Degradation Pathways of Acetochlor by γ-Radiolysis

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The degradation of acetochlor by γ-irradiation was investigated. Acetochlor was decomposed with an efficiency of 40% with a dose rate of 92 Gy min^{-1} in 2 h. Its radiolytic products under oxidative and reductive conditions were analyzed by GCMS and FTIR. Six products under oxidative conditions and four products under reductive conditions were identified by their mass spectra. With the products identified, the oxidative and reductive degradation pathways of acetochlor by γ-irradiation were proposed.

Acetochlor, 2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide, is a chloroacetanilide herbicide widely used for controlling grass weeds in various areas of the world in recent years. Acetochlor-caused pollution problems have attracted increasing attention. Its toxicity to creatures has been reported.[1,2] Since acetochlor and its metabolites have become widely present in surface and ground waters, and even in soils in the past several years, its decomposition in natural or artificial environments has also become an important subject.[3–6]

Radiation-induced degradation is a promising method against organic contaminations.[7] Efficient radiolysis of various pollutants, such as chlorinated benzaldehydes,[8] methyl *tert*-butyl ether[9] and nitrobenzene[10] has been reported. However, the information about the degradation of acetochlor by γ-irradiation is still sparse. In the present work, the radiolysis of acetochlor was investigated. Radiolytic products under both oxidative and reductive conditions were identified by using GCMS and FTIR, in order to obtain essential information about the intermediates and pathways of the degradation. Based on the products identified, degradation pathways were proposed.

Acetonitrile, ethyl acetate, anhydrous magnesium sulfate, and sodium formate, all purchased from Shanghai Chemical Reagent Company, were of analytical grade. Methanol was of chromatographic purity grade. Acetonitrile and ethyl acetate were redistilled prior to use. Acetochlor, purchased from Shandong Vicome Chemicals Ltd., had a purity of over 92%. Prior to use, it was purified by 25-cm silica gel column chromatography with redistilled ethyl acetate as an eluent. Acetochlor solutions were prepared using a mixed solvent composed of acetonitrile and water at a ratio of 20 to 80 in volume. Double distilled water was used throughout the experiments.

The concentration of acetochlor was measured by using an HPLC (Model 1100, Agilent Co.) equipped with a UV detector at a wavelength of 220 nm and a 5 µm × 4 mm × 250 mm Hypersil ODS column. The radiolytic products were analyzed and identified using an Agilent 6890 GC (Angilent Inc., USA) system coupled to a GCTMS (Micromass Ltd., UK) through an electron impact interface. Chromatographic measurements were performed with a capillary column DB-5 (30 m × 0.25 mm × 0.25 µm). Irradiated samples were extracted with redistilled ethyl acetate. The extracts were merged and dried over anhydrous magnesium sulfate and were concentrated under reduced pressure. Concentrated extracts of 0.2 µL were subjected to GCMS determination and FTIR (Magna-IR 750, Nicolet Instrument Co., USA) analysis.

Acetochlor solutions with initial concentration of 0.5 mmol L^{-1} were irradiated in sealed Pyrex glass vessels at a γ-ray dose rate of 92 Gy min^{-1} at ambient temperatures. The degradation efficiency reached 40% after 2-h irradiation.

As dilute acetochlor solutions were irradiated, several radical species, e.g. $\cdot OH$, e_{aq}^{-} and $H\cdot$, and molecular products e.g. H_2 and H_2O_2, were formed.[7] Nitrous oxide could scavenge the reductive species (e_{aq}^{-}), whereas sodium formate could scavenge oxidative ones ($\cdot OH$ and H_2O_2) during irradiation.[7]

To identify the radiolytic products of acetochlor under oxidative and reductive conditions respectively, two experiments were performed in parallel. The original sample for oxidative condition experiment was 50-mL acetochlor solutions of 0.6 mmol L^{-1} saturated with nitrous oxide before irradiation, while the sample for reductive one was composed of 1-mL sodium formate of 5 mol L^{-1} and 49-mL acetochlor of 0.6 mmol L^{-1}, and was saturated with high-pure argon. The both sample solutions were irradiated in sealed Pyrex glass vessels at a dose rate of 86 Gy min^{-1} under ambient temperatures for 5 h.

Infrared spectra of acetochlor and its degradation products are illustrated in Figure 1. New peaks, e.g. at wavenumber of 3344 cm^{-1} in spectrum B and 1296 cm^{-1} in spectrum C, appeared, indicating the formation of metabolites and the degradation of acetochlor under both conditions. The peaks at wavenumber of around 3400 cm^{-1} in spectra B and C were attributed to the stretching vibration of amido group or hydroxy group, suggesting the formation of amido group and/or hydroxy group in the radiolysis. Some differences can be found between spectra B and C, e.g., a new band appeared at 1296 cm^{-1} and the bands at 1069 cm^{-1} strengthened significantly in spectrum C. The two

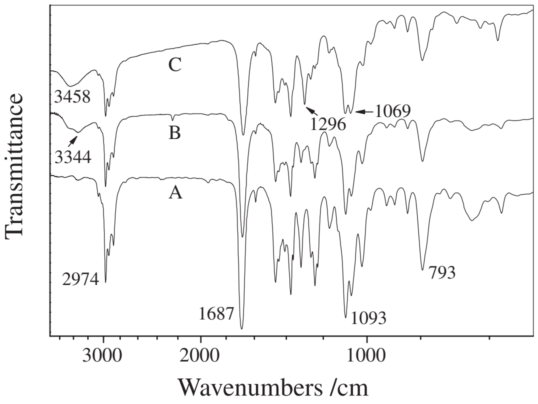


Figure 1. FTIR spectra of acetochlor and its degradation products: **A**: acetochlor; **B**: degradation products under oxidative conditions; **C**: degradation products under reductive conditions.

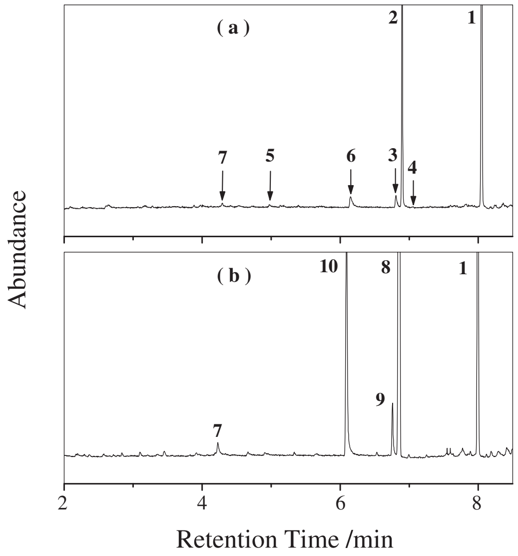
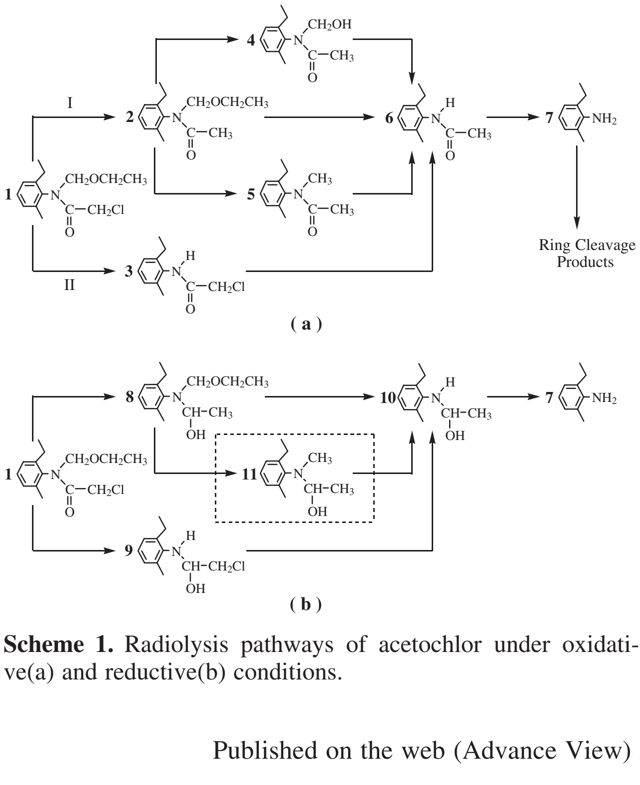


Figure 2. GC chromatogram of the extracts from acetochlor radiolytic products: (a) under oxidative conditions and (b) reductive conditions.

bands should be attributed to hydroxy groups, implying more hydroxy groups were present in the reductive products than in the oxidative ones.

Figure 2a shows the GC chromatogram of the extracts from the irradiated samples. Acetochlor (**1**) and six degradation products, labeled as **2**, **3**, **4**, **5**, **6**, and **7**, were qualitatively identified by their mass spectra. Among the six products, only the low abundance product **3** kept the chlorine atom, indicating that dechlorination of acetochlor might be a fast reaction under irradiation.

Based on the degradation products identified, possible radiolysis pathways of acetochlor under oxidative conditions were proposed and illustrated in Scheme 1a. Two alternative pathways existed for the preliminary degradation. In pathway I, dechlorination of acetochlor was the first step, forming product **2**. In spite of their low relative abundances, products **4** and **5** were detected, both of which were formed through losing the ethoxyl from product **2**. It suggests that there were three degradation processes from product **2** to product **6**, i.e. losing the ethoxymethyl directly from product **2**, or degrading into product **4** or **5** first. In pathway II, acetochlor lost its ethoxymethyl directly, yielding product **3**. Then product **3** was dechlorinated with the formation of product **6**. Product **6** was formed through two pathways, and was further degraded into product **7**. It is well known that the active species generated from radiolysis, such as hydroxyl radicals, could cleave benzene rings.[9] Therefore, product **7** would be degraded into even smaller molecules until complete mineralization was achieved.



Scheme 1. Radiolysis pathways of acetochlor under oxidative(a) and reductive(b) conditions.

The GC chromatogram of the extracts obtained under reductive conditions is shown in Figure 2b. Acetochlor (**1**) and other identified degradation products **8**, **9**, **10**, and **7** were labeled. Products **8**, **9**, and **10** were similar to products **2**, **3**, and **6** respectively. The only difference between the reductive products and the corresponding oxidative products was that the –CO– groups in oxidative products were changed into –CHOH– groups due to the reductive conditions.

The radiolysis pathways under reductive conditions are shown in Scheme 1b. Acetochlor (**1**) was degraded into product **10** via two alternative intermediates, product **8** or **9**. Product **10** was readily converted into product **7**. Considering the radiolysis pathways under oxidative conditions, product **11** might be an intermediate. However, it was not observed in this work, probably owing to its very low concentration.

Product **7**, 2-ethyl-6-methylaniline, was the sole degradation product identified under both conditions. It is well known that aromatic amino compounds are readily biodegraded.[11] Therefore, the irradiation treatment would not only decompose acetochlor directly, but also improve the biodegradability of acetochlor.

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