Degradation of 2,4-Dichlorophenoxyacetic Acid (2,4-D) by Cobalt-60 Gamma Radiation in a Methanolic Solution Containing Humic Acid

Sandro X. Campos and Eny M. Vieira*
São Carlos Institute of Chemistry, University of São Paulo, CP 780, 13566-590 São Carlos, SP, Brazil

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In this study, cobalt-60 gamma radiation was used to degrade 2,4-dichlorophenoxyacetic acid herbicide (2,4-D) in methanol in the presence of humic acid. The 2,4-D solution was irradiated with different doses. The herbicide was completely degraded after treatment with a dose of 150 kGy. The influence of humic acids was verify in higher doses (75 and 100 kGy) only. ESI/MS and MS/MS identified 3-chlorophenol as the intermediate product. The radiolytic yield (G) of 2,4-D degradation was calculated.

Herbicides are an important class of pollutants that have been introduced into the environment. An example includes the herbicides with chlorophenol in their structure. These compounds are generally resistant to chemical, photochemical, and biological degradation in the environment, making disposal difficult. The possibility of utilizing ionizing radiation (gamma radiation, electrons, and X-rays) to induce the decomposition of a wide variety of organic pollutants has proved to be an efficient tool for environmental decontamination, as well as being economically viable.[1–4] Owing to its great penetration capacity, gamma radiation can be used to degrade pesticides in different mediums, such as soils and humic substances. Many works have been made also showing the interaction of γ-radiation with different substances in alcohol solutions. These results are important to understand the effect of γ-radiation in different solvent. Some show the degradation of pesticides, such as polychlorinated biphenyls (PCBs).[5] When methanol is irradiated with ionizing radiation, as γ-rays, free radicals are formed. In methanol, the most common radicals are $H^{\bullet}$, $^{\bullet}CH_2OH$, and $^{\bullet}CH_3$. Hydroxyl radicals ($^{\bullet}OH$) and hydrated electrons ($e^{-}_{aq.}$) are found in small quantities.[6] The 2,4-dichlorophenoxyacetic acid herbicide (2,4-D) and its by-products are among the first herbicides registered in the United States and have been widely employed in the control of broadleaf forests, roadways, parks, and farmland. It was our goal in this study to determine not only the effects of different radiation doses on the degradation of herbicide 2,4-D in a methanolic solution, but also to verify the influence of humic acid added to the solution and to determine the G-value for radiolysis degradation. The structure of one of the degradation products was also elucidated by mass spectrometric techniques.

A "JS 7500" (Nordion International Inc. Canada, 92 curie ^{60}Co source), providing a dose rate of 2.7 kGy h^{-1}, was used as a γ-ray source. The irradiation experiments were conducted at the Brazilian Radiation Company, EMBRARAD, in Cotia, state of São Paulo, at room temperature and in air. Solutions of 2,4-D were prepared by dissolving 25 mg of herbicide in one liter of HPLC grade methanol (MALLINCKRODT). The irradiated solutions containing humic acid were prepared by adding humic acid extracted from soil (Aldrich). A sufficient amount of humic acid mass was added to obtain a concentration of 30 mg L^{-1} in the 2,4-D (25 mg L^{-1}) solution. The humic acid was used to study the influence of organic matter in the degradation of 2,4-D by γ-radiation.

The solutions of 2,4-D, with and without humic acid, were irradiated in 5-mL borosilicate glass tubes. The tubes were purged with nitrogen to remove oxygen, labeled and sent for irradiation treatment in doses of 1 to 150 kGy, at a dose rate of 2.7 kGy h^{-1}. The irradiations were repeated three times in different periods of year. After irradiation, the tubes were opened and the contents were stored in amber glass flasks in a refrigerator prior to their analysis.

The herbicide that remained undegraded in the solution in different irradiation doses was quantified, using the external standard method, using an analytical curve having concentrations of 2.26×10^{-5}, 4.52×10^{-5}, 6.78×10^{-5}, 9.05×10^{-4}, and 1.13×10^{-4} mol L^{-1}. The analytical curve was obtained by liquid chromatography (Shimadzu LC-9). An RP-18 HP column ($200 \times 4.6 \times 10$ mm^3), a UV–vis detector with wavelength set at 280 nm, and a mobile phase with 40% acetronitrile + 60% water with 2% acetic acid added were used, operating in the isocratic mode with a 1 mL min^{-1} flow rate and an injected volume of 20 µL. These conditions were selected after experimental studies.

After irradiation and analysis by HPLC, samples of the herbicide were selected to identify the degradation products. The samples were analyzed by ESI/MS and MS/MS in a Micromass Quattro LC mass spectrometer equipped with a triple quadrupole analyser. MS data were collected by direct introduction of the sample solution ($MeOH/H_2O$ 70/30 v/v) into the ion source. The optimal voltages defined for the probe and ion source components to produce maximum intensity of the ions $[M + H]^+$ were 3.30 kV for the capillary, 17 V for the sample cone, and 8 V for the extractor cone. The parent/daughter runs were performed by adding Ar to the collision cell to produce a pressure of 2×10^{-3} mbar for collision activation dissociation (CAD). The optimal collisional energy used to decompose the ions $[M + H]^+$ was 10/30 eV.

The radiolysis yield (G) is the number of produced or decomposed molecules per 100 eV of absorbed energy. For conversion into SI units, the G-values are multiplied by 0.10364 to obtain the value in µmol J^{-1}. The initial G-value is calculated from extrapolation of the linear part of the corresponding yield-dose-curve. The solutions of herbicide with and without humic acid were irradiated in doses of 1, 5, 10, 20, 30, 40, 75, 100, and 150 kGy at a dose rate of 2.7 kGy h^{-1}. The Table 1 shows the results obtained after irradiation.

Total degradation of the herbicide was achieved with a dose of 150 kGy. The influence of humic acid in the degradation of 2,4-D was verify in dosages 75 and 100 kGy, only. This behavior may be due to the fact that humic substances play a role in scavenger of hydroxyl radicals ($^{\bullet}OH$). The production of hydroxyl

Table 1. Concentration of 2,4-D (mol L^{-1} × 10^{-4}) irradiated in methanol, with and without humic acid, as a function of radiation dosage

Dose /kGy	Without humic acid	With humic acid
0	1.1 ± 0.10	1.1 ± 0.11
10	1.0 ± 0.09	1.0 ± 0.10
20	0.8 ± 0.02	0.8 ± 0.10
30	0.7 ± 0.02	0.7 ± 0.10
40	0.6 ± 0.05	0.6 ± 0.10
75	0.3 ± 0.10	0.5 ± 0.10
100	0.04 ± 0.10	0.08 ± 0.10
150	0.0	0.0

radicals ($^{\bullet}$OH) is smaller in methanol than in water (sixth species in yielding[6]). This fact explains why a higher dose γ-radiation (150 kGy) is necessary to degrade the herbicide in methanolic solution than in aqueous solution.[2] These data show that the degradation of 2,4-D occurs by indirect action of γ-radiation. In the first moment the products resulting from the radiolysis of solvents are attained and subsequently they attack the molecule of pesticide. Trillas et al.[7] reports that $^{\bullet}$OH is the main oxidizing specie in the photodegradation and chemical degradation of the 2,4-D molecule in aqueous solutions. Luchini et al.[8] found the same occurrence when irradiated parathion insecticide. It was necessary 1 kGy to degraded 98% of insecticide in water while that in methanolic solution it was necessary 30 kGy dose to degraded 99% of insecticide. In an attempt to identify some radiolytic degradation products of the 2,4-D herbicide, the samples were irradiated with a dose of 100 kGy without humic acid. Figure 1 shows the mass spectrum obtained by ESI/MS and the product ion spectrum of MS/MS of m/z 127, with collision energy of 30 eV. This ion was selected as it presents the same molar mass as 4-chlorophenol, an intermediate product formed by the photodegradation of 2,4-D.[7] Figure 2 shows the mechanism proposed for the fragmentation of the ion at m/z 127. In the first step, the degraded herbicide, which was ionized in the negative ion mode, undergoes a loss of the HCl group with the formation of the ion detected at m/z 91, followed by a loss of carbon monoxide (CO) to form the peak at m/z 63. Although Baglio et al.[9] reported a rupture of the aromatic ring after the loss of an HCl molecule, we have found that, on the basis of their proposal, it would be very difficult to explain the subsequent fragmentations.

Our results revealed that the radiolytic degradation products formed from 2,4-D can be toxic and as more than 2,4-D, as in the case of 3-chlorophenol, which is an organochlorine compound. However, after a radiation dose of 150 kGy, the 2,4-D peak has disappeared and there was a significant decrease of the peaks corresponding to the degradation products.

The degradation rate of the solutions without humic acid was 1.08 × 10^{-6} mol L^{-1} kGy^{-1}, with G = 0.10 mmol/J, while the rate for the solutions containing humic acid was 9.69 × 10^{-7} mol L^{-1} kGy^{-1} with G = 0.09 mmol/J. This values are smaller than values of G of degradation of 2,4-D in water[2] (8.4 mmol/J without humic acid and 5.4 mmol/J with humic acid) showing again the action of solvent in the degradation. This value may have occurred owing to the formation of a small amount of reactive species in the medium and requires high doses of radiation to significantly degradation of 2,4-D.

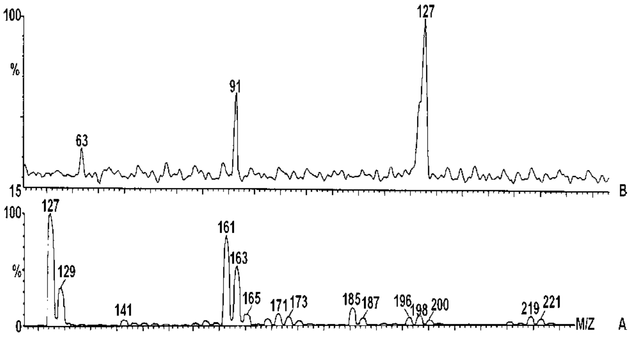

Figure 1. Mass spectra obtained for 2,4-D irradiated in methanol with a dose of 100 kGy and at a dose rate of 2.7 kGy h^{-1}, A) ESI/MS (full scan); B) MS/MS from m/z 127 ion with a collision energy of 30 eV.

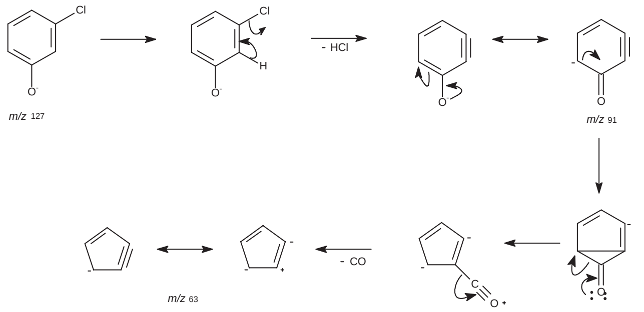

Figure 2. Fragmentation path suggested for the m/z 127 ion.

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