations by oxidative degradation of $1 \times 10^{-3}\,mol\,dm^{-3}$ 4-ClBzAl as a function of treatment time. Temperature 32°C, pH_i 6, $[O_3]_i$ $6 \times 10^{-4}\,mol\,dm^{-3}$, $TiO_2 = 1\,mg\,ml^{-1}$.

in a solution containing a surplus of substrate and initiate chemical reactions. In ozonated photocatalytic process, the presence of ozone can inhibit the electron–hole recombination on TiO_2 surface by reacting with e^-. In addition to this effect, ozone can increase the oxidation efficiency by producing hydroperoxyl and hydroxyl radicals [26]. Having strong oxidizing power these radicals can also be produced in photocatalytic reaction.

In this study, the substrate decomposition was additionally followed by measuring the formation of Cl^-, H^+ ions and

Table 2
k_i, Q_i and G_i and values for chloride, formaldehyde and total acid formation observed by various processes

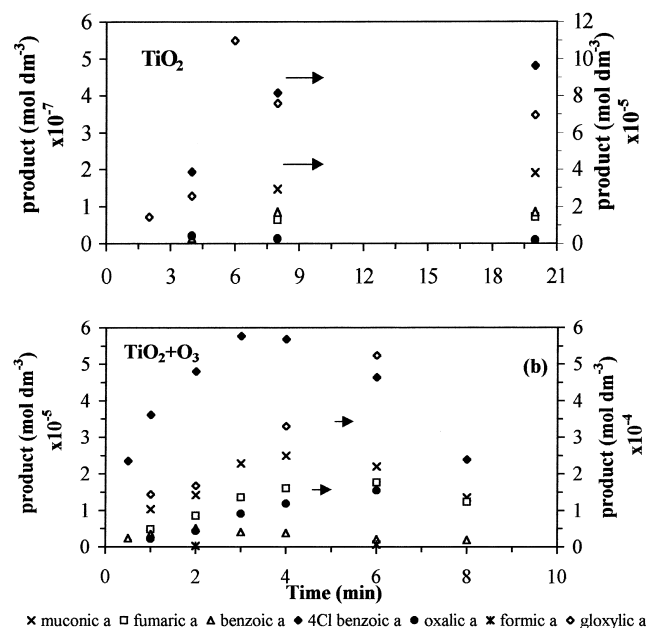| Type of process	(H^+)		(Cl^-)		(HCHO)	
	G_i	k_i (mol dm^{-3} min^{-1})	G_i	ki (mol dm^{-3} min^{-1})$_i$	G_i	k_i (mol dm^{-3} min^{-1})
O_3	–	1.25×10^{-4}		0.60×10^{-5}		0.48×10^{-5}
γ-Radiation	1.18	0.053×10^{-4}	0.64	0.30×10^{-5}	0.4	0.18×10^{-5}
$O_3 + \gamma$-radiation	16.38	0.75×10^{-4}	0.96	0.43×10^{-5}	0.66	0.31×10^{-5}
Type of process	Q_i	k_i (mol dm^{-3} min^{-1})	Q_i	k_i (mol dm^{-3} min^{-1})	Q_i	k_i (mol dm^{-3} min^{-1})
UV/TiO$_2$	0.6	1.25×10^{-4}	1.096	1.70×10^{-5}	0.18	0.27×10^{-5}
O_3+UV/TiO$_2$	11.8	1.83×10^{-4}	0.44	0.68×10^{-5}	1.032	11.6×10^{-5}

Fig. 3. Photo-induced formation in the presence of products by TiO_2/UV and O_3+TiO_2/UV by decomposition of 1×10^{-3} mol dm^{-3} 4-ClBzAl (pH=6.1) in the presence of air.

Fig. 4. Formation of products by γ-radiation as well as by γ-radiation in the presence of O_3 by decomposition of 1×10^{-3} mol dm^{-3} 4-ClBzAl (pH 6.1) in the presence of air.

formaldehyde (Fig. 2a–c) and initial reaction rate constants (k_i), G_i and Q_i values are compiled in Table 2.

An inspection of the k_i, G_i and Q_i values of H^+, Cl^- ions and formaldehyde in Table 2, showed that the highest reaction rate was obtained for H^+ ion and formaldehyde formation by the simultaneous application of O_3 and TiO_2. The chloride ions were one of the reaction by-products of the UV/TiO_2 photocatalytic reaction as well as the γ-radiation of 4-ClBzAl in the presence of oxygen. For Cl^- ion formation, the most rapid initial reaction rate was observed for the photocatalytic reaction of 4-ClBzAl. In most cases, e_{aq}^- is known to lead to a quantitative reductive dehalogenation [27–29]. However, this is not the case with 4-ClBzAl, as has been shown previously by pulse radiolysis experiments in connection with product analysis of aqueous 2-, 3- and 4-chlorobenzaldehydes. The e_{aq}^- attacks specifically the
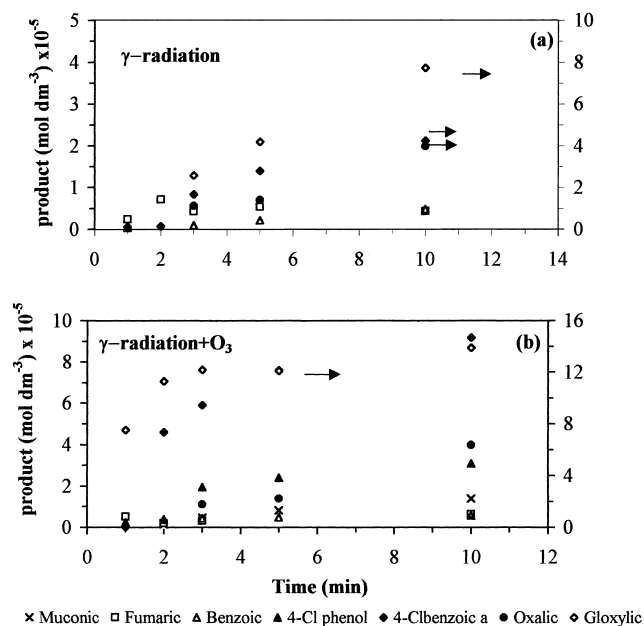
aldehyde group of these substrates, resulting in the formation of radical anions. In the present case, the OH-radicals are forming the corresponding OH-adduct of 4-ClBzAl, which is subsequently leading to H^+ and Cl^- formation.

A thorough search was made for other decomposition products, which were identified and analyzed by the HPLC-method. In Fig. 3a and b, the products obtained for the photocatalytic oxidation of 4-ClBzAl are displayed as a function of reaction time.

From the course of the curves, the corresponding initial quantum yields were calculated and are compiled in Table 3. Oxalic and glyoxalic acids were the main products of 4-ClBzAl detected during the application of O_3+UV/TiO_2 and UV/TiO_2 processes while the other acidic products were found at lower concentrations.

In case of γ-radiation and the combined application of γ-radiation and O_3, glyoxalic and 4-Cl benzoic acids were

Table 3

Q_i and k_i values or the product formation from 1×10^{-3} mol dm^{-3} 4-ClBzAl (pH 6.1) irradiated with UV-light ($\lambda=254$ nm) in the presence of 1 mg TiO_2 ml^{-1} and air ($O_2=2.5\times10^{-4}$ mol dm^{-3}) as well as for solutions saturated with O_3 under the same conditions

Product	TiO_2		TiO_2+O_3	
	Q_i	k_i (mol dm^{-3} min^{-1})	Q_i	k_i (mol dm^{-3} min^{-1})
Benzoic acid	0.0006	0.0106×10^{-6}	0.22	0.35×10^{-4}
4-Chlorobenzoic acid	0.003	0.048×10^{-6}	3.03	0.48×10^{-4}
Formic acid	[a]	–	[b]	–
Fumaric acid	0.0005	0.008×10^{-6}	0.29	0.45×10^{-4}
Glyoxalic acid	0.46	7.2×10^{-6}	5.41	0.84×10^{-4}
Muconic acid	0.0011	0.018×10^{-6}	0.45	0.71×10^{-4}
Oxalic acid	0.068	1.05×10^{-6}	1.93	3.04×10^{-4}

[a] Because of the low yield initial value was not determined.

[b] Product formation was not observed.

Table 4
G_i and k_i values for the formation of products using 1×10^{-3} mol dm^{-3} 4-ClBzAl (pH 6.1) by γ-irradiation in the presence of air as well as by combined γ-irradiation and O_3

Product	γ-Radiation		γ-Radiation+O_3	
	G_i	k_i (mol dm^{-3} min^{-1})	G_i	k_i(mol dm^{-3} min^{-1})
Benzoic acid	0.19	0.085×10^{-5}	0.4	0.19×10^{-5}
4-Chlorobenzoic acid	1.24	0.56×10^{-5}	4.9	2.3×10^{-5}
4-Chlorophenol	a	a	1.42	0.65×10^{-5}
Citric acid	b	b	a	a
Glyoxalic acid	1.86	0.838×10^{-5}	3.33	1.5×10^{-5}
Fumaric acid	0.14	0.238×10^{-5}	0.23	0.1×10^{-5}
Muconic acid	a	a	0.35	0.15×10^{-5}
Oxalic acid	a	a	0.82	0.37×10^{-5}
Tartaric acid	a	a	b	b

[a] No product formation was observed.
[b] Because of the low yield initial value was not determined.

the main reaction products. The course of the product formation is shown for both cases in Fig. 4a and b, respectively. The calculated G_i and k_i values are represented in Table 4.

As can be seen from Table 4, the distribution of the products in both cases is different, indicating that the involved reaction mechanisms are differential. Although application of both combined processes yields high degradation rates, a number of by-products were observed. Practically the same type of reaction by-products were formed by application of γ-radiation, photocatalytic reaction, ozonation or combination of these processes. As a conclusion, comparing the substrate degradation by application of four different oxidizing methods, it can be seen that combination of photocatalytic reaction and ozonation is the most efficient method for the oxidation reaction. Further experiments need to be performed to determine whether CO_2 is formed by one of these oxidation reactions of 4-ClBzAl.

Acknowledgements

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