

ORTHO-CHLOROANILINE DEGRADATION UNDER THE INFLUENCE OF OZONE IN AQUEOUS SOLUTION

Ermin Katrin Winarno*

Center for The Application of Isotopes and Radiation Technology, National Nuclear Energy Agency
Jl. Cinere Pasar Jumat, Lebak Bulus, Jakarta Selatan, 12440

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ABSTRACT

The degradation study on 2-chloroaniline (2-CIA) used as a model of water pollutant by ozonation was performed. The change of spectrum and substrate concentration of treated solutions were measured by spectrophotometer as well as by HPLC method. The change of solutions pH after ozonation was observed. The yields of the products formed (chloride ions, ammonium ions, and formaldehyde) were investigated as a function of ozonation time. The results showed that the ozonation gave to an efficient degradation of 2-CIA.

Keywords: degradation, ortho-chloroaniline, ozone

INTRODUCTION

The increasing chloro-organic compounds contamination in the environment is one of the biggest problems for the human future. The production and usage of various chlorine-containing pesticides, various chemicals, as well as fertilizer in modern agriculture, largely contribute to the contamination in the ground water [1]. On the other hand, advanced oxidation processes (AOP) based on various techniques have been studied mostly on laboratory scale and proposed for purification of drinking water, industrial wastewater, groundwater and landfill leachate [1-3]. Those techniques are not still efficient yet, hence the development of new and efficient methods for the radiation-induced degradation of water pollutants is necessary [3-5]. For that purpose ozonation is proposed [6-7].

Ozone is a powerful oxidizing agent and is used on a technical scale for purification of drinking water as well as wastewater [8,9]. The chemistry of ozone reactivity with various substances has been studied by several researchers [1,10,11]. Ozone (O_3) may react with solutes either by direct oxidation, O_3 attack on the electron rich site of the solute or by indirect reaction, OH radicals resulted from the decomposition of O_3 reactions are highly selective in terms of the solutes having double bonds. However, at pH > 6, OH radicals become the predominant oxidants. Although these radicals react very rapidly with organic and inorganic solutes ($k = 10^9$ to $10^{10} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) [12], they are less selective to attack on the solute.

EXPERIMENTAL SECTION

Material

Ortho-chloroaniline (2-CIA) used as a model compound in this work was purchased from Fluka AG

(high purity, > 99.5 %). All other chemicals were of p.a. quality and used as obtained. The solutions 100 mL of $1 \times 10^{-4} \text{ mol.L}$ 2-CIA were prepared using at least three times freshly distilled water. Ozone ($6.6 \times 10^{-2} \text{ mol.L}^{-1}$) was flowed into the aqueous substrate solution.

Instrumentation

Ozone generator used was Ozonia AG, Type CFS-1, 3A model. The absorption band was measured with a Perkin Elmer UV-Vis spectrophotometer Lambda 16. The pH of the solution was measured with a pH meter. The concentration of undegraded 2-CIA after each irradiation was determined using HPLC Hewlett-Packard, model 1046A/1050. The electrochemical-amperometry detector and Kromasil 100-C18 column (150 mm x 4.6 mm) were used. Carboxylic acids were measured using HPLC Shimadzu, LC 7A model, uv detector and Shodex KC-811 column (300 mm x 8 mm) were used.

Procedure

Ozonation treatment of 2-CIA

The substrate solution was put into a special designed radiation vessel. Ozone was flowed into the aqueous substrate solution. Each ozonation was conducted at a gas flow rate of $1 \text{ L} \cdot \text{min}^{-1} O_3$. Ozonation time were 1, 2, 4, 5, 7, 9, 13, 18, and 22 minutes. Samples after certain treatment times were taken.

Analysis

Absorption Spectra. The result of degradation was first followed by measuring the change of the absorption spectra of 2-CIA solutions without ozone and with ozone treatment, using UV-Vis spectrophotometer. Significant changes of the spectra (depending of the pH of the solution) were observed at

* Email address : erminkk@batan.go.id

λ 232 nm and 285 nm. The changes of the optical density (OD/cm) at these wavelengths as a function of the absorbance were studied as indicator for the radiation-induced degradation of 2-CIA.

Determination of 2-CIA using HPLC. The concentration of undegraded 2-CIA after each irradiation was determined using HPLC method. The eluent was MeOH / H₂O = 5 / 1 and the flow rate was 1 mL/minute.

Determination of chloride ions. The formation of chloride ions as one of the degradation products was performed following Florence method [13]. The OD/cm-values were registered at λ = 460 nm. A calibration curve was used for the determination of the yield.

Determination of ammonia. Ammonia (measured as NH₄⁺ ions) appeared to be one of the degradation products. The yield was determined by means of Nessler's reagent and the absorption was measured at λ = 410 nm [14].

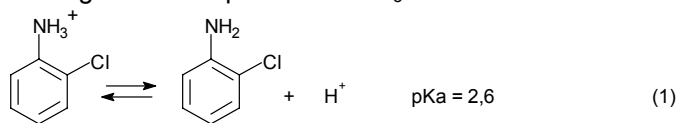
Determination of formaldehyde. For this purpose the method by Nash was applied [15]. The formation of formaldehyde was measured spectrophotometrically at 412 nm. The obtained yields were calculated based on a calibration curve.

Determination of carboxylic acids. Carboxylic acids were measured using HPLC method. The eluent was H₃PO₄ 0.03 % and flow rate was 1 mL/min.

RESULT AND DISCUSSION

Absorption Spectra of Aqueous 2-CIA

The 2-CIA substrate has pK_a = 2.6. The pH of 2-CIA solutions used in this work were kept at pH = 6.85. Hence, the unprotonated form of the substrate was investigated in the presence of O₃.



The absorption spectrum of 2-CIA ($1 \times 10^{-4} \text{ mol.L}^{-1}$) shows two maxima at 232 nm and 285 nm (see insert I in Fig 2). Chlorinated anilines are frequently used as starting substances for chemical synthesis and appear as pollutants in the industrial wastewater. Since up to now very little known upon the degradation of this group of substances using ozonation, so 2-chloroaniline (2-CIA) was chosen as a model-substrate for this experiment. In Fig 1 it is shown that absorption of the solution decreased with the increase of ozonation time. After 13 min the absorption peak disappeared, it is suggested that a lot of 2-CIA substrates were degraded. The percentage of absorption after 13 min was decreased to 44 %, this shows that there are still other compounds as the degradation products, which have double bond conjugation. The compounds increased with rising the ozonation time.

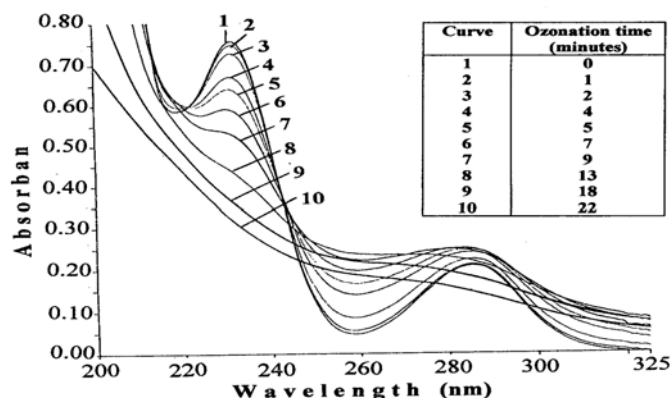


Fig 1. The change of absorption spectra from 2-CIA ($1 \times 10^{-4} \text{ mol.L}^{-1}$) before and after ozonation

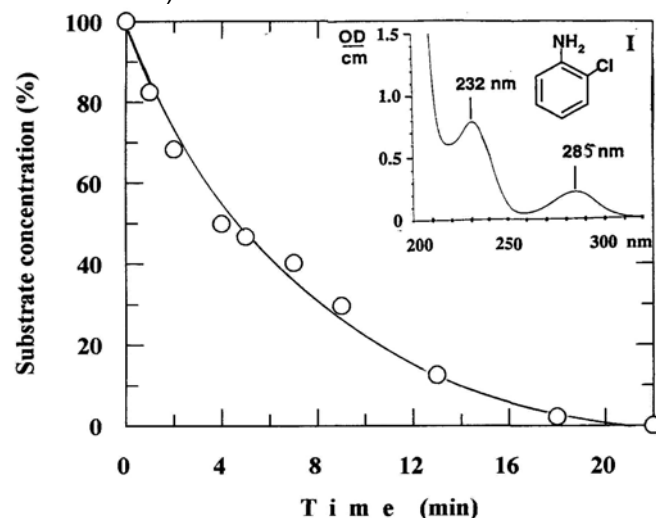


Fig 2. Degradation of aqueous $1 \times 10^{-4} \text{ mol.dm}^{-3}$ 2-CIA in the presence of O₃ ($6.6 \times 10^{-2} \text{ mol.L}^{-1}$ O₃) as a function time (starting pH 6.85)

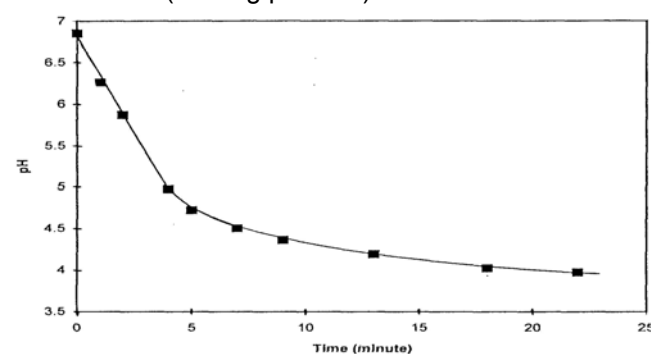


Fig 3. pH-decrease as a sequence of the ozonation of aqueous $1 \cdot 10^{-4} \text{ mol.L}^{-1}$ 2-CIA as a function of time (starting pH = 6.85)

The result of the degradation of 2-CIA using ozone are plotted in Fig 2. The concentration of ozone was high ($6.6 \times 10^{-2} \text{ mol.dm}^{-3}$), so the degradation of 2-CIA was very fast, destruction was achieved 100 % within 22 min.

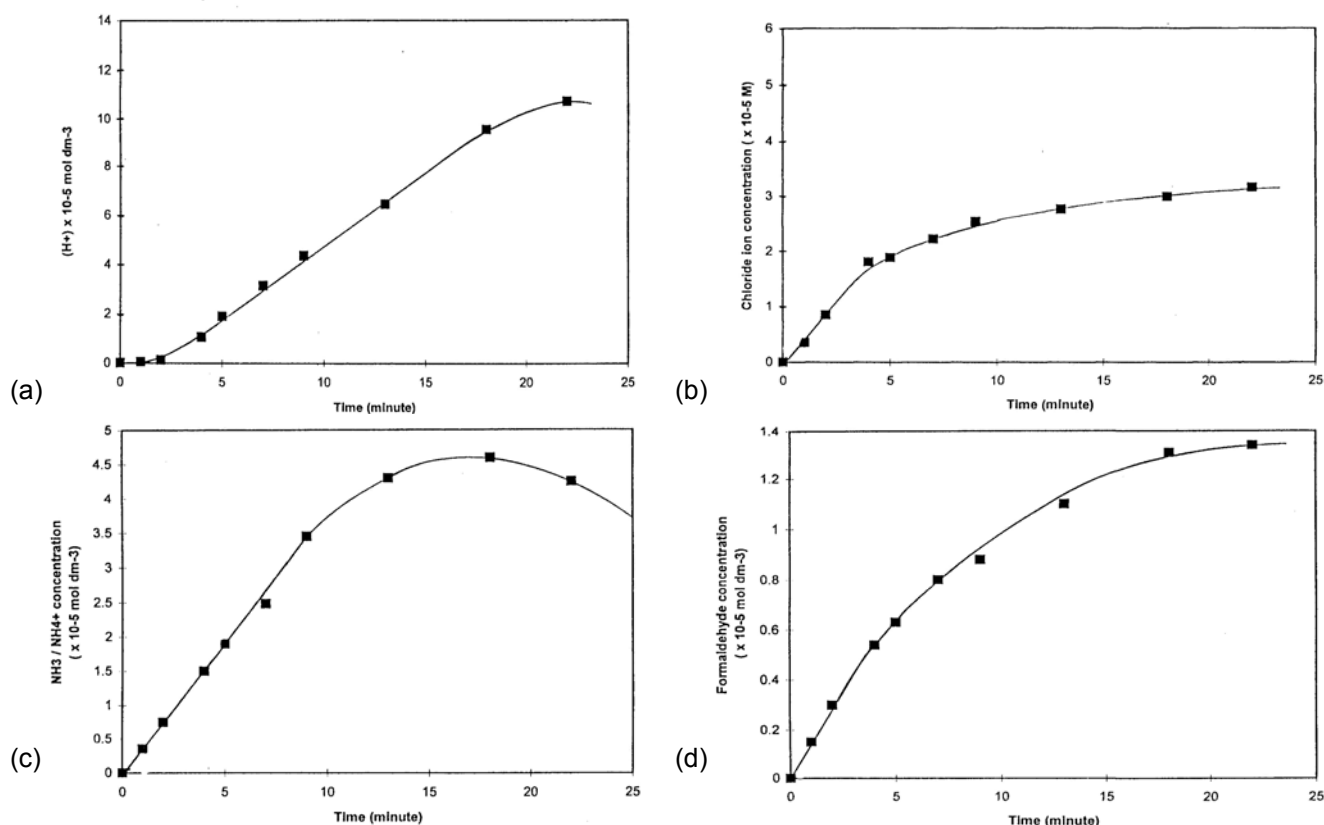


Fig 4. H^+ (4a), chloride ions (4b), NH_3/NH_4^+ (4c), and formaldehyde (4d) Formation as a sequence of the ozonation of aqueous $1 \times 10^{-4} \text{ mol L}^{-1}$ 2-CIA as a function of time (starting pH = 6.85)

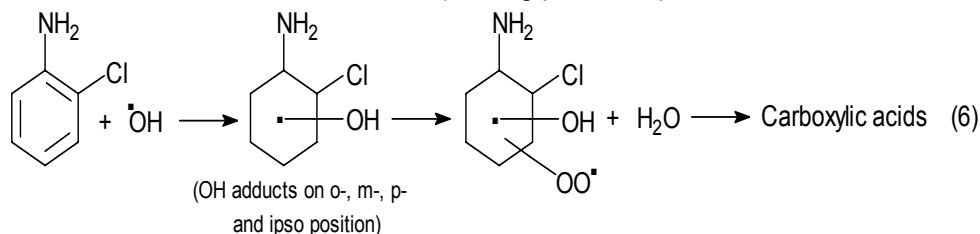
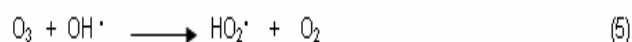
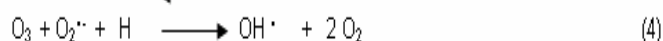
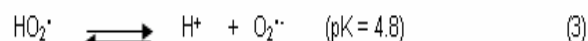
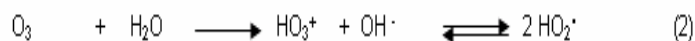


Fig 5. The possibilities of OH-attack on various positions of the 2-CIA molecule

During degradation for various period of time, decreasing pH of solutions was observed (Fig 3), and H^+ formation can be seen in Fig 4. The starting pH 6.85 of aqueous substrate solution was decreased to 3.97 after ozonation for 22 min. It indicated that acid compound products are formed.

The observed result of chloride ions is shown in Fig 4b, then Fig 4c and 4d are shown Cl^- ions, NH_4^+ ions and formaldehyde formation. They are taken as an indicator for substrate degradation in the presence of ozone only in the solution. After 22 minutes the ozonation of 2-CIA resulted in some products of the degradation (chloride ions $3.15 \times 10^{-5} \text{ mol L}^{-1}$, NH_4^+ ions $4.25 \times 10^{-5} \text{ mol L}^{-1}$, and formaldehyde $1.34 \times 10^{-5} \text{ mol L}^{-1}$).

Based on the instability of O_3 in water at room temperature can initiate reactions as follows :



The possibilities of OH-attack on various positions (*o*-, *m*-, *p*-, and *ipso*-position) of the 2-CIA molecule are illustrated as Fig 5. Based on the observed results that chloride ions, NH_4^+ ions and formaldehyde are formed, the possibility of OH-attack can be explained as Fig 6.

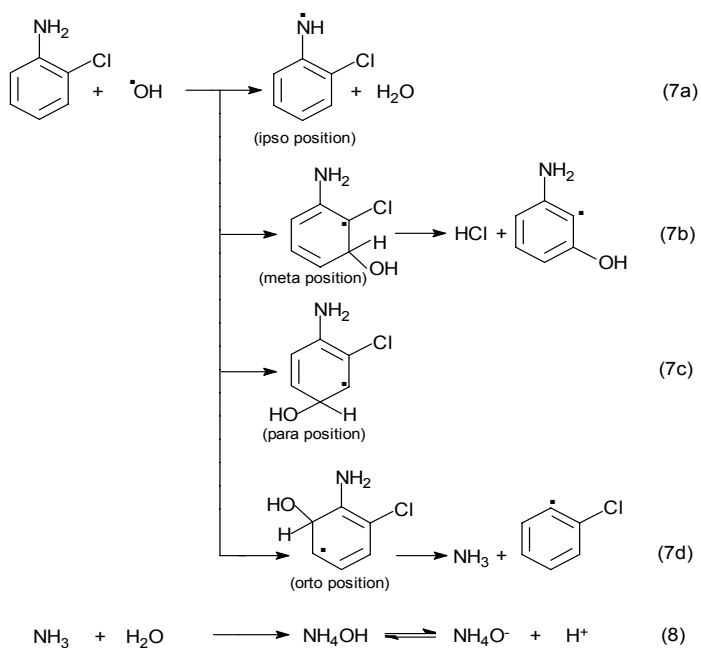
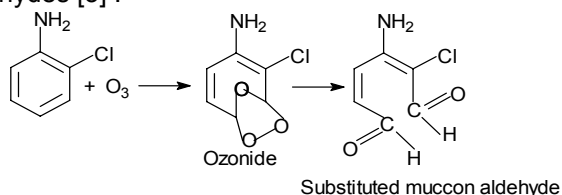


Fig 6. The possibilities of OH-attack

In the presence of O_3 , the substrate can form ozonides which is easily decomposed to form aldehydes [3] :



The mucon aldehyde as well as the muconic acid can undergo further reaction with ozone resulting in carboxylic acids. The oxidizing species HO_2^{\cdot} / $O_2^{\cdot-}$ can attack the substrate forming adducts in similar manner as the OH radicals (see eq. 7a-7d). Furthermore, a number of carboxylic acids (oxalic acid), aldehydes (formaldehyde), etc. can be formed.

CONCLUSION

Based on the results obtained, it can be concluded that the ozonation can decompose 2-chloroaniline quickly. The ozonation after 22 minutes gave the degradation of 2-CIA 100 % ($6.6 \times 10^{-2} \text{ mol dm}^{-3} O_3$). Degradation of 2-CIA in aqueous solution using ozonation produced H^+ ions, chloride ions, NH_4^+ ions, formaldehyde and oxalic acid.

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