Degradation of Aqueous 4-Chloroaniline by Ozonolysis and Combined γ-Rays-Ozone Processing

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The decomposition of 4-chloroaniline (4-ClA), used as a model for water pollutants, was studied by ozonolysis as well as by γ-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_3/min) introduced into the aqueous solution the substrate is decomposed to a mixture of carboxylic acids, which can be entirely degradated by prolonged treatment.

The combined processing of 4-ClA by γ-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-ClA) 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^-_{aq}, H, OH, $HO_2^\bullet/O_2^{\bullet-}$) the solutions were saturated with air, pure oxygen, N_2O, argon and argon in the presence of tert-butanol (OH-scavenger), respectively. Using HPLC the initial G-values[**]) of the 4-ClA degradation as well as a number of degradation products were determined. The most efficient substrate decomposition was achieved in the presence of N_2O, where e^-_{aq} are converted into OH radicals (90% OH and 10% H-atoms). The yields of the main products observed under these conditions are: G(-4-ClA) = 4.0, $G(Cl^-)$ = 1.6, $G(NH_4^+)$ = 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-ClA under comparable conditions by ozonolysis and by γ-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 (γ-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 γ-rays dose rate of 74 Gy/min. A modified Fricke dosimeter $G(Fe^{3+})$ = 15.6 was used for determination of the dose rate (Getoff, 1967). Ozone of desired flow concentration (mg O_3/

[**]) **) 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 $\mu mol.J^{-1}$

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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.

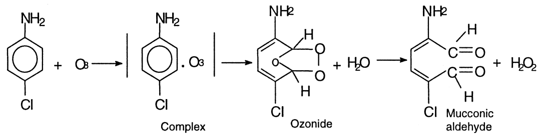
The absorption spectra of the solutions were measured with a "Perkin Elmer UV/VIS, Lambda 16" spectrophotometer. A 10^{-4} mol/l 4-ClA solution, (pH = 6.5) showed an absorption maximum at 238 nm, having a molar extinction coefficient, $\varepsilon_{238}= 1.3 \times 10^4 \, l \cdot mol^{-1} \cdot cm^{-1}$. 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 µm, 125 × 4 mm, 30 °C). The eluent mixture was an aqueous solution of 0.1% H_3PO_4 (80–95%) and methanol (20%–5%) with a flow rate of 1 ml/min. A multiple wavelength detector was applied.

Results and Discussion

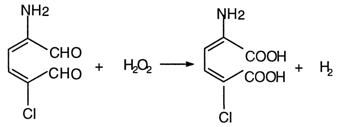
Ozonolysis of 4-ClA

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 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 degradated to more than 90% within 20 min treatment with 0.8 mg O_3/min. Using even lower O_3 concentration (0.32 mg O_3/min) a strong pH-change of the ozonated 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 Equs. 1 and 2:



(1)



(2)

The double bonds of both products, mucconic aldehyde and mucconic acid molecules are subsequently attacked by 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 CO_2 and H_2O can be expected (see Getoff, 1996).

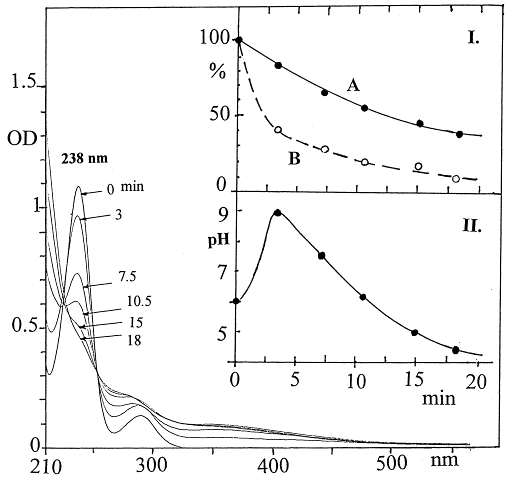


Fig. 1. Ozonolysis of aqueous 10^{-4} mol/l 4-Cl-aniline. Individual absorption spectra resulting by ozone-treatment a different times (min). The observed degradation-process is given in insert **I**. (A) 0.32 mg O_3/min (B) 0.8 mg O_3/min bubbled through the solution. Insert **II**: pH–change as a function 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 γ-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-ClA 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-ClA by γ-rays and ozone can be in general explained by the cooperative action of the radiolysis and ozonolysis.

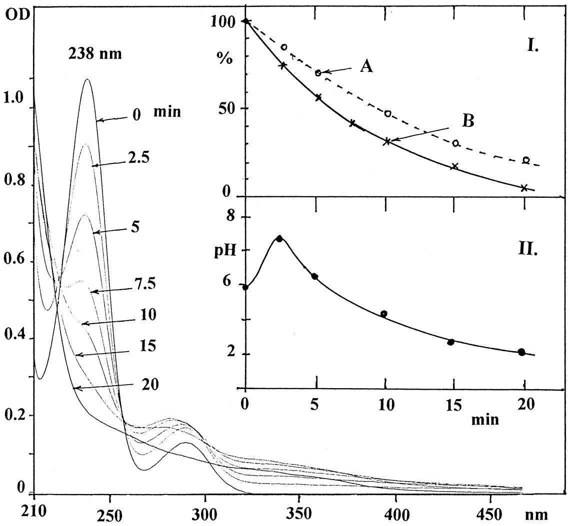


Fig. 2. Degradation of aqueous 10^{-4} mol/l 4-Cl-aniline by simultaneous action of ozone and γ-rays (74 Gy/min), illustrated through the individual absorption spectra at different times (min).
Insert I. (A) 0.32 mg O_3/min and γ-rays; (B) 0.80 mg O_3/min and γ-rays.
Insert II. pH-change using 0.32 mg O_3/min and γ-rays as a function of time (min.).

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

$$H_2O \longrightarrow H_2O^* \rightarrow H + OH \tag{3a}$$

$$\hookrightarrow H_2O^+ + e^- \tag{3b}$$

$$e^- \rightarrow e^-_{th} + nH_2O \rightarrow e^-_{aq} \text{ (solvated electron)} \tag{4}$$

$$H_2O^+ + H_2O \rightarrow H_3O^+(H^+_{aq}) + OH \tag{5}$$

$$e^-_{aq} + OH \rightarrow {}^-OH_{aq} \tag{6}$$

$$e^-_{aq} + H^+_{aq} \rightarrow H \tag{7}$$

The resulting primary products of water radiolysis are:

$$H_2O \rightsquigarrow e^-_{aq}, H, OH, H_2, H_2O_2, H^+_{aq}, OH^-_{aq} \tag{8}$$

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:

$$H^+_{aq} + OH^-_{aq} \rightarrow H_2O \ (k = 1.4 \times 10^{11}\ l\ mol^{-1}s^{-1}) \tag{9}$$

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

$$H + O_2 \rightarrow HO_2^\bullet \ (k = 2.1 \times 10^{10}\ l\ mol^{-1}s^{-1}) \tag{10}$$

$$e^-_{aq} + O_2 \rightarrow O_2^{\bullet-} \ (k = 1.9 \times 10^{10}\ l\ mol^{-1}s^{-1}) \tag{11}$$

$$HO_2^\bullet \leftrightarrow H^+ + O_2^{\bullet-} \ (pK = 4.8) \tag{12}$$

It is known that the radiolysis of aqueous ozone results in a number of very strong oxidizing transients (*e.g.* $HO_3^\bullet$, $HO_3^{\bullet-}$,$O_3^{\bullet-}$, HO_4, $HO_2^\bullet/O_2^{\bullet-}$ etc. (Getoff, 1997). All these species are certainly involved in the decomposition process of 4-ClA, together with the primary products of water radiolysis. Naturally, there is a competition between 4-ClA 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-ClA 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-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-ClA) = 4.4, shows that the substrate degradation in the presence of 0.8 mg O_3/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

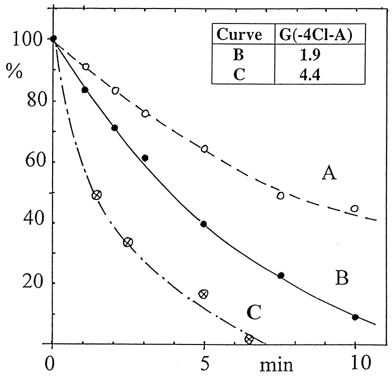


Fig. 3. Degradation of aqueous 10^{-4} mol/l 4-Cl-aniline as a function of time (min) registered by HPLC analysis.
(A) Ozonolysis using 0.32 mg O_3/min.
(B) Combined radiolysis (74 Gy/min) and ozonolysis (0.32 mg O_3/min).
(C) Combined radiolysis (74 Gy/min) and ozonolysis (0.80 mg O_3/min).

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