

FORMATION OF POLYCHLORINATED PHENOLS FROM PHOTODEGRADATION OF 2,4,5-TRICHLOROPHENOXYACETIC ACID HERBICIDE (2,4,5-T)

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Introduction

The phenoxyacetic acid type herbicides were used for more than half of the century to control broad leave weeds, brush and certain aquatic weeds. However, the use of 2,4,5-trichlorophenoxyacetic acid herbicide (2,4,5-T) was phased out in the 1970's once it was established that it was often contaminated with the highly toxic 2,3,7,8-TCDD. Polychlorinated phenols, which are parent chromophores for phenoxyacetic acid type herbicides, are themselves highly toxic compounds.

The toxicity of polychlorinated phenols depends on the number of chlorine atoms in the molecule, and their relative position with respect to the hydroxyl group⁴. Most chlorinated phenols are released in natural environment from pulp bleaching process, wood preservative, chemical spillage and illegal dumping of waste disposal. Due to its high persistence and generally high stability, traces of these compounds (with their degradation products) are widespread in soils and water. In addition to concerns about their own toxicity, it has been reported that polychlorinated phenols can act as precursors to PCDD/Fs formation^{5,6}.

The formation of PCDD/Fs from polychlorinated phenols has been investigated previously⁷. While the release of PCDD/Fs into the environment is often associated with high temperature thermal processing of commercial materials, it has been speculated that polychlorinated dioxin can be formed from a polychlorinated phenol (pentachlorophenol) via low temperature photolysis in aqueous conditions with⁸ or without⁹ the aid of a sensitizer. However, previous attempts to establish a mechanism for the formation of dioxin via photodecomposition decomposition of 2,4,5-T were fruitless¹.

The research to be presented in this paper was undertaken in order to assess the formation of polychlorinated phenols from photodecomposition of 2,4,5-T in pure water under UVC radiation at room temperature. The motivation for this study is associated with a desire to understand the sources, transportation and reaction mechanisms involved when toxic materials are released into the natural environment. We report the formation of chlorinated phenols from 2,4,5-T; other photodegradation products, which were also detected, will not be discussed in this paper.

Materials and methods

The herbicide 2,4,5-T (97%), 1,2-dihydroxybenzene (pyrocatechol also known as PYRCL) and 2,4,5-trichlorophenol (2,4,5-TCP) (99%) were obtained from Sigma-Aldrich. The other primary reactants 2,5-dichlorophenol (2,5-DCP), 2-chlorophenol (2-CP) were obtained from Alfa Aesar (USA). For liquid-liquid extraction procedures used for gas chromatography mass spectrometry (GCMS) sample preparation, diethyl ether (DE) was purchased from Chem Supply. Acetonitrile (HPLC grade) and formic acid were obtained Ajax Finechem Pty Ltd. All irradiated solutions were prepared in double distilled water supplied by ELGA labwater (resistivity 18.2 MΩcm).

Photodegradation experiments were undertaken in a Rayonet photochemical reactor purchased from South New England Ultraviolet Company. This reactor has 8 built-in UV lamps. The UV radiation applied for each experiment was at a wavelength of 254 nm, while the light intensity measured using ferrioxalate actinometry method¹⁰ was $4.316 \times 10^{-9} \text{ E.s}^{-1}$. The initial pH of the pesticide solution was adjusted to an initial pH of 2.23 by adding drops of diluted hydrochloric acid (HCl). All sample solutions in this study were placed in a 100 mL quartz tube and subjected to UV radiation for up to 1 h, unless stated otherwise. An aliquot of the irradiated solution was taken at predetermined time intervals for identification and quantification of feed and product species. For experiments performed in the absence of O₂, N₂ gas was bubbled into the system for at

least 30 mins prior to experiment to purge O₂ from the system. The N₂ gas was continuously bubbled throughout the duration of experiment. To determine the optimum purging time for N₂, a series of experiments were undertaken at intervals of 10, 20 and 30 min of N₂ flow. No significant difference was found for 2,4,5-T concentration after 1 h of irradiation, and thus it was assumed that 30 min is sufficient time to eliminate the oxygen from the reaction flask.

The formation of different anions was monitored on Dionex ion chromatography (IC) using a mixture of 800 mM (Na₂CO₃)/100 mM (NaHCO₃) as the eluent. Identification of water-soluble products was undertaken on an Agilent GCMS using a HP-5MS column (0.25 mm × 30 m × 0.25 μm). The GC temperature program used for separation used an initial temperature of 70 °C and held for 1 min followed by ramping of the temperature to 320 °C at 12.50 °C/min and with a hold time of 3.60 min. Total analysis time was 25.00 min and the injection mode was splitless. Prior to analysis, the organic species dissolved in the aqueous solution were extracted (3 times) with DE before further concentrated to 1 ml for GCMS analysis. Further quantisation of unreacted initial reactants and associated photodegradation products was undertaken on an Agilent high pressure-liquid chromatography (HPLC), comprising of 2 pumps and 100 μL injector, a Microsorb 100 5μm C18 column coupled to a UV detector (set at 289 nm).

Results and discussion

Photodecomposition of 2,4,5-T yielded chlorinated and unchlorinated phenols which were identified as 2,4,5-TCP, 2,5-DCP, 2,4-DCP, 2-CP and PYRCL (Figure 1). The pK_a of 2,4,5-T is 2.88, and at a pH of 2.32 and in a system without oxygen, under these conditions, it is primarily in its undissociated form. Thus the photodecomposition process mainly involved the 2,4,5-T molecule, water and UVC radiation.

One reaction product whose concentration steadily increased with time was 2-CP. It is also one of the final chlorinated phenols produced from photodecomposition process of dichlorophenol¹¹ and trichlorophenol. As shown in figure 1, more than 95% of the 2,4,5-T herbicide degraded following 60 minutes of irradiation, and almost 60% of the total chloride initially in 2,4,5 T was detected in ionic form following exposure of 2,4,5 T to UVC radiation for 60 minutes (Figure 2). The observed decrease in the pH of irradiated sample is consistent with the formation of hydrochloric acid (HCl) from each mole of 2,4,5-T in the system¹.

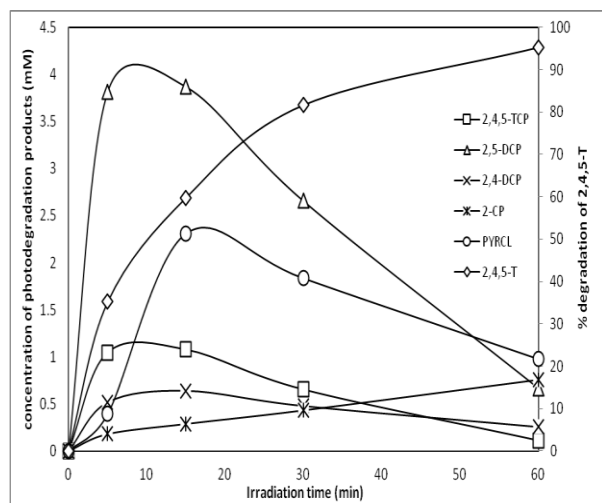


Figure 1 : % degradation of 2,4,5-T and concentration of the photodecomposition products

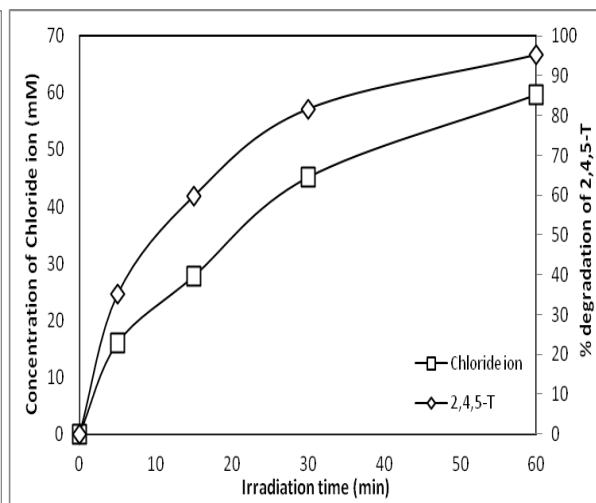


Figure 2 : % degradation of 2,4,5-T and concentration of chloride ion detected

The release of chlorine from 2,4,5-T is likely to be influenced by the position of the chlorine atom on the benzene ring. As suggested by others, chlorine at the *para* position is photo liable, while the chlorine atom at position 5- is not photoreactive³. Thus, it is expected that the dechlorination of 2,4,5-T occurs primarily at the chlorine at 4- position, and would explain why *p*-chlorophenol was not observed in our system. During the photodegradation of 2,4,5-T, formic acid was detected, which is in agreement with measurements of previous researcher, who also studied the photodecomposition of phenoxyacetic acid herbicides¹³.

The photodecomposition of 2,4,5-T was accelerated in the system when the initial pH was adjusted to 4.50, especially during the early period of the irradiation (figure 3). This could be a result of the comparatively high concentration of OH⁻ in the system at higher pH conditions, thus aiding the decomposition process of 2,4,5-T. as was suggested by others¹. Under the studied conditions, 2,4,5-T yielded 59.7% of HCl from its undissociated molecules and 70.2% of HCl in its dissociated molecules (figure 4), which again associated with the availability of OH⁻ that could replace the Cl atoms on the benzene ring.

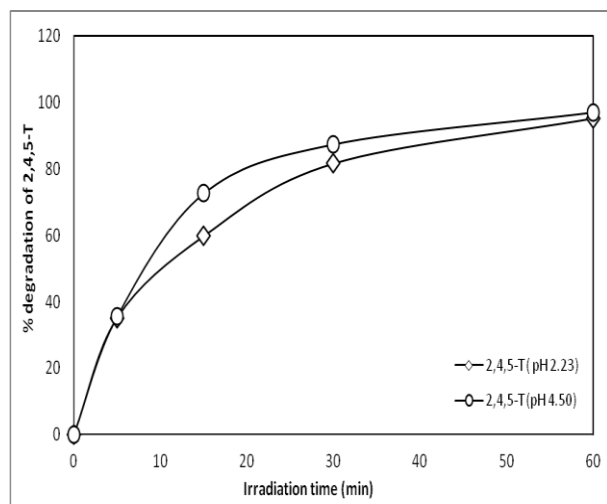


Figure 3: % degradation of 2,4,5-T at pH of 2.23 and 4.50

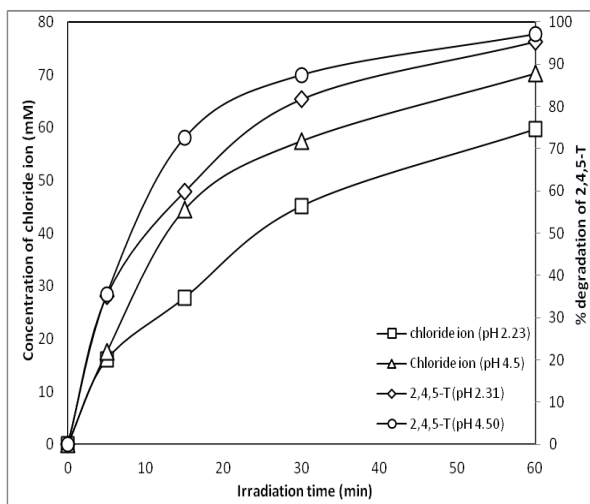
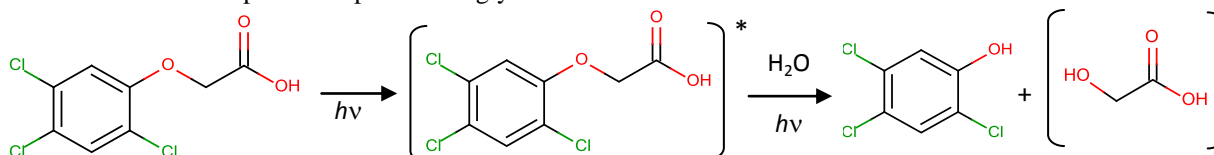


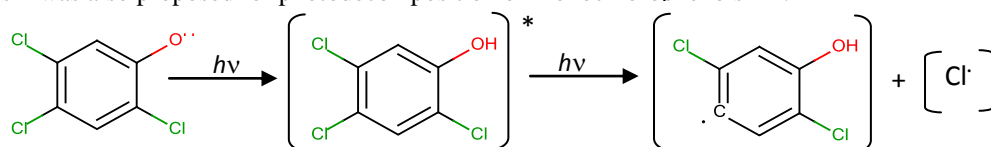
Figure 4 : % degradation of 2,4,5-T at pH of 2.23 and 4.50

Photodegradation of 2,4,5-T generally involves the photohydrolysis of the side chain group and replacement of the chlorine atoms by hydroxyl group (OH)¹. In its undissociated form, upon absorption of a photon from UV radiation, 2,4,5-T molecule was electronically excited to its singlet state, which then underwent intersystem crossing to triplet state where most of reactions took place. In the presence of H₂O molecule, the excited 2,4,5-T molecule undergoes photohydrolysis to form 2,4,5-TCP and glycolic acid, as reported by previous researchers^{1,3}. In the present study, only formic acid was observed in the irradiated system, which could be due to the rapid decomposition of glycolic acid to form formic acid under the studied condition.



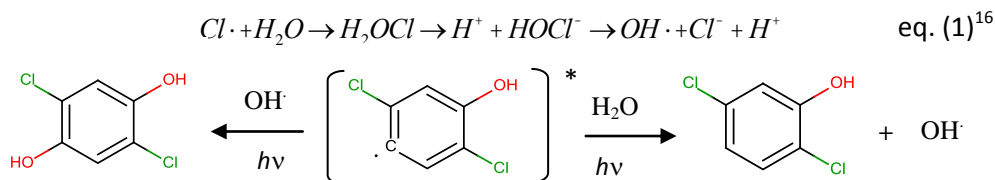
Scheme 1: proposed mechanism for the formation of 2,4,5-TCP from 2,4,5-T^{1,3}

Further exposure of 2,4,5-TCP to UV will generate electronically-excited 2,4,5-TCP molecule and through the homolytic cleavage of C-Cl bond¹³ (scheme 2), chlorophenoxy radical and Cl[•] radical were formed¹⁴. The same mechanism was also proposed for photodecomposition of monochlorophenols^{12,15}.



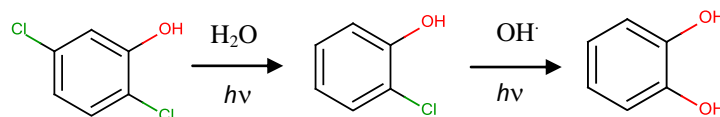
Scheme 2: proposed mechanism for the formation of radical intermediates from 2,4,5-TCP².

In aqueous solution, OH[•] radicals can be generated from the reaction of Cl[•] radical through reaction with H₂O¹⁶ (eq. 1). Further interaction of chlorophenoxy radicals with OH[•] radicals yields dichlorohydroquinone, which was also identified from 2,4,5-TCP². Dichlorophenols are subsequently produced from 2,4,5-TCP via reaction of chlorophenoxy radical with OH[•] or via photohydrolysis⁷ (Scheme 3)¹⁴.



Scheme 3: proposed mechanism for formation of dichlorophenol and dichlorohydroquinone

Finally, homolytic cleavage of C-Cl bond of 2-CP produced electronically excited phenol radical which then underwent reaction with OH[•]/H[•] to produce non-chlorinated phenol, 1,2-dihydroxybenzene (Scheme 4). Coincidentally, a molecule of HCl was produced as the parent phenol molecule was dechlorinated. 1,2-dihydroxybenzene has been reported to be one of the main photodegradation products of 2-CP⁹.



Scheme 4: proposed mechanism for formation of 2-CP and 1,2-dihydroxybenzene

Acknowledgments

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