

Lawrence Berkeley National Laboratory

Recent Work

Title

Photodegradation of Oryzalin in aqueous isopropanol and acetonitrile.

Permalink

<https://escholarship.org/uc/item/5c5287zd>

Journal

Journal of environmental science and health. Part. B, Pesticides, food contaminants, and agricultural wastes, 51(5)

ISSN

0360-1234

Authors

Pramanik, Sukhendu Kumar
Joarder, Soumen
Das, Saktipada
[et al.](#)

Publication Date

2016

DOI

10.1080/03601234.2015.1128741

Peer reviewed

of Oryzalin in aqueous isopropanol and acetonitrile

[Sukhendu Kumar Pramanik](#), [Soumen Joarder](#), [Saktipada Das](#), [Sankhajit Roy](#) & [Anjan Bhattacharyya](#)

- [Download citation](#)
- <https://doi.org/10.1080/03601234.2015.1128741>
-

In this article

- [ABSTRACT](#)
- [Introduction](#)
- [Materials and methods](#)
- [Results and discussion](#)
- [References](#)
 - [Full Article](#)
 - [Figures & data](#)
 - [References](#)
 - [Citations](#)
 -
 - [Metrics](#)
 - [Reprints & Permissions](#)
 - [PDF](#)

ABSTRACT

The phototransformation of Oryzalin was studied under UV light ($\lambda_{\max} \geq 290$ nm) and sunlight ($\lambda_{\max} \geq 250$ nm) in aqueous isopropanol and acetonitrile solution in absence and presence of TiO_2 as sensitizer. The rate of photodegradation of Oryzalin in different solvent system followed first-order kinetics, and calculated half-lives were found to be in the range of 23.52-53.75 h for UV light and 41.23-61.43 h for sunlight. From this study, total 12 photoproducts were identified and characterized on the basis of column

chromatography and Q-ToF micromass spectral data. The plausible mechanism of phototransformation involved was hydrolysis, breaking of sulfonic bond, and loss of amino and sulfonic acid group.

KEYWORDS: [Oryzalin](#), [photoproduct](#), [isopropanol](#), [acetonitrile](#), [titanium dioxide](#), [UV light](#), [sunlight](#)

Introduction

Investigation on photodegradation of pesticides has a vital importance in connection with the environmental quality and public health as well as importance for understanding of the optimum conditions of pesticides use. The use of semiconductor catalyzed photodegradation of organic and inorganic substrates as a method of treatment of waste water is currently attracting considerable attention. Photodegradation of different pesticides of agricultural importance has rapidly become a significant part of studies on the fate of those chemicals in the environment.

Pesticides absorb UV light at ≥ 290 nm wavelength and undergo direct photolysis. The sunlight photolysis, is highly dependent not only on the UV absorption profile of the pesticides but also on the surroundings medium and the emission spectrum of the sunlight.^[1]Mandal, S.; Joardar, S.; Das, S.; Bhattacharyya, A. Photodegradation of hexythiazox in different solvent systems under the influence of ultraviolet light and sunlight in the presence of TiO_2 , H_2O_2 and KNO_3 and identification of the photoproducts. *J. Agric. Food Chem.* 2011, 59, 11727–11734. [[Crossref](#)], [[PubMed](#)], [[Web of Science](#)], [[Google Scholar](#)] The energy needed for/to break the chemical bonds in pesticide molecules was in the range of 70–120 Kcal mol⁻¹, corresponding to light having wavelength of 250–400 nm.^[2]Watkins, D.A.M. Some implications of the photochemical decomposition of pesticides. *Chem. Ind.* 1974, 5, 185–190. [[Google Scholar](#)] Various photodegradation experiments have already been done on the variety of organic molecules in the presence of TiO_2 as catalyst to determine the photocatalytic effect of TiO_2 . TiO_2 is being widely used as an ideal photocatalyst for photodegradation of various organic compounds since it is stable, inexpensive, non-toxic and photoactive.^[3]^[4]Daneshvar, N.; Salari, D.; Niaei, A.; Khataee, A.R. Photocatalytic degradation of the herbicide erioglaucine in the presence of nano-sized titanium dioxide: comparison and modeling of reaction kinetics. *J. Environ. Sci. Health, Part B.* 2006, 41, 1273–1290. Lapertot, M.; Pichat, P.; Parra, S.; Guillard, C.; Pulgarin, C. Photocatalytic degradation of p-halophenols in TiO_2 aqueous suspensions: halogen effect on removal rate, aromatic intermediates and toxicity variations. *J. Environ. Sci. Health, Part A.* 2006, 41, 1009–1025. Zayani, G.; Bousselmi, L.; Pichat, P.; Mhenni, F.; Ghrabi, A. Photocatalytic degradation of the acid blue 113 textile azo dye in aqueous suspensions of four commercialized TiO_2 samples. *J. Environ. Sci. Health, Part A.* 2008, 43, 202–209. Konstantinou, I.K.; Albanis, T.A. TiO_2 -assisted photocatalytic degradation of azo dyes in aqueous solution: kinetics and mechanistic investigation A review. *Appl. Catal. B.* 2004, 49, 1–14. Blake, D.M. *Bibliography of Work on the Heterogeneous Photocatalytic Removal of Hazardous Compounds from Water and Air: Update Number 3 to January 1999*; National Renewable Energy Laboratory Report, NREL/TP-570-26797; National

Technical Information Service (NTIS): Springfield, VA, 1999. Available at <http://www.nrel.gov/docs/fy99osti/26797.pdf> (accessed April 2008).

The photodegradation of pesticides by UV light in the presence of TiO_2 is generally initiated by the hydroxyl radical (OH^\cdot), which is formed by reacting electron holes on the excited TiO_2 surface and OH^- (or H_2O) from the surrounding water.^[8]

^[10]Behnajady, M.A.; Modirshahla, N.; Shokri, M.; Elham, H.; Zeininezhad, A. The effect of particle size and crystal structure of titanium dioxide nanoparticles on the photocatalytic properties. *J. Environ. Sci. Health, Part A*. 2008, *43*, 460–467.

Ollis, D.F.; Hsiao, C.; Budiman, L.; Lee, C. Heterogeneous photoassisted catalysis: conversions of perchloroethylene, dichloroethane, chloroacetic acids, and chlorobenzenes. *J. Catal.* 1984, *88*, 89–95.

Graetzel, M. Molecular engineering in photoconversion systems. In *Energy Resources through Photochemistry and Catalysis*; Graetzel, M., Ed.; Academic Press: New York, 1983; 71–98. Irradiation of aqueous suspension of TiO_2 at wavelengths shorter than the band gap energy (E_{bg} ; $\lambda < 410 \text{ nm}$) leads to electron-hole pair generation.^[11]

^[13]Roy, U.; Bhattacharyya, A.; Kole, R.K.; Chakraborty, S.; Mitra, S.R. Phototransformation of bifenoxy in aqueous isopropanol. *Toxicol. Environ. Chem.* 2004, *86*(1–4), 45–53.

Das, S.; Muneer, M.; Gopidas, K.R. Photocatalytic degradation of waste water pollutants. Titanium dioxide-mediated oxidation of polynuclear aromatic hydrocarbons. *J. Photochem. Photobiol. A. Chem.* 1994, *77*, 83–88.

Oliver, B.G.; Carey, J.H. Photodegradation of wastes and pollutants in aquatic environment. In *Homogeneous and Heterogeneous Photocatalysis*; Pelizzetti, E.; Serpone, N. Eds.; Reidel: Dordrecht, Netherlands, 1986; 629–650. Both these species can recombine with the liberation of heat but in the presence of adsorbed oxygen and an electron donor, chemical reactions can occur at the surface of TiO_2 .

After the reaction of the valence band holes (h_{vb}^+) and the TiO_2 surface, active OH^- groups (or oxidizable species, viz., H_2O , H_2O_2 , or organic substrates) recombine to form $\cdot\text{OH}$ radicals.^[14] Mansour, M.; Feicht, E.A.; Behechti, A.; Scheunert, I. Experimental approaches to studying the photolysis of selected pesticides in water and soil. *Chemosphere*. 1997, *35*, 39–50. [[Crossref](#)], [[Web of Science ®](#)], [[Google Scholar](#)]

It is well known that surface adsorbed O_2 delays the electron hole recombination process by trapping the conduction band electron (e_{cb}^-) to form a superoxide ion $\text{O}_{2(\text{surface})}^\cdot$.

The electrons may also react with reducing species (such as O_2 or H^+) in the solution yielding OH^- or H^\cdot radicals as follows:

The hydroxyl radical is very strong oxidants and oxidizes most of the organic molecules^[15,16]Bruggeman, W.A.; Burns, L.A.; Choudhury, G.C.; Daum, K.A.; Gehring, P.J.; Newland, L.W.; Paris, D.F.; Parke, D.V.; Reitz, R.H.; Roof, A.A.M.; Steen, W.C.; Zepp, R.G. *The Handbook of Environmental Chemistry*; Hutzinger, O., Ed.; Reaction and Processes: Aquatic Photochemistry; Springer-Verlag: Berlin, 1982; Vol. 2, Part B. Benedix, R.; Dehn, F.; Quaas, J.; Orgass, M. Application of titanium dioxide photocatalysis to create self-cleaning building materials. *LACER*. 2006, 5, 157–168. to give the oxidative products as follows:

Pesticides suffer photodegradation by hydroxyl radicals^[17]Draper, W.M.; Crosby, D.G. Photochemistry and volatility of drepamon in water. *J. Agric. Food Chem.* 1984, 32(4), 728–733.[\[Crossref\]](#), [\[Web of Science ®\]](#), [\[Google Scholar\]](#) that have been shown to be present in sunlight irradiated natural waters.^[18]Mill, T.; Hendry, D.G.; Richardson, H. Free-radical oxidants in natural waters. *Science*. 1980, 207, 886–887.[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#), [\[Google Scholar\]](#) The formation of some of the photoproducts under the present experiment could be rationalized by direct incorporation of OH[•] radicals into the pesticide molecule, which is generated by irradiation of TiO₂ in water.

Oryzalin (4-(Dipropylamino)-3,5-dinitrobenzenesulfonamide), a dinitroaniline group of herbicide, is used as a selective post emergence herbicide for control of annual grasses, certain broadleaf and sedge weeds in transplanted and direct seeded rice.^[19]Dvorakova, K.; Dorr, R.T.; Gallegos, A.; McClure, T.; Powis, G. Pharmacokinetic studies of the herbicide and antitumor compound Oryzalin in mice. *J. Chromatogr. B.* 1997, 696, 275–281.[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#), [\[Google Scholar\]](#) However, the fate and phototransformation pathways of Oryzalin in different photochemical environments in the presence and/or absence of sensitizer (e.g., TiO₂) have not been systematically studied yet. The present experiment was, therefore, undertaken to determine the nature of photodegradation of Oryzalin under the influence of UV and sunlight in presence and/or absence of TiO₂ as catalyst, to determine the kinetics of phototransformation, identification of the photoproducts if formed and to determine the probable mechanism of the formation of photoproducts. Some of the photoproducts were prepared synthetically in the laboratory and other photoproducts were identified with the help of Q-ToF MSMS.

Materials and methods

Chemicals, reagents and materials

The crystalline orange colored analytical grade Oryzalin (purity 99%; m.p. 141–142°C; molecular weight 346.36) was supplied by M/s Excel Crop Care Ltd., Mumbai, India. The crystalline solid of Oryzalin was also isolated from its formulation (24% EC) in the laboratory. The Oryzalin formulation was triturated with silica gel and kept in a soxhlet

apparatus. It was first extracted with hexane for 5 h and then extracted with chloroform for 10 h. The chloroform extract was evaporated to dryness (at rotary vacuum evaporator at $\sim 40^{\circ}\text{C}$), which yielded the crystalline solid of Oryzalin. The crystalline solid was recrystallized from mixture of hexane and chloroform until homogeneous on thin-layer chromatography (TLC) and high pressure liquid chromatography (HPLC). Its purity was also determined by direct comparison with authentic sample of Oryzalin (Co-IR and mixed m.p.) and finally, the purity (99%) was confirmed by direct comparison with analytical grade Oryzalin by HPLC. Solvents, such as isopropanol, acetonitrile (all HPLC grade), hexane, dichloromethane and chloroform (all analytical reagent grade), were obtained from Merck India Ltd. HPLC grade water was obtained from SISCO Research Laboratory (India). Silica Gel (60–120 mesh) used for TLC and column chromatography was supplied by Spectrochem (India) and titanium di-oxide (TiO_2) used for photolysis was obtained from Rankem Fine Chemicals Ltd. (India). All analytical grade solvents were redistilled before use. Water was double glass distilled.

Preparation of working standard solution

A stock standard solution (generally containing $100\ \mu\text{g mL}^{-1}$ in methanol) was prepared from the reference standard material. From the stock standard solution, a $10\ \mu\text{g mL}^{-1}$ working standard solution was prepared in methanol.

Chromatographic analysis

TLC was performed on 20×20 cm glass plates coated with 0.5 mm layer of silica gel. The spots were developed using iodine as a chromogenic reagent. Column chromatography was conducted using a glass column packed with slurry of silica gel (60–120 mesh, SRL, India) in hexane (b.p. 69.5°C). Most of the breakdown products were separated by column chromatography on silica gel and further purified by preparative TLC on silica gel. The bands on preparative TLC plates were scrapped off and extracted with ethyl acetate. The combined suspension was then filtered through a medium of porosity glass filter to yield a filtrate that was then dried over anhydrous sodium sulfate and concentrate to give pure compound. HPLC analysis was carried out on a JASCO-JAPAN make instrument (model: PU-1580), equipped with UV-VIS detector set at $\lambda_{\text{max}} = 212\ \text{nm}$ and coupled with chemito 5000 data processor. The column used was reverse phase thermo hypersil ($250 \times 4.6\ \text{mm}$) $5\ \mu$ Hypersil® ODS; mobile phase was acetonitrile:water (7:3, v/v) at a flow rate of $1\ \text{mL min}^{-1}$; volume injected was $20\ \mu\text{L}$; retention time (RT) was 2.25 min; limit of quantification (LOQ) and limit of detection (LOD) were determined as 0.1 and 0.05 ppm, respectively. The above HPLC parameters were employed in the entire study. All melting points were uncorrected.

Spectroscopic analysis

UV spectra

Ultraviolet (UV) spectra was taken on UV-VIS Recording Spectrometer, Shimadzu (Japan, Model no. UV-2401 PC).

IR spectra

Infra-red (IR) spectra was taken on 1.0 mm KBr pellets by using a PerkinElmer (Waltham, MA, USA, model name: Spectrum One; model no: L 120-000A) Infra-red Spectrophotometer.

¹H NMR spectra

Proton nuclear magnetic resonance spectra (¹H NMR) were recorded on Bruker DRX spectrometer (Germany, 500 MHz) using TMS as an internal standard.

¹³C NMR spectra

Carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on Bruker DRX spectrometer (125 MHz).

Mass spectra

Mass spectra were obtained using a Jeol JMSDX 300 instrument (Jeol, Peabody, MA, USA) at 70 eV using electron impact ionization with the source at ambient temperature.

Q-ToF mass spectrometric study of the photoproducts of Oryzalin

In the present investigation, Micromass® Q-ToF Micro™ Mass Spectrometer (Waters, Milford, MA, USA), one of the most modern tool, was used for separation and identification of the compound in mixture. Micromass® Q-ToF Micro™ Mass Spectrometer with NanoLockSpray™ and Water CapIC® Pump and Autosampler using MassLynx™ 4.0 Software was used for characterization of the photoproducts.

Synthesis of photoproducts

Synthesis of 3-amino-4-(dipropylamino)-5-nitro-1-benzenesulfonamide

Sodium polysulfide was prepared by dissolving 8 g (102.56 mmol, 5.25 eqv.) of sodium sulfide (Na₂S, 9H₂O) in 20 mL of water and to it 2 g (62.5 mmol, 3.2 eqv.) finely

powdered sulfur was added. The reaction mixture was warmed and 5 g (19.53 mmol) of Oryzalin was added to 25 mL of water and the mixture was boiled gently. Then the sodium polysulfide solution was added dropwise to the boiling mixture and boiling was continued for further 15 min. The resulting reaction mixture was cooled and the solid was filtered with the help of a vacuum pump and washed with cold water. The solid was dissolved in a 25 mL mixture of water and conc. hydrochloric acid (20 mL water + 5 mL conc. hydrochloric acid) and warmed gently. Unreacted reagent was filtered off and the filtrate was made alkaline with slow addition of saturated NaHCO₃ solution to precipitate the compound. The solid (m.p. 114 – 116°C) was recrystallized from boiling water and identified as 3-amino-4-(dipropylamino)-5-nitro-1-benzenesulfonamide on the basis of different spectral properties (see Tables A1 (i)–(iv) in the Appendix).

Synthesis of 3,5-diamino-4-(dipropylamino)-1-benzenesulfonamide

Oryzalin (5 g; 19.53 mmol) was dissolved in 70 mL of methanol in a 100 mL RB flask. Then 1 g of 10% Pd-C was added to the reaction mixture and H₂ gas was passed for 3 h at 45 psi. The resulting reaction mixture was filtered through celite pad and concentrated in rotary vacuum evaporator at ~40°C. On concentration, the reaction mixture yielded a brownish crystal that was purified by crystallization with 10% ethyl acetate in hexane. The m.p. range of the purified crystal was 132–134°C and the compound was identified as 3,5-diamino-4-(dipropylamino)-1-benzenesulfonamide on the basis of different spectral properties (see Tables A2 (i)–(iv) in the Appendix).

Synthesis of 7-amino-2-ethyl-1-propyl-1H-benzo[d]imidazole-5-sulfonamide

Oryzalin (5 g; 19.53 mmol) was dissolved in 70 mL of methanol in a 100 mL RB flask. Then 1 g of 10% Pd-C was added to the reaction mixture and catalytic amount of conc. H₂SO₄ was added dropwise to the reaction mixture. After that, H₂ gas was applied for 5 h at 60 psi to the resulting mixture and the mixture was filtered through celite pad. The mixture on concentration under vacuum yielded the desired compound, which was purified by crystallization with 10% methanol in hexane. The m.p. of the purified product was 216–218°C and the product was characterized as 7-amino-2-ethyl-1-propyl-1H-benzo[d]imidazole-5-sulfonamide on the basis of different spectral properties (see Tables A3 (i)–(iv) in the Appendix).

Synthesis of N¹,N¹-dipropyl-2,6-dinitroaniline

In a 100 mL RB flask, 5 g (24.69 mmol) of 2,6-dinitro chlorobenzene was dissolved in 50 mL of DMF. To it, 1.75 g (29.63 mmol, 1.2 eqv.) of *N,N*-dipropyl amine as well as 5 g (49.38 mmol, 2 eqv.) of triethylamine were added dropwise and the reaction mixture was refluxed at 60°C for 8 h. Then the reaction mixture was cooled at room temperature and

400 mL water was added to it. The resulting reaction mixture was extracted twice with 2 × 200 mL of ethyl acetate. Finally, the compound was obtained by concentrating the solvent in vacuum and recrystallized from 20% of dichloromethane in hexane that yielded 3.85 g N¹,N¹-dipropyl amine determined on the basis of different spectral properties (see Tables A4 (i)–(iv) in the Appendix).

Synthesis of N¹-propyl-2,6-dinitro aniline

In a 100 mL RB flask, 5 g (24.69 mmol) of 2,6-dinitro chlorobenzene was dissolved in 70 mL DMF. The reaction mixture was charged under N₂ atmosphere. Then 2.23 mL (27.16 mmol, 1.1 eqv.) of n-propylamine was added dropwise to the reaction mixture. The resulting reaction mixture was stirred at 60°C for 16 h. After addition of 300 mL water to the reaction mixture, it was extracted with ethyl acetate and the extract was washed with 1N HCl, saturated NaHCO₃ followed by brine solution, dried and evaporated to dryness. A brown solid (m.p. 90–92°C) was obtained and the compound was identified as N¹-propyl-2,6-dinitro aniline on the basis of different spectral properties (see Tables A5 (i)–(iv) in the Appendix).

Synthesis of 2,6-dinitro aniline

2,6-dinitro chlorobenzene (5 g; 24.69 mmol) was taken in a 250 mL sealed tube. To the reaction mixture, 50 mL of 20% ammonia solution was added and the reaction mixture was allowed to be heated for 10 h with constant stirring. Finally, a yellow precipitate was obtained and filtered off. After crystallization from 20% ethyl acetate in hexane, a yellow crystalline solid (m.p. 136–138°C) was obtained and the product was characterized as 2,6-dinitro aniline on the basis of different spectral properties (see Tables A6 (i)–(iv) in the Appendix).

Irradiation experiment

In the present experiment, Oryzalin was irradiated in the solvent systems of isopropanol:water (1: 1, v/v) and acetonitrile:water (1:1, v/v) separately, in the absence and/or presence of sensitizer (TiO₂) under the influence of both UV and sunlight. The concentration of the Oryzalin solution was 250 µg mL⁻¹ and the solution was prepared by dissolving 250 mg of Oryzalin in 1,000 mL of mixed solvent and stirred thoroughly. In total, eight batches of solution were prepared for each system. A dark control without TiO₂ was kept under UV and sunlight. The solutions were irradiated in a photoreactor using a high-pressure mercury lamp (HPK 125 W, Phillips) to achieve maximum intensity of UV light at λ_{max} ≥ 290 nm under continuous stirring using a magnetic stirrer. The photoreactor was jacketed with a water cooled Pyrex filter to maintain a constant solution temperature (25°C). The same amount of Oryzalin was irradiated in a borosilicate flask for 75 h under natural sunlight (at Kalyani, 22°57' N latitude, 7.8 m altitude, West Bengal, India) under clear sky, at 20 ± 5°C temperature in the wavelength of λ_{max} ≥ 250 nm. The mouth of the flasks was tightly covered with a polythene sheet to

prevent contamination. Samples were collected periodically and analyzed by HPLC to monitor the rate of photodegradation of Oryzalin.

Results and discussion

Isolation of photoproducts

(i) The combined UV irradiated aqueous isopropanolic solutions of Oryzalin in absence of sensitizer (TiO_2) was concentrated at rotary vacuum evaporator ($\leq 40^\circ\text{C}$). After addition of 50 mL saturated sodium chloride solution, the remaining aqueous portion was partitioned thrice with (100 + 100 + 50) mL dichloromethane and the organic fraction was collected. The combined organic fraction was passed through anhydrous sodium sulfate and after filtration, the filtrate was allowed to stand for evaporation. The same extraction procedure was followed with (ii) the sunlight-irradiated aqueous isopropanolic solution in the absence of TiO_2 ; (iii) UV-irradiated aqueous isopropanolic solution in the presence of TiO_2 ; (iv) sunlight-irradiated aqueous isopropanolic solution in the presence of TiO_2 ; (v) UV-irradiated aqueous acetonitrile solution in the absence of TiO_2 ; (vi) sunlight-irradiated aqueous acetonitrile solution in the absence of TiO_2 ; (vii) UV-irradiated aqueous acetonitrile solution in the presence of TiO_2 and (viii) sunlight-irradiated aqueous acetonitrile solution in the presence of TiO_2 . In each case, the concentrated crude extracts were subjected to column chromatography (60 × 1 cm glass column) over silica gel (100–200 mesh) and the column was eluted with solvent systems of increasing polarity to isolate the photodegradation products from each solvent system in pure form.

Isolation and identification of the photodegradation products of Oryzalin in isopropanol:water (1:1, v/v) under UV light in absence of TiO_2

The dark yellow gummy residue obtained from the above UV irradiation experiment was column chromatographed over silica gel (15 g). Elution of the column with Hexane:Benzene (2:3; v/v) afforded a brownish extract. From the Co-TLC and mass fragmentation data of the solid, it was rationalized as N¹-propyl-2,6-dinitroaniline. On evaporation of Benzene:Ethyl Acetate (7:3; v/v), the extract yielded a dark yellow solid that showed some overlapping spots on TLC and the compounds (2-ethyl-7-nitro-2,3-dihydro-1H-benzo[d]imidazole-5-sulfonamide; 3,5-dinitro-4-(propylamino)-1-benzenesulfonamide; 2-ethyl-7-nitro-1-propyl-1H-benzo[d]imidazole-5-sulfonamide; 4-(dipropylamino)-3,5-dinitro-1-benzenesulfonic acid) were identified on the basis of Q-Tof micromass analysis data. A yellow crystal obtained from Benzene:Ethyl acetate (1:1; v/v) was identified as 3,5-diamino-4-(dipropylamino)-1-benzenesulfonamide on the basis of Co-TLC and Q-Tof micromass analysis data.

Isolation and identification of the photodegradation products of Oryzalin in isopropanol:water (1:1, v/v) under UV light in presence of TiO₂

The Hexane:Benzenesulfonic acid (1:9; v/v) afforded a yellow solid and identified as 2,6-dinitroaniline on the basis of TLC and mass fragmentation data. A dark brown solid obtained from the Benzene:Ethyl Acetate (3:2, v/v) was found to be a mixture of several compounds on TLC. On the basis of Q-ToF micromass analysis data of the solid, the identified compounds were 2-ethyl-7-nitro-2,3-dihydro-1H-benzo[d]imidazole-5-sulfonamide; 7-amino-2-ethyl-1-propyl-1H-benzo[d]imidazole-5-sulfonamide; 3,5-diamino-4-(dipropylamino)-1-benzenesulfonic acid; 3,4-dinitro-4-(propylamino)-1-benzenesulfonamide; 2-ethyl-7-nitro-1-propyl-1H-benzo[d]imidazole-5-sulfonamide; and 4-(dipropylamino)-3,5-dinitro-1-benzenesulfonic acid.

Isolation and identification of photodegradation products Oryzalin in isopropanol:water (1:1, v/v) under sunlight in absence of TiO₂

The Benzene:Ethyl Acetate (3 : 2, v/v) extract yielded dark yellow gummy solid that was found to be a mixture of several compound on TLC and the compounds were identified as 2-ethyl-7-nitro-2,3-dihydro-1H-benzo[d]imidazole-5-sulfonamide; 3,5-dinitro-4-(propylamino)-1-benzenesulfonamide; and 4-(dipropylamino)-3,5-dinitro-1-benzenesulfonic acid on the basis of Q-ToF micromass analysis data. A cream color crystal was obtained from Benzene:Ethyl acetate (3:7; v/v), which was identified as 3,5-diamino-4-(dipropylamino)-1-benzenesulfonamide on the basis of Co-TLC and mass fragmentation data.

Isolation and identification of the photodegradation products of Oryzalin in isopropanol:water (1:1, v/v) under sunlight in presence of TiO₂

A dark yellow residue obtained from Benzene:Ethyl Acetate (3:2, v/v) that was found to be a mixture of several compound on TLC and the compounds were identified as 2-ethyl-7-nitro-2,3-dihydro-1H-benzo[d]imidazole-5-sulfonamide; 3,5-diamino-4-(dipropylamino)-1-benzenesulfonic acid; 3,5-dinitro-4-(propylamino)-1-benzenesulfonamide; 2-ethyl-7-nitro-1-propyl-1H-benzo[d]imidazole-5-sulfonamide; and 4-(dipropylamino)-3,5-dinitro-1-benzenesulfonic acid on the basis of Q-ToF micromass analysis data.

Isolation and identification of the photodegradation products of Oryzalin in acetonitrile:water (1:1, v/v) under UV light in absence of TiO₂

Elution with Hexane:Benzen (3:2; v/v) afforded a dark yellow extract that was identified as N¹-propyl-2,6-dinitroaniline on the basis of Co-TLC and mass fragmentation data. The dark yellow gum obtained from Benzene:Ethyl Acetate (3:2, v/v) contains traces of solid that was found to be a mixture of several compound on TLC and the compounds were identified as 2-ethyl-7-nitro-2,3-dihydro-1H-benzo[d]imidazole-5-sulfonamide; 3,5-dinitro-4-(propylamino)-1-benzenesulfonamide; 2,2-dimethyl-7-nitro-2,3-dihydro-1H-benzo[d]-imidazole-5-sulfonamide; 3-amino-4-(dipropylamino)-5-nitro-1-benzenesulfonamide; and 4-(dipropylamino)-3,5-dinitro-1-benzenesulfinic acid on the basis of Q-Tof MSMS data.

Isolation and identification of the photodegradation products of Oryzalin in acetonitrile:water (1:1, v/v) under UV light in presence of TiO₂

The yellow extract obtained from the Hexane:Benzen (1:4; v/v) was identified as 2,6-dinitroaniline on the basis of Co-TLC and mass fragmentation data. Elution with Benzene:Ethyl acetate (7:3; v/v) afforded a dark yellow residue that was found to be a mixture of several compound on TLC and the compounds were identified as 2-ethyl-7-nitro-2,3-dihydro-1H-benzo[d]-imidazole-5-sulfonamide; 7-amino-2-ethyl-1-propyl-1H-benzo[d]imidazole-5-sulfonamide; 3,5-diamino-4-(dipropylamino)-1-benzenesulfonic acid; 3,5-dinitro-4-(propylamino)-1-benzenesulfonamide; 2-ethyl-7-nitro-1-propyl-1H-benzo[d]imidazole-5-sulfonamide; and 4-(dipropylamino)-3,5-dinitro-1-benzenesulfinic acid on the basis of Q-Tof MSMS data. Further Benzene:Ethyl acetate (1:1, v/v) yielded yellow crystal that was characterized as 3-amino-4-(dipropylamino)-5-nitro-1-benzenesulfonamide on the basis of Co-TLC and mass fragmentation data.

Isolation and identification of the photodegradation products of Oryzalin in acetonitrile:water (1:1, v/v) under sunlight in absence of TiO₂

A dark yellow extract was obtained from Hexane:Benzen (3:2; v/v) and rationalized as N¹,N¹-dipropylamino-2,6-dinitroaniline. Elution with Benzene:Ethyl Acetate (7:3, v/v) afforded a dark yellow gum that was found to be a mixture of several compound on TLC. The compounds were identified as 4-amino-3,5-dinitro-1-benzenesulfonamide; 3,5-dinitro-4-(propylamino)-1-benzenesulfonamide; 2-ethyl-7-nitro-1-propyl-1H-benzo[d]imidazole-5-sulfonamide; and 4-(dipropylamino)-3,5-dinitro-1-benzenesulfinic acid on the basis of Q-Tof MSMS data. The Benzene:Ethyl Acetate (1:1; v/v) extract

yielded yellow solid and characterized as 3,5-diamino-4-(dipropylamino)-1-benzenesulfonamide on the basis of Co-TLC and mass fragmentation data.

Isolation and identification of the photodegradation products of Oryzalin in acetonitrile:water (1:1, v/v) under sunlight in presence of TiO_2

Elution with Hexane:Benzenes (7:3; v/v) afforded a dark yellow extract and identified as N^1, N^1 -dipropylamino-2,6-dinitroaniline on the basis of Co-TLC and mass fragmentation data. The Benzenes:Ethyl Acetate (7:3; v/v) extract yielded brownish gummy residue, showed some overlapping spots on TLC and the compounds were identified as 4-amino-3,5-dinitro-1-benzenesulfonamide; 2-ethyl-7-nitro-2,3-dihydro-1H-benzo[d]imidazole-5-sulfonamide; 3,5-dinitro-4-(propylamino)-1-benzenesulfonamide; 2-ethyl-7-nitro-1-propyl-1H-benzo[d]imidazole-5-sulfonamide; and 4-(dipropylamino)-3,5-dinitro-1-benzenesulfonic acid on the basis of Q-Tof micromass analysis data. A yellow crystal obtained from Benzenes:Ethyl acetate (1:1; v/v) was characterized as 3,5-diamino-4-(dipropylamino)-1-benzenesulfonamide on the basis of Co-TLC and mass fragmentation data.

Kinetics of Oryzalin

The rate of dissipation of 10 ppm Oryzalin under UV/sunlight in different solvent system is presented in Tables 1 and 2. The Sample (5 mL) was taken at an interval of 0, 5, 15, 25, 40, 60 and 75 h from all the solutions and the residue at different time intervals was analyzed and calculated. From Tables 1 and 2, it was observed that the rate of disappearance of Oryzalin has increased with the time of irradiation in all the cases. The results revealed that the degradation of Oryzalin in different solvent systems followed first-order kinetics. The half-life values were calculated from the corresponding regression equations. From Tables 1 and 2, it is revealed that the rate of degradation of Oryzalin under UV irradiation in both the solvent system was faster as compared to sunlight irradiation. Sensitizer (TiO_2) in both the solvent system had almost no effect on the rate of degradation of Oryzalin in UV and sunlight irradiation. It was also observed that the rate of disappearance of Oryzalin in aqueous isopropanolic system was faster than in aqueous acetonitrile system. In all the cases, a dark control was kept and no reaction was observed during the entire irradiation period.

Table 1. Persistence of Oryzalin in different solvent systems under the influence of UV light.

[CSV Display Table](#)

Table 2. Persistence of Oryzalin in different solvent systems under the influence of sunlight.

CSVD:showTable

Characterization of photoproducts

In the present investigation, total 12 photodegradation products of Oryzalin (F₁, F₂, F₃, F₄, F₅, F₆, F₇, F₈, F₉, F₁₀, F₁₁ and F₁₂) were identified from different solvent mixtures. Out of the total, six photodegradation products (F₁, F₂, F₃, F₄, F₅, F₆) were synthetically prepared in the laboratory. Due to meager amount formation of the photoproducts, it was not possible to separate out these products in pure form. The structure of these compounds was elucidated by Co-TLC with the synthetically prepared compounds and Q-Tof micromass spectra; the detailed nomenclature of all the photoproducts is provided in Table 3. The different photoproducts obtained from aqueous isopropanol and acetonitrile solution after irradiation under UV and sunlight in absence and/or presence of sensitizer (TiO₂) are listed in Table 4.

Table 3. List of photoproducts identified.

CSVD:showTable

Table 4. List of photoproducts identified from different solvent systems.

CSVD:showTable

Degradation mechanism of dinitroaniline group herbicide

From environmental and agronomic point of view, the products of photodegradation of Oryzalin and an idea of the rate of degradation of Oryzalin have great importance. The effect of ultraviolet irradiation on phytotoxic amines with *ortho*-nitro substituent has been previously studied.^[20-21]

Crosby, D.G.; Li, M. Herbicide Photodecomposition. In *Degradation of Herbicides*; Kearney, P.C.; Kaufman, D.D., Eds.; Marcell Dekker: New York, 1969, p. 321–363.

Probst, G.W.; Tepe, J.B. Trifluralin and related compounds. In *Degradation of Herbicides*; Kearney, P.C.; Kaufman, D.D., Eds.; Marcell Dekker: New York, 1969, p. 255–282. Trifluralin, a dinitroaniline group of herbicide, undergo loss in herbicidal activity and a change in its ultraviolet absorption on exposure to sunlight, both on soil and on glass plates.^[22] Wright, W.L.; Warren, G.F. Photochemical decomposition of trifluralin. *Weeds*. 1965, *13*, 329–331. [\[Crossref\]](#), [\[Google Scholar\]](#) There were several studies that have already been reported to describe probable photodegradation path of dinitroaniline group of herbicide. Photocatalysis of pendimethalin and alachlor under UV light in the presence of TiO₂ followed first-order kinetics.

^[23] Moza, P.N.; Hustert, K.; Pal, S.; Sukul, P. Photocatalytic decomposition of pendimethalin and Alachlor. *Chemosphere*. 1992, *25*(11), 1675–1682. [\[Google Scholar\]](#) Hydroxyl radical formed during the photolysis affected the oxidation of the herbicides. The fast disappearance of the chemical was because of the enhanced

reactivity of the substance towards hydroxyl radicals. These radicals oxidize the side chain on the aromatic ring and hydroxylate the benzene ring. The photodegradation of trifluorfen was the result of competitions between nucleophilic substitutions by hydroxyl ion and a radical mechanism (photodecarboxylation and H-abstraction).

^[24]Vialaton, D.; Pilichowski, J.F.; Bagilo, D.; Paya-Perez, A.; Larsen, B.; Richard, C. Photo transformation of propiconazole in aqueous media. *J. Agric. Food Chem.* 2001, 49, 5377–5382. [\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#), [\[Google Scholar\]](#) The photoproducts formed, in their turn, can be phototransformed. As the photodegradation progressed, the increasing concentration of byproducts yielded other competitive absorption and reactions, so the prediction of the involved mechanism was not easy. The photodecomposition of dinitroaniline group of herbicides mainly involved N-dealkylation and arylmethyl oxidation in addition to processes like nitro-group reduction, nitro-group elimination and cyclization.^[25]

^[27]Leitis, E.; Crosby, D.G. Photodecomposition of trifluralin. *J. Agric. Food Chem.* 1974, 22(5), 842–848.

Newsom, H.C.; Woods, W.G. Photolysis of herbicide dinitramine (N³, N³-diethyl-2,4-dinitro-6-trifluoromethyl-m-phenylenediamine). *J. Agric. Food Chem.* 1973, 21(4), 598–601.

Dureja, P.; Walia, S. Photodecomposition of pendimethalin. *Pestic. Sci.* 1989, 25, 105–114. It was suggested that photochemical N-dealkylation of 2,6-dinitroaniline herbicides proceeds via free radical oxidation by atmospheric oxygen.^[25,28]

^[31]Leitis, E.; Crosby, D.G. Photodecomposition of trifluralin. *J. Agric. Food Chem.* 1974, 22(5), 842–848.

Plimmer, J.R.; Klingebiel, U.I. Photochemistry of *N*-sec-butyl-4-ter-butyl-2,6-dinitroaniline. *J. Agric. Food Chem.* 1974, 22, 689–693.

Crosby, D.G.; Tang, C.S. Photodecomposition of 3-(*p*-chlorophenyl) -1,1-dimethylurea (monuron). *J. Agric. Food Chem.* 1969, 17(5), 1041–1044.

Abdel-Wahab, A.M.; Casida, J.E. Photooxidation of two 4-dimethylaminoaryl methylcarbamate insecticides (Zectran and Matacil) on bean foliage and of alkylamino-phenyl methylcarbamate on silica gel chromoplates. *J. Agric. Food Chem.* 1967, 15(3), 479–487.

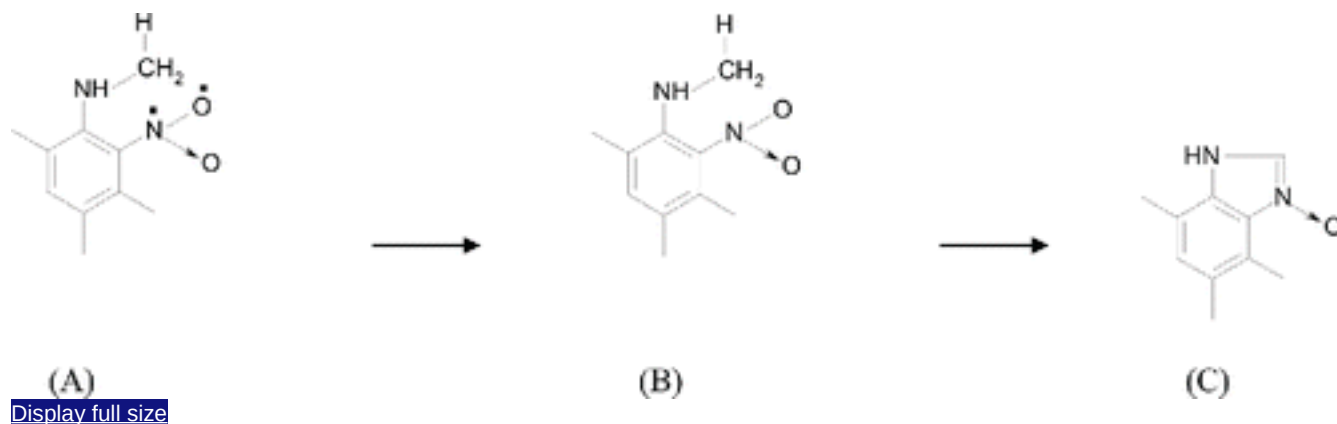
Sharkey, W.H.; Mochel, W.E. Mechanism of the photooxidation of amides. *J. Agric. Food Chem. Soc.* 1959, 81(12), 3000–3005. The reduction in methanol represented the well-known abstraction of hydrogen atoms from the medium.^[32,33] Plimmer, J.R. The photochemistry of halogenated herbicides. *Residue Rev.* 1970, 33, 47–74.

Crosby, D.G.; Hamadmad, N. Photoreduction of pentachlorobenzenes. *J. Agric. Food Chem.* 1971, 19(6), 1171–1174. An ionic mechanism for the formation of benzamidazoles and benzamidazole N-oxide from photodegradation of *o*-nitro-*tert*-anilines in the presence of acid has already been postulated earlier.^[34] Fielden, R.; Meth-Cohn, O.; Suschitzky, H. Thermal and photolytic cyclisation, rearrangement and denitration reactions of *o*-nitro-*t*-anilines. *Tetrahedron Lett.* 1970, 15, 1229–1234. [\[Crossref\]](#), [\[Google Scholar\]](#) Since our photodegradation was carried in the absence of added acid and the pH of the reaction mixture remained constant, we follow the mechanism proposed by Leitis and Crosby.

^[25]Leitis, E.; Crosby, D.G. Photodecomposition of trifluralin. *J. Agric. Food Chem.* 1974, 22(5), 842–848. [\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#), [\[Google](#)

[\[Scholar\]](#) The proposed plausible pathway for the photochemical formation of benzimidazole-N-oxide by slight modification of the free radical mechanism was as proposed earlier ([Fig. 1](#)).^[35]Döpp, D. Photochemistry of aromatic nitro compounds, on the mechanism from *o*-nitro-*tert*-butyl benzenes. Chem. Ber. 1971, 104, 1043–1047. [\[Crossref\]](#), [\[Google Scholar\]](#)

Figure 1. Plausible pathway for the formation of benzimidazole-3-oxide.

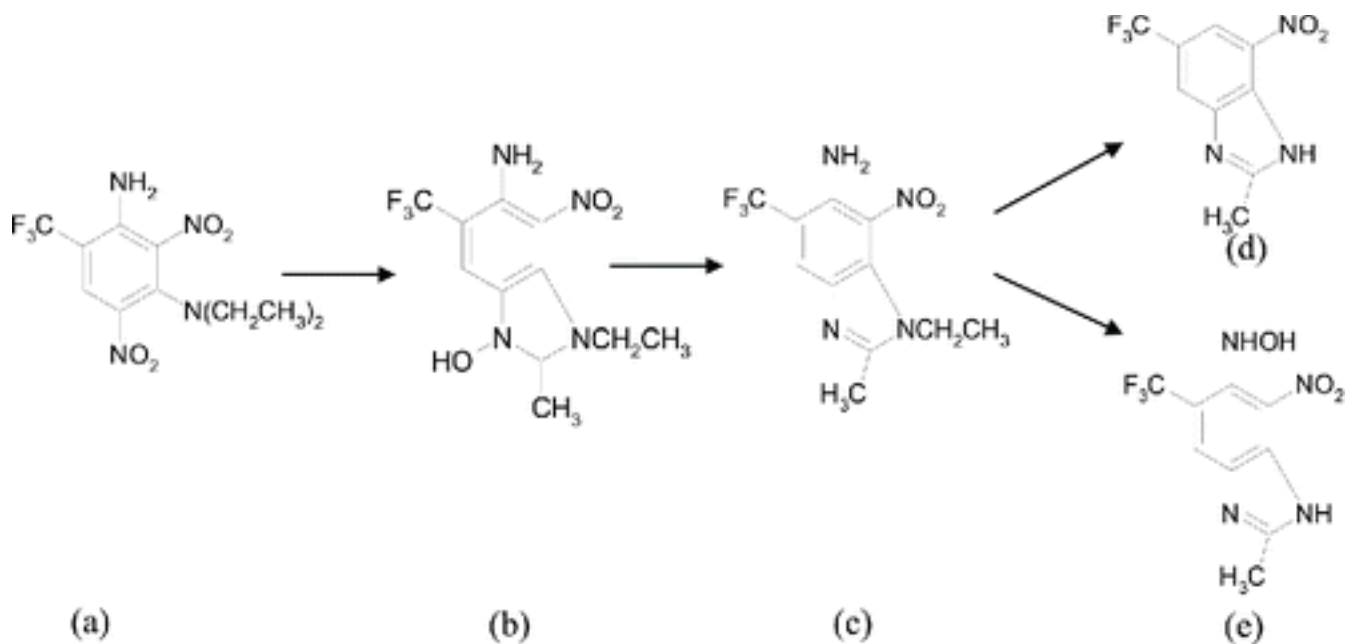


A detailed mechanism for the formation of cyclic photoproducts from dinitramine, a dinitroaniline group of herbicide, has already been established.

^[26]Newsom, H.C.; Woods, W.G. Photolysis of herbicide dinitramine (N³, N³-diethyl-2,4-dinitro-6-trifluoromethyl-*m*-phenylenediamine). J. Agric. Food Chem. 1973, 21(4), 598–601. [\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#), [\[Google Scholar\]](#) The plausible sequence to account for the observed products is depicted in [Figure 2](#). Condensation at the α -carbon leads to benzimidazoline (b), which may lose water and oxygen to provide benzimidazole (c). Formation of (c) from (b) was established in a separate experiment in which the benzimidazoline itself was photolyzed in methanol and found to yield benzimidazole (c). Dealkylation and oxidation of (c) could account for (d) and (e), respectively. Photochemical dealkylation of amine is already well documented.

^[36]Schonberg, A. Preparative organic photochemistry. Springer-Verlag: New York, 1968, p. 255. [\[Crossref\]](#), [\[Google Scholar\]](#) The ring-closed compounds obtained from dinitramine suggest the possible formation of similar cyclic photoproducts from other herbicides having a nitro group *ortho* to an alkyl-amino group.

Figure 2. Plausible pathway for the formation of cyclic products from dinitramine.



[Display full size](#)

The photodecomposition of Oryzalin involved only N-dealkylation and aryl methyl oxidation in addition to processes like nitro-group reduction, nitro-group elimination and cyclization. It was suggested that photochemical N-dealkylation of 2,6-dinitroaniline herbicides proceeds via free-radical oxidation by atmospheric oxygen.

^[37]Plimmer, J.R.; Klingebiel, U.I. Photochemistry of *N*-sec-butyl-4-tert-butyl-2,6-dinitroaniline. *J. Agric. Food Chem.* 1974, 22(4), 689–693.[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#), [\[Google Scholar\]](#) The formation of benzimidazoles and benzimidazole-N-oxides was investigated by free radicals in soil as well as light energy. Leitis and Crosby^[25]Leitis, E.; Crosby, D.G. Photodecomposition of trifluralin. *J. Agric. Food Chem.* 1974, 22(5), 842–848.[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#), [\[Google Scholar\]](#) proposed a plausible pathway to explain the photochemical formation of benzimidazole-N-oxide by slight modification of the free-radical mechanism as proposed by Döpp^[35]Döpp, D. Photochemistry of aromatic nitro compounds, on the mechanism from *o*-nitro-tert-butyl benzenes. *Chem. Ber.* 1971, 104, 1043–1047.[\[Crossref\]](#), [\[Google Scholar\]](#) (Fig. 1). The replacement of the NO₂ group and hydroxyl group could be explained by a radical process through photonucleophilic displacement.

^[38]Havinga, E.; Kronenberg, M.E. Some problems in aromatic photosubstitution. *Pure Appl. Chem.* 1968, 16, 137–152.[\[Crossref\]](#), [\[Google Scholar\]](#) Previous investigations has already shown the involvement of photochemical N-dealkylation, nitro-group reduction and cyclization of dinitroaniline herbicide.^[25]

^[27]Leitis, E.; Crosby, D.G. Photodecomposition of trifluralin. *J. Agric. Food Chem.* 1974, 22(5), 842–848.

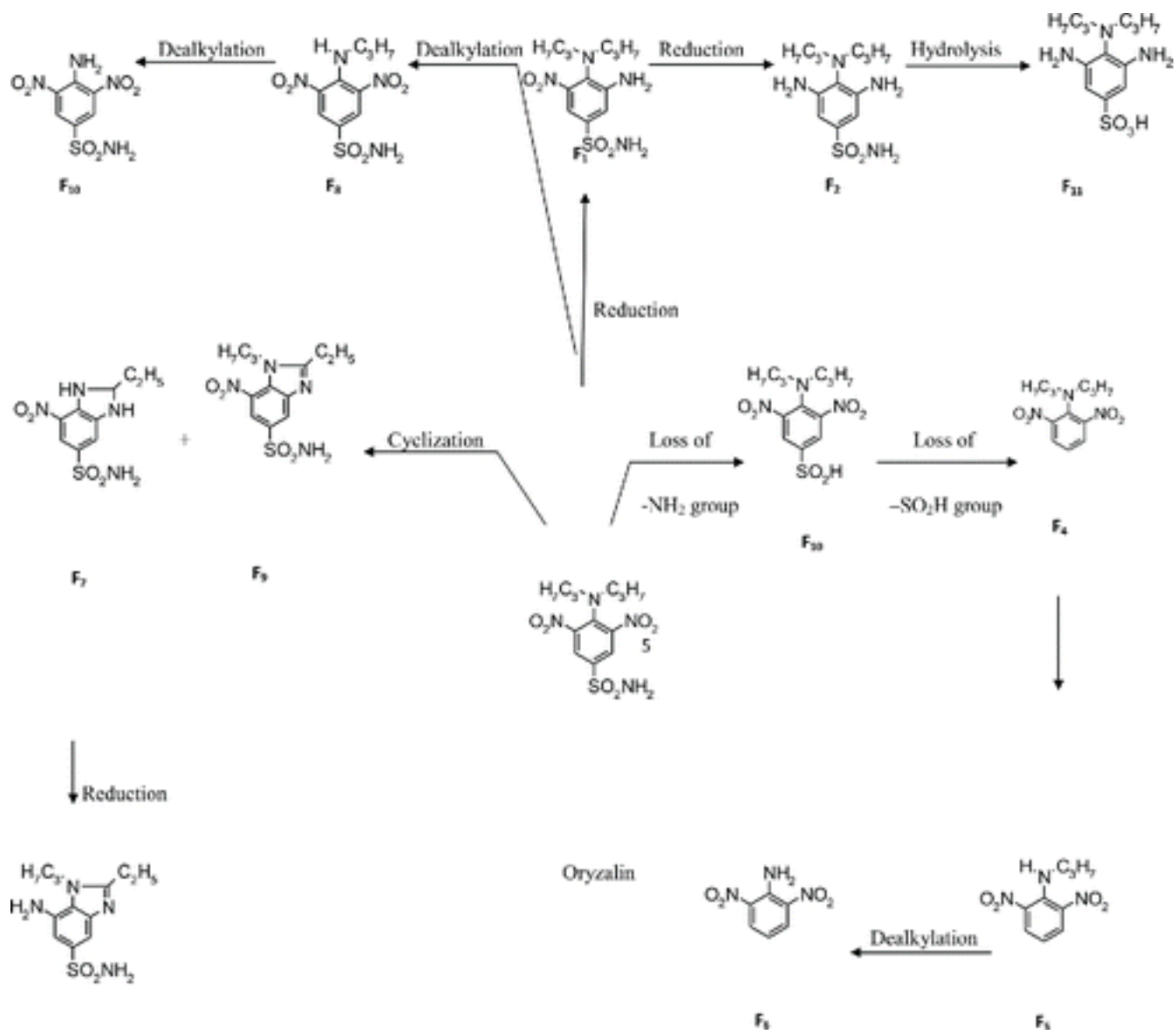
Newsom, H.C.; Woods, W.G. Photolysis of herbicide dinitramine (N³, N³-diethyl-2,4-dinitro-6-trifluoromethyl-*m*-phenylenediamine). *J. Agric. Food Chem.* 1973, 21(4), 598–601.

Dureja, P.; Walia, S. Photodecomposition of pendimethalin. *Pestic. Sci.* 1989, 25, 105–114.

Degradation mechanism of Oryzalin

The plausible mechanism of phototransformation of Oryzalin is depicted in [Figure 3](#). Sequential dealkylation of the aniline nitrogen, reduction of at least one nitro ($-\text{NO}_2$) group, cyclization and loss of $-\text{NH}_2$ from $-\text{SO}_2\text{NH}_2$ group appeared to be primary degradative reactions. Quantitatively, the partially N-dealkylated product F_9 , completely reduced product F_2 , cyclic product F_7 and the compound F_{11} formed due to loss of $-\text{NH}_2$ group were the major product of degradation. On partial N-dealkylation of Oryzalin yielded the compound F_9 , which was converted to F_{10} after complete N-dealkylation. Product F_1 was formed from the partial reduction of at least one $-\text{NO}_2$ group, and after complete reduction of two $-\text{NO}_2$ group, Oryzalin yielded F_2 . The photoproduct F_2 hydrolyzed to give F_8 . Cyclization of Oryzalin yielded the product F_7 and reduction of the $-\text{NO}_2$ group of F_7 yielded the product F_3 . Compound F_7 also yielded product F_6 after partial N-dealkylation and reduction. Loss of $-\text{NH}_2$ group from $-\text{SO}_2\text{NH}_2$ group of Oryzalin yielded the photoproduct F_{11} . The compound F_{12} was formed from F_{11} due to loss of $-\text{SO}_2\text{H}$ group. Partial and complete N-dealkylation of the compound F_{12} yielded the compounds F_4 and F_5 , respectively.

Figure 3. Plausible photometabolic pathways of photodegradation of Oryzalin in different solvent systems.



[Display full size](#)

The photodegradation of Oryzalin in different solvent systems in presence of TiO_2 has been suggested in view of the different researches depicted earlier, which were discussed earlier. Thus, it may be stated from the present study that the main phototransformation pathways of Oryzalin involved dealkylation, reduction, cyclization and loss of $-\text{NH}_2$ and $-\text{SO}_2\text{H}$ groups. A plausible photodegradation pathway of Oryzalin has been portrayed in [Figure 3](#).

The faster degradation in isopropanol was probably due to the hydrogen atom abstraction, which was more facile from isopropanol than from acetonitrile because of much greater stability of the component radical species generated from isopropanol than from acetonitrile.

Acknowledgments

We are grateful to IICB, Kolkata, for Q-Tof micromass spectral analysis and to Bidhan Chandra Krishi Viswavidyalaya (BCKV) for infrastructural facilities.

Appendix

Table A1(i). TLC of 3-amino-4-(dipropylamino)-5-nitro-1-benzenesulfonamide.

[CSVDisplay Table](#)

Table A1(ii). ^1H NMR spectrum of 3-amino-4-(dipropylamino)-5-nitro-1-benzenesulfonamide.

[CSVDisplay Table](#)

Table A1(iii). ^{13}C NMR spectrum of 3-amino-4-(dipropylamino)-5-nitro-1-benzenesulfonamide.

[CSVDisplay Table](#)

Table A1(iv). Mass spectrum of 3-amino-4-(dipropylamino)-5-nitro-1-benzenesulfonamide.

[CSVDisplay Table](#)

Table A2(i). TLC of 3,5-diamino-4-(dipropylamino)-1-benzenesulfonamide.

[CSVDisplay Table](#)

Table A2(ii). ^1H NMR spectrum of 3,5-diamino-4-(dipropylamino)-1-benzenesulfonamide.

[CSVDisplay Table](#)

Table A2(iii). ^{13}C NMR of 3,5-diamino-4-(dipropylamino)-1-benzenesulfonamide.

[CSVDisplay Table](#)

Table A2(iv). Mass spectrum of 3,5-diamino-4-(dipropylamino)-1-benzenesulfonamide.

[CSV Display Table](#)

Table A3(i). TLC of 7-amino-2-ethyl-1-propyl-1H-benzo[*d*]imidazole-5-sulfonamide.

[CSV Display Table](#)

Table A3(ii). ¹H NMR spectrum of 7-amino-2-ethyl-1-propyl-1H-benzo[*d*]imidazole-5-sulfonamide.

[CSV Display Table](#)

Table A3(iii). ¹³C NMR spectrum of 7-amino-2-ethyl-1-propyl-1H-benzo[*d*]imidazole-5-sulfonamide.

[CSV Display Table](#)

Table A3(iv). Mass spectrum of 7-amino-2-ethyl-1-propyl-1H-benzo[*d*]imidazole-5-sulfonamide.

[CSV Display Table](#)

Table A4(i). TLC of N¹,N¹-dipropyl-2,6-dinitroaniline.

[CSV Display Table](#)

Table A4(ii). ¹H NMR spectrum of N¹,N¹-dipropyl-2,6-dinitroaniline.

[CSV Display Table](#)

Table A4(iii). ¹³C NMR spectrum of N¹,N¹-dipropyl-2,6-dinitroaniline.

[CSV Display Table](#)

Table A4(iv). Mass spectrum of N¹,N¹-dipropyl-2,6-dinitroaniline.

[CSV Display Table](#)

Table A5(i). TLC of N¹-propyl-2,6-dinitro aniline.

[CSV Display Table](#)

Table A5(ii). ¹H NMR spectrum of N¹-propyl-2,6-dinitro aniline.

[CSV Display Table](#)

Table A5(iii). ¹³C NMR spectrum of N¹-propyl-2,6-dinitro aniline.

[CSV Display Table](#)

Table A5(iv). Mass spectrum of N¹-propyl-2,6-dinitro aniline.

[CSV Display Table](#)

Table A6(i). TLC of 2,6-dinitro aniline.

[CSV Display Table](#)

Table A6(ii). ¹H NMR spectrum of 2,6-dinitro aniline.

[CSV Display Table](#)

Table A6(iii). ¹³C NMR spectrum of 2,6-dinitro aniline.

[CSV Display Table](#)

Table A6(iv). Mass spectrum of 2,6-dinitro aniline.

[CSV Display Table](#)

References

1. Mandal, S.; Joardar, S.; Das, S.; Bhattacharyya, A. Photodegradation of hexythiazox in different solvent systems under the influence of ultraviolet light and sunlight in the presence of TiO₂, H₂O₂ and KNO₃ and identification of the photoproducts. J. Agric. Food Chem. 2011, 59, 11727–11734.
[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#)
,
[\[Google Scholar\]](#)
2. Watkins, D.A.M. Some implications of the photochemical decomposition of pesticides. Chem. Ind. 1974, 5, 185–190.

[\[Google Scholar\]](#)

3. Daneshvar, N.; Salari, D.; Niaei, A.; Khataee, A.R. Photocatalytic degradation of the herbicide erioglaucine in the presence of nano-sized titanium dioxide: comparison and modeling of reaction kinetics. *J. Environ. Sci. Health, Part B.* 2006, *41*, 1273–1290.

[\[Taylor & Francis Online\]](#), [\[Web of Science ®\]](#)

[\[Google Scholar\]](#)

4. Lapertot, M.; Pichat, P.; Parra, S.; Guillard, C.; Pulgarin, C. Photocatalytic degradation of p-halophenols in TiO₂ aqueous suspensions: halogen effect on removal rate, aromatic intermediates and toxicity variations. *J. Environ. Sci. Health, Part A.* 2006, *41*, 1009–1025.

[\[Taylor & Francis Online\]](#), [\[Web of Science ®\]](#)

[\[Google Scholar\]](#)

5. Zayani, G.; Bousselmi, L.; Pichat, P.; Mhenni, F.; Ghrabi, A. Photocatalytic degradation of the acid blue 113 textile azo dye in aqueous suspensions of four commercialized TiO₂ samples. *J. Environ. Sci. Health, Part A.* 2008, *43*, 202–209.

[\[Taylor & Francis Online\]](#), [\[Web of Science ®\]](#)

[\[Google Scholar\]](#)

6. Konstantinou, I.K.; Albanis, T.A. TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetics and mechanistic investigation A review. *Appl. Catal. B.* 2004, *49*, 1–14.

[\[Crossref\]](#), [\[Web of Science ®\]](#)

[\[Google Scholar\]](#)

7. Blake, D.M. *Bibliography of Work on the Heterogeneous Photocatalytic Removal of Hazardous Compounds from Water and Air: Update Number 3 to January 1999*; National Renewable Energy Laboratory Report, NREL/TP-570-26797; National Technical Information Service (NTIS): Springfield, VA, 1999. Available at <http://www.nrel.gov/docs/fy99osti/26797.pdf> (accessed April 2008).

[\[Crossref\]](#)

[\[Google Scholar\]](#)

8. Behnajady, M.A.; Modirshahla, N.; Shokri, M.; Elham, H.; Zeininezhad, A. The effect of particle size and crystal structure of titanium dioxide nanoparticles on the photocatalytic properties. *J. Environ. Sci. Health, Part A.* 2008, *43*, 460–467.

[\[Taylor & Francis Online\]](#), [\[Web of Science ®\]](#)

[\[Google Scholar\]](#)

9. Ollis, D.F.; Hsiao, C.; Budiman, L.; Lee, C. Heterogeneous photoassisted catalysis: conversions of perchloroethylene, dichloroethane, chloroacetic acids, and chlorobenzenes. *J. Catal.* 1984, 88, 89–95.
[\[Crossref\]](#), [\[Web of Science ®\]](#)
,
[\[Google Scholar\]](#)
10. Graetzel, M. Molecular engineering in photoconversion systems. In *Energy Resources through Photochemistry and Catalysis*; Graetzel, M., Ed.; Academic Press: New York, 1983; 71–98.
[\[Crossref\]](#)
,
[\[Google Scholar\]](#)
11. Roy, U.; Bhattacharyya, A.; Kole, R.K.; Chakraborty, S.; Mitra, S.R. Phototransformation of bifenoxy in aqueous isopropanol. *Toxicol. Environ. Chem.* 2004, 86(1–4), 45–53.
[\[Taylor & Francis Online\]](#)
,
[\[Google Scholar\]](#)
12. Das, S.; Muneer, M.; Gopidas, K.R. Photocatalytic degradation of waste water pollutants. Titanium dioxide-mediated oxidation of polynuclear aromatic hydrocarbons. *J. Photochem. Photobiol. A. Chem.* 1994, 77, 83–88.
[\[Crossref\]](#), [\[Web of Science ®\]](#)
,
[\[Google Scholar\]](#)
13. Oliver, B.G.; Carey, J.H. Photodegradation of wastes and pollutants in aquatic environment. In *Homogeneous and Heterogeneous Photocatalysis*; Pelizzetti, E.; Serpone, N. Eds.; Reidel: Dordrecht, Netherlands, 1986; 629–650.
[\[Crossref\]](#)
,
[\[Google Scholar\]](#)
14. Mansour, M.; Feicht, E.A.; Behechti, A.; Scheunert, I. Experimental approaches to studying the photolysis of selected pesticides in water and soil. *Chemosphere.* 1997, 35, 39–50.
[\[Crossref\]](#), [\[Web of Science ®\]](#)
,
[\[Google Scholar\]](#)
15. Bruggeman, W.A.; Burns, L.A.; Choudhury, G.C.; Daum, K.A.; Gehring, P.J.; Newland, L.W.; Paris, D.F.; Parke, D.V.; Reitz, R.H.; Roof, A.A.M.; Steen, W.C.; Zepp, R.G. *The Handbook of Environmental Chemistry*; Hutzinger, O., Ed.; Reaction and Processes: Aquatic Photochemistry; Springer-Verlag: Berlin, 1982; Vol. 2, Part B.

[\[Google Scholar\]](#)

16. Benedix, R.; Dehn, F.; Quaas, J.; Orgass, M. Application of titanium dioxide photocatalysis to create self-cleaning building materials. *LACER*. 2006, *5*, 157–168.

[\[Google Scholar\]](#)

17. Draper, W.M.; Crosby, D.G. Photochemistry and volatility of drepamon in water. *J. Agric. Food Chem.* 1984, *32*(4), 728–733.

[\[Crossref\]](#), [\[Web of Science ®\]](#)

,

[\[Google Scholar\]](#)

18. Mill, T.; Hendry, D.G.; Richardson, H. Free-radical oxidants in natural waters. *Science*. 1980, *207*, 886–887.

[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#)

,

[\[Google Scholar\]](#)

19. Dvorakova, K.; Dorr, R.T.; Gallegos, A.; McClure, T.; Powis, G. Pharmacokinetic studies of the herbicide and antitumor compound Oryzalin in mice. *J. Chromatogr. B*. 1997, *696*, 275–281.

[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#)

,

[\[Google Scholar\]](#)

20. Crosby, D.G.; Li, M. Herbicide Photodecomposition. In *Degradation of Herbicides*; Kearney, P.C.; Kaufman, D.D., Eds.; Marcell Dekker: New York, 1969, p. 321–363.

[\[Google Scholar\]](#)

21. Probst, G.W.; Tepe, J.B. Trifluralin and related compounds. In *Degradation of Herbicides*; Kearney, P.C.; Kaufman, D.D., Eds.; Marcell Dekker: New York, 1969, p. 255–282.

[\[Google Scholar\]](#)

22. Wright, W.L.; Warren, G.F. Photochemical decomposition of trifluralin. *Weeds*. 1965, *13*, 329–331.

[\[Crossref\]](#)

,

[\[Google Scholar\]](#)

23. Moza, P.N.; Hustert, K.; Pal, S.; Sukul, P. Photocatalytic decomposition of pendimethalin and Alachlor. *Chemosphere*. 1992, *25*(11), 1675–1682.

[\[Google Scholar\]](#)

24. Vialaton, D.; Pilichowski, J.F.; Bagilo, D.; Paya-Perez, A.; Larsen, B.; Richard, C. Phototransformation of propiconazole in aqueous media. *J. Agric. Food Chem.* 2001, *49*, 5377–5382.

[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#)

,
[\[Google Scholar\]](#)

25. Leitis, E.; Crosby, D.G. Photodecomposition of trifluralin. *J. Agric. Food Chem.* 1974, *22*(5), 842–848.

[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#)

,
[\[Google Scholar\]](#)

26. Newsom, H.C.; Woods, W.G. Photolysis of herbicide dinitramine (N³, N³-diethyl-2,4-dinitro-6-trifluoromethyl-m-phenylenediamine). *J. Agric. Food Chem.* 1973, *21*(4), 598–601.

[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#)

,
[\[Google Scholar\]](#)

27. Dureja, P.; Walia, S. Photodecomposition of pendimethalin. *Pestic. Sci.* 1989, *25*, 105–114.

[\[Crossref\]](#)

,
[\[Google Scholar\]](#)

28. Plimmer, J.R.; Klingebiel, U.I. Photochemistry of *N*-sec-butyl-4-ter-butyl-2,6-dinitroaniline. *J. Agric. Food Chem.* 1974, *22*, 689–693.

[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#)

,
[\[Google Scholar\]](#)

29. Crosby, D.G.; Tang, C.S. Photodecomposition of 3-(*p*-chlorophenyl)-1,1-dimethylurea (monuron). *J. Agric. Food Chem.* 1969, *17*(5), 1041–1044.

[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#)

,
[\[Google Scholar\]](#)

30. Abdel-Wahab, A.M.; Casida, J.E. Photooxidation of two 4-dimethylaminoaryl methylcarbamate insecticides (Zectran and Matacil) on bean foliage and of alkylamino-phenyl methylcarbamate on silica gel chromoplates. *J. Agric. Food Chem.* 1967, *15*(3), 479–487.

[\[Crossref\]](#), [\[Web of Science ®\]](#)

,
[\[Google Scholar\]](#)

31. Sharkey, W.H.; Mochel, W.E. Mechanism of the photooxidation of amides. *J. Agric. Food Chem. Soc.* 1959, *81*(12), 3000–3005.

[\[Google Scholar\]](#)

32. Plimmer, J.R. The photochemistry of halogenated herbicides. *Residue Rev.* 1970, 33, 47–74.

[\[PubMed\]](#)

,

[\[Google Scholar\]](#)

33. Crosby, D.G.; Hamadmad, N. Photoreduction of pentachlorobenzenes. *J. Agric. Food Chem.* 1971, 19(6), 1171–1174.

[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#)

,

[\[Google Scholar\]](#)

34. Fielden, R.; Meth-Cohn, O.; Suschitzky, H. Thermal and photolytic cyclisation, rearrangement and denitration reactions of *o*-nitro-*t*-anilines. *Tetrahedron Lett.* 1970, 15, 1229–1234.

[\[Crossref\]](#)

,

[\[Google Scholar\]](#)

35. Döpp, D. Photochemistry of aromatic nitro compounds, on the mechanism from *o*-nitro-*tert*-butyl benzenes. *Chem. Ber.* 1971, 104, 1043–1047.

[\[Crossref\]](#)

,

[\[Google Scholar\]](#)

36. Schonberg, A. Preparative organic photochemistry. Springer-Verlag: New York, 1968, p. 255.

[\[Crossref\]](#)

,

[\[Google Scholar\]](#)

37. Plimmer, J.R.; Klingebiel, U.I. Photochemistry of *N*-*sec*-butyl-4-*tert*-butyl-2,6-dinitroaniline. *J. Agric. Food Chem.* 1974, 22(4), 689–693.

[\[Crossref\]](#), [\[PubMed\]](#), [\[Web of Science ®\]](#)

,

[\[Google Scholar\]](#)

38. Havinga, E.; Kronenberg, M.E. Some problems in aromatic photosubstitution. *Pure Appl. Chem.* 1968, 16, 137–152.

[\[Crossref\]](#)

,

[\[Google Scholar\]](#)