

# Degradation of Aqueous 4-Chloroaniline by Ozonolysis and Combined $\gamma$ -Rays-Ozone Processing

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The decomposition of 4-chloroaniline (4-CIA), used as a model for water pollutants, was studied by ozonolysis as well as by  $\gamma$ -rays in the presence of ozone under comparable conditions. The degradation process was followed by absorption spectroscopy and by HPLC-method as well. Depending on the ozone concentration (mg O<sub>3</sub>/min) introduced into the aqueous solution the substrate is decomposed to a mixture of carboxylic acids, which can be entirely degraded by prolonged treatment.

The combined processing of 4-CIA by  $\gamma$ -irradiation in the presence of ozone proved to lead even to more efficient degradation of the substrate. Some primary reaction steps are briefly discussed.

## Introduction

Very recently the radiation-induced degradation of 4-chloroaniline (4-CIA) in aqueous solution has been studied under various experimental conditions as a function of the absorbed radiation dose (Sanchez *et al.*, 2002). In order to establish the specific action of the involved primary radicals (e<sup>-</sup><sub>aq</sub>, H, OH, HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup>) the solutions were saturated with air, pure oxygen, N<sub>2</sub>O, argon and argon in the presence of tert-butanol (OH-scavenger), respectively. Using HPLC the initial G-values<sup>\*\*</sup>) of the 4-CIA degradation as well as a number of degradation products were determined. The most efficient substrate decomposition was achieved in the presence of N<sub>2</sub>O, where e<sup>-</sup><sub>aq</sub> are converted into OH radicals (90% OH and 10% H-atoms). The yields of the main products observed under these conditions are: G(-4-CIA) = 4.0, G(Cl<sup>-</sup>) = 1.6,

G(NH<sub>4</sub><sup>+</sup>) = 0.8, G(aldehydes) = 0.06, G(carboxylic acids) = 0.12, G(4-aminophenol) = 0.12 in addition to small amounts of 4-chlorophenol and aniline.

The aim of the present work was to investigate the degradation of 4-CIA under comparable conditions by ozonolysis and by  $\gamma$ -irradiation in the presence of ozone. For practical reasons the obtained results will be then collated with the previously reported data (Sanchez *et al.*, 2002).

Ozone is well known to act as a powerful oxidizing agent of organic water pollutants (Hoigne, 1998). The combined use of ozone and radiation ( $\gamma$ -rays, high energy electrons) for degradations of various water pollutants, *e.g.* humic acid (Arai *et al.*, 1986), chlorinated ethylenes (Gehringer *et al.*, 1992), chlorinated phenols (Getoff and Solar, 1988), various phenols (Kubesch, 2001), EDTA in aqueous solution (Krapfenbauer and Getoff, 1999) etc. has been successfully applied.

A “Gammacell 220” (Nordion International Inc., Canada) provided a  $\gamma$ -rays dose rate of 74 Gy/min. A modified Fricke dosimeter G(Fe<sup>3+</sup>) = 15.6 was used for determination of the dose rate (Getoff, 1967). Ozone of desired flow concentration (mg O<sub>3</sub>/

\*\*\*) G-value = number of decomposed molecules per 100 eV absorbed energy. For conversion in SI-units multiply the G-value by 0.10364 to obtain G(x) in  $\mu\text{mol}\cdot\text{J}^{-1}$

min) was supplied by a ozone unit (type: Ozat CFS-1A, Ozonia Corp., 8600 Dübendorf, Switzerland).

The aqueous solutions of  $10^{-4}$  mol/l 4-ClA, Merck p. a. quality were prepared using four times distilled water.

The absorption spectra of the solutions were measured with a "Perkin Elmer UV/VIS, Lambda 16" spectrophotometer. A  $10^{-4}$  mol/l 4-ClA solution, (pH = 6.5) showed an absorption maximum at 238 nm, having a molar extinction coefficient,  $\epsilon_{238} = 1.3 \times 10^4 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ . The degradation process of the substrate was followed by the changes of the absorption spectra. In addition also the HPLC-method was used for a precise determination of the 4-ClA-degradation as well as for the measurement of the products. The HPLC apparatus (Hewlett-Packard, series 1050 and 1100) was equipped with a spherisorb ODS2 RP-18 column (5  $\mu\text{m}$ ,  $125 \times 4$  mm, 30 °C). The eluent mixture was an aqueous solution of 0.1%  $\text{H}_3\text{PO}_4$  (80–95%) and methanol (20%–5%) with a flow rate of 1 ml/min. A multiple wavelength detector was applied.

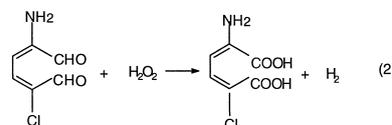
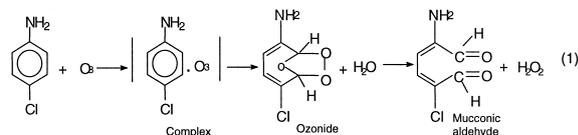
## Results and Discussion

### Ozonolysis of 4-ClA

First, several series of experiments using samples of 30 ml of  $10^{-4}$  mol/l 4-ClA in aqueous solution (pH = 6) were bubbled at room temperature with air, containing a known concentration of ozone. The absorption spectra of the treated solutions were measured in the range of 210 to about 550 nm. Based on the optical density (OD) change at 238 nm the degradation of the substrate was followed as a function of time (min) for a given input of ozone (mg  $\text{O}_3$ /min) in the solution. It was established that the absorption spectrum of the substrate was superimposed with those of the degradation products. Hence, HPLC-analysis have been also performed, which permit precise measurements of the degradation products (see letter).

Fig. 1 shows the absorption spectra obtained at different times of ozone treatment, where the OD-decrease at 238 nm is clearly illustrated. Insert I presents the ozonolysis of the substrate for two different ozone concentrations as a function of ozonisation time. Obviously, 4-ClA is degraded to more than 90% within 20 min treatment with 0.8 mg  $\text{O}_3$ /min. Using even lower  $\text{O}_3$  concentration (0.32 mg  $\text{O}_3$ /min) a strong pH-change of the ozo-

nated solution was observed (see insert II). Within the first 3 min of treatment the pH of the solution was increased from 6 up to 9, due to formation of ammonia, but subsequently rapidly decreased up to pH = 4.4. This fact indicates that the 4-ClA molecule is degraded as a consequence of several oxidizing processes to a mixture of carboxylic acids. For illustration of the involved reaction mechanisms some possible primary steps of ozonolysis are presented in Eqs. 1 and 2:



The double bonds of both products, muconic aldehyde and muconic acid molecules are subsequently attacked by  $\text{O}_3$  leading to the formation of simple carboxylic acids, such as fumaric, malonic, oxalic and formic acid. As final products of the substrate oxidation  $\text{CO}_2$  and  $\text{H}_2\text{O}$  can be expected (see Getoff, 1996).

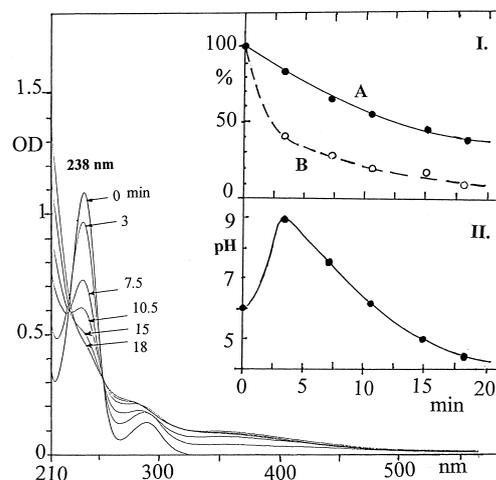


Fig. 1. Ozonolysis of aqueous  $10^{-4}$  mol/l 4-Cl-aniline. Individual absorption spectra resulting by ozone-treatment a different times (min). The observed degradation-process is given in insert I. (A) 0.32 mg  $\text{O}_3$ /min (B) 0.8 mg  $\text{O}_3$ /min bubbled through the solution. Insert II: pH-change as a function of treatment time (min).

### Combined radiolysis and ozonolysis

The results obtained under these conditions are embraced in Fig. 2. The OD-values at 238 nm show a progressive substrate degradation by the combined treatment of  $\gamma$ -rays and ozone. At about 280 nm an increase of the OD-values is observable, which indicates the formation of products having mostly aromatic character. In the range of 210 to 220 nm the formation of more simple compounds is noticeable. The effect of ozone on the radiolysis of 4-CIA is demonstrated by the data, given in the insert I, Fig. 2 for the same  $O_3$ -concentrations (0.32 and 0.8 mg  $O_3$ /min) as in Fig. 1. The achieved substrate degradation is in this case more efficient compared to that of ozonolysis, especially in the presence of 0.8 mg  $O_3$ /min input (see Fig. 2, insert I, curve B). The curve showing the pH-change with treating time (Fig. 2, insert II) has the same shape as the corresponding one in Fig. 1, but it decreases to pH = 2, indicating a very high yield of produced carboxylic acids.

The combined degradation of 4-CIA by  $\gamma$ -rays and ozone can be in general explained by the cooperative action of the radiolysis and ozonolysis.

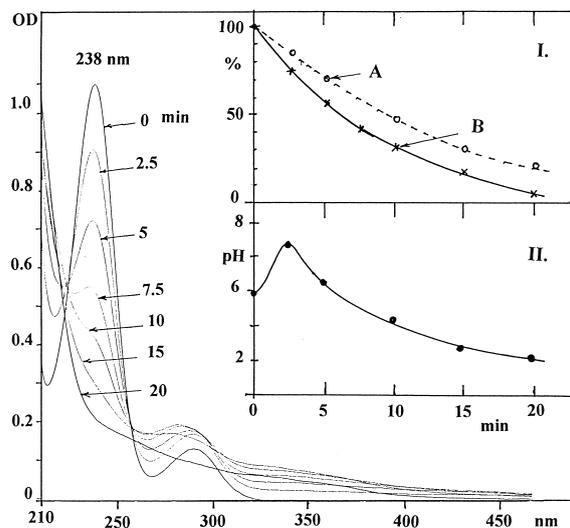
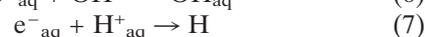
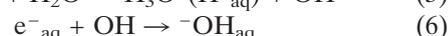
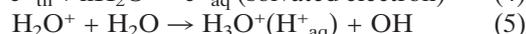
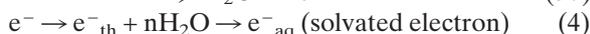
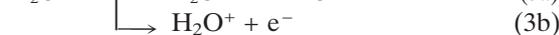
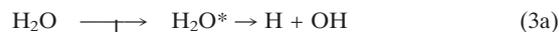


Fig. 2. Degradation of aqueous  $10^{-4}$  mol/l 4-Cl-aniline by simultaneous action of ozone and  $\gamma$ -rays (74 Gy/min), illustrated through the individual absorption spectra at different times (min).

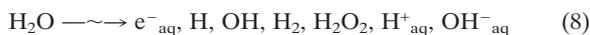
Insert I. (A) 0.32 mg  $O_3$ /min and  $\gamma$ -rays; (B) 0.80 mg  $O_3$ /min and  $\gamma$ -rays.

Insert II. pH-change using 0.32 mg  $O_3$ /min and  $\gamma$ -rays as a function of time (min.).

The radiolysis of water is summarized in Eqs. (3) to (8) given below.



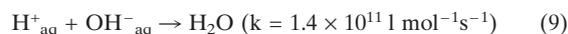
The resulting primary products of water radiolysis are:



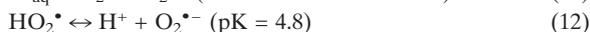
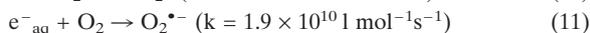
at pH = 5–10 is: G = (2.7) (0.6) (2.8) (0.45)

(0.72) (3.2) (0.5)

Thereby  $e^-_{aq}$  and H are reducing agents, whereas OH and  $H_2O_2$  are oxidizing ones.  $H^+_{aq}$  and  $OH^-_{aq}$  are combining to water:



In the presence of oxygen H and  $e^-_{aq}$  are converted to peroxy radicals ( $HO_2^*/O_2^{\bullet-}$ ), which are involved in the degradation process.



It is known that the radiolysis of aqueous ozone results in a number of very strong oxidizing transients (*e.g.*  $HO_3^*$ ,  $HO_3^{\bullet-}$ ,  $O_3^{\bullet-}$ ,  $HO_4$ ,  $HO_2^*/O_2^{\bullet-}$  etc. (Getoff, 1997). All these species are certainly involved in the decomposition process of 4-CIA, together with the primary products of water radiolysis. Naturally, there is a competition between 4-CIA and  $O_3$  for the primary products of the water radiolysis.

Based on the present state of the art it is obvious that the reaction mechanisms in the present system are rather complicated.

As already mentioned the absorption spectra obtained from the individual samples of the substrate degradation by ozonation (Fig. 1) as well those resulting from the radiolysis in the presence of ozone (Fig. 2), are superimposed. They represent the absorption of the corresponding final products and the remaining 4-CIA concentration at any given time. Therefore, the exact substrate degradation was also determined by HPLC-analysis. The obtained data for both degradation treatments are presented in Fig. 3. It is obvious, that

the combination of radiolysis and ozonolysis of 4-ClA is much more efficient than this observed by ozonolysis only. The combined procedure is strongly enhanced with increasing the concentration of  $O_3$ -input (compare curve B and C, Fig. 3). The calculated G-values are given as insert in Fig. 3. Comparing the previously reported degradation yield,  $G(4\text{-ClA}) = 4.0$  observed by OH-attack on 4-ClA only (Sanchez *et al.*, 2002) with that based on curve C, Fig. 3  $G(4\text{-ClA}) = 4.4$ , shows that the substrate degradation in the presence of  $0.8 \text{ mg } O_3/\text{min}$  is more efficient.

### Conclusion

4-Chloroaniline (4-ClA) was used as a pollutant model for degradation studies of chlorinated organic compounds in aqueous solution. The investigations included ozonolysis as well as radiolysis of the substrate in the presence of ozone. Although the treatment of the substrate with ozone leads to a very strong degradation, the combined procedure was found to be even much more efficient. The reaction mechanisms involved in both degradation procedures are rather complicated, but some primary reactions steps of degradation are briefly discussed

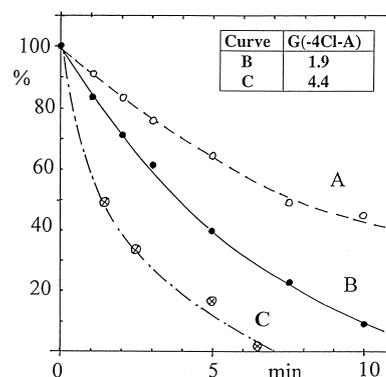


Fig. 3. Degradation of aqueous  $10^{-4} \text{ mol/l}$  4-Cl-aniline as a function of time (min) registered by HPLC analysis. (A) Ozonolysis using  $0.32 \text{ mg } O_3/\text{min}$ . (B) Combined radiolysis ( $74 \text{ Gy/min}$ ) and ozonolysis ( $0.32 \text{ mg } O_3/\text{min}$ ). (C) Combined radiolysis ( $74 \text{ Gy/min}$ ) and ozonolysis ( $0.80 \text{ mg } O_3/\text{min}$ ).

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