Original Article

Ga₂O₃-Photoassisted and Photolytic Degradation of the Flubendiamide Agrochemical in Aqueous Media under UVC Irradiation

Tohru Tsukamoto ^{a*}, Yoshihiro Mitsutsuka ^a, Takeji Takamura ^b^a Department of Chemistry, Meisei University, Hino, Japan^b Division of Applied Chemistry, Kanagawa Institute of Technology, Atsugi, Japan**ABSTRACT**

The photoassisted degradation of the recalcitrant and persistent Flubendiamide insecticide was examined in the presence of the metal-oxide semiconductor Ga₂O₃ in air-equilibrated and inert conditions (Ga₂O₃/air and Ga₂O₃/N₂, respectively) under Ultraviolet C (UVC) irradiation at 254 nm; for comparison, the degradation of this insecticide was also investigated in catalyst-free/air and catalyst-free/N₂ under UVC irradiation. The time course of the degradation was monitored by examining the yields of inorganic ions formed (fluoride, iodide, sulfate, nitrate and ammonium ions) and analyzed quantitatively by ion chromatographic techniques. Mechanistic considerations are described from calculating partial charges and electron densities on each of the functionalities in the Flubendiamide structure in aqueous media. Reactive oxygen species, such as the electrophilic •OH radicals and singlet oxygen, are inferred to attack the insecticide at positions where the functional groups possess the highest electron densities and highest negative partial charges, which led ultimately to defluorination, deiodination, desulfonation, and denitrogenation (i.e., formation of ammonium and nitrate ions). The total yields of decomposition followed expectations in the increasing order: N₂ < Ga₂O₃/N₂ < air < Ga₂O₃/air.

Keywords: Flubendiamide, Ga₂O₃, photodegradation, UVC, Ames test

INTRODUCTION

Various fluorinated agrochemicals and pharmaceuticals have been synthesized and used extensively in several applications. The effects of fluorine substituents on the physicochemical and conformational properties of many substrates have been investigated and reviewed in the context of medicinal chemistry [1], as fluoro functionalities possess striking electrophilic and hydrophilic characteristics. Trifluoromethyl group (s) and fluorine atom (s) bonded to aromatic rings act as fat-soluble functions that enhance the penetration and permeability of fluorinated substrates into membranes and tissues [2]. The medicinal action of these substrates in living cells is their aggressive impact on the carcinogenic behavior that causes cancers in humans and animals at cell positions where the fluorinated substrate is shielded through hydrogen

bonding. To the extent that the van der Waals radius of the hydrogen atom is similar to that of the fluorine atom, an organism has difficulty in distinguishing between fluorinated and non-fluorinated compounds [3]. Fluorinated anti-cancer medicinals intercept the growth of cancer cells and accelerate their extinction. Unfortunately, too often these pharmaceutical anti-cancer agents are released into the environment through excretion by a human body.

Cleavage of the C–F bond is uncommonly difficult so that fluorinated substrates tend to accumulate in the environment for some time causing substantive ecological contamination, even in slight amounts. To the extent that they are fat-soluble and hydrophobic, such substrates are not adsorbed on the surface of solids and, of relevance here, on the surface of metal-oxide nanoparticulates. Although photoassisted mineralizations of cyanuric acid [4], methyl parathion [5],

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Received: March 15, 2019, Accepted: June 17, 2019, Published online: October 10, 2019

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and dimethoate [6] by such metal oxides as ZnO and TiO₂ have been investigated, the photoactivity of ZnO toward the degradation of fluorinated substrates has received but scant attention. In earlier studies, we examined the photoassisted degradation of such fluorinated substrates as fluoxetine, fluvoxamine, fluazinam, and others by the Ga₂O₃ and TiO₂ metal oxides [7]. Our previous investigation of the Ga₂O₃-photoassisted decomposition of the insecticide Fipronil in aqueous media by Ultraviolet C (UVC) irradiation [8,9] showed that this insecticide could be converted in relatively short time (ca. 30 min; mass spectral analysis) to the photoproduct fipronil-desulfinyl through loss of the S=O fragment, followed by significant degradation of this photoproduct in less than 1 hr of continued UVC irradiation. And degradation and mineralization of fluorinated compound which is insoluble by Ga₂O₃ was higher about 10% than that of TiO₂. Defluorination of soluble fluorinated substance (Fluoxetine) by Ga₂O₃/N₂ system was over 85%, in TiO₂/O₂ system case, it was defluorinated 5%. Photocatalytic degraded intermediates by Ga₂O₃/N₂ system didn't have toxicity from results of Ames test.

The insecticide Flubendiamide (a benzenedicarboxamide insecticide) has a high insect-killing activity against moths that harm vegetables, teas, fruits and others. In safety evaluation of residual agrochemicals, the acceptable daily intake (ADI) of this insecticide is 0.024 mg kg⁻¹ day⁻¹ in the USA, 0.010 mg kg⁻¹ day⁻¹ in Australia and 0.020 mg kg⁻¹ day⁻¹ according to the Joint Meeting on Pesticide Residues (JMPR). Flubendiamide is commonly utilized in many countries of Asia, North and South America, and Africa. The harvest yield of more than 200 crops that include a variety of different fruits (e.g., peach, apple, watermelon, pear and persimmon), and various vegetables (e.g., soybeans, almonds, peanuts, cotton, lettuce, tomatoes, carrot, cabbage, onion and potato) increases subsequent to spreading this insecticide. The U.S. Environmental Protection Agency has recently moved to prohibit the use of Flubendiamide/Products because of significant harmful risks to aquatic animals and to different environments [10]. (Fig. 1)

Several studies have been published on the photoassisted degradation of Flubendiamide with the composite metal oxides subjected to artificial light irradiation in aqueous media [11] and to sunlight irradiation under soil conditions at various pHs [12]. In this regard, Fenoll and coworkers [11] examined the photodegradation of Flubendiamide in aqueous suspensions of binary (ZnO and TiO₂) and ternary (Zn₂TiO₄ and ZnTiO₃) oxides under artificial light (300–460 nm) irradiation. They showed that addition of ZnO and TiO₂, in

Fig. 1 Flubendiamide.

tandem with an electron acceptor (Na₂S₂O₈), enhanced the degradation rate of this insecticide in comparison with those carried out photolytically and with other metal oxides alone. They also identified the desiodoflubendiamide intermediate during the degradation process [11].

Under soil conditions, Das and Mukherjee [12] exposed Flubendiamide as thin films on petri-plates and on soil to UV light and to sunlight; the residues of Flubendiamide dissipated with half-lives $t_{1/2}$ = 7.0 and 9.1 days under UV light and 12.0 and 19.1 days under sunlight, respectively. By contrast, in aqueous media under different pH conditions they showed that Flubendiamide residues persisted in water beyond 250 days with half-lives from ca. 251 to 301 days, with dissipation occurring faster in water at pH 4.0 ($t_{1/2}$ = 251 days), followed at pH 9.2 ($t_{1/2}$ = 274 days) and pH 7.0 ($t_{1/2}$ = 301 days).

Processes that occur in active sludge typically detoxify/purify environmental pollutants by means of microorganisms, but fail to cleave the rather strong C–F bond. The photocatalytic techniques to decompose environmental pollutants have been explored actively toward the destruction of fluorinated substrates. The cleavage of the C–F bond has proven rather difficult even in cases where the metal oxide was TiO₂. By contrast, the environment-unfriendly perfluorooctanoic acid (PFOA) with several such C–F bonds could be degraded in the presence of gallium sesquioxide (β-Ga₂O₃) upon 254-nm irradiation, even under an inert nitrogen atmosphere [13]. In fact, several studies have demonstrated that Ga₂O₃ is more photoactive toward the decomposition of PFOA than is TiO₂ [14–16]. However, with a bandgap larger (4.8–5.0 eV) than TiO₂ (anatase; bandgap 3.2 eV; absorption edge, 387 nm), activation of Ga₂O₃ requires shorter wavelength radiation (e.g. 254 nm) so as to generate reductive (conduction band electrons) and oxidative (valence band holes) charge carriers. The present study was undertaken to examine the Ga₂O₃-photoassisted and photolytic degradation of Flubendiamide as part of our systematic studies into disposing of undesirable agrochemicals once part of the agricultural environment.

EXPERIMENTAL METHOD

Reagents

The neonicotinoid insecticide Flubendiamide {1-N-[4-(1,1,1,2,3,3,3-heptafluoropropan-2-yl)-2-methylphenyl]-3-iodo-2-N-(2-methyl-1-methylsulfonylpropan-2-yl)benzene-1,2-dicarboxamide} was purchased from Wako Pure Chem. Ind. Co. Ltd., Osaka, Japan; purity was 99.4% (reagent grade) and was used as received. The β -gallium sesquioxide (β -Ga₂O₃) was also supplied by Wako Pure Chem. Ind. Co. Ltd., Osaka, Japan; all other chemicals were of reagent grade. The acute dermal Lethal Dose 50 (LD₅₀) for rat for Flubendiamide was greater than 2000 mg kg⁻¹ [17].

Photodegradation set-ups and analytical assays

A starting tested mixture of the insecticide Flubendiamide (68.2 mg L⁻¹) in aqueous media was equivalent to 0.10 mM of Flubendiamide. To 100 mL of the Flubendiamide suspension contained in a tightly closed 115-mL quartz cylindrical photoreactor was added, when necessary, 50 mg of β -Ga₂O₃; the suspension was subsequently irradiated with two low-pressure Hg lamps (Toshiba Lighting & Technology Corp, Tokyo, Japan, GL 20-A sterilization lamp; ca. 60 cm length; light irradiance at 254 nm was 10.4 mW cm⁻² (Topcon Corp. UVR-2 and UD-25 radiometers, Tokyo, Japan)). The magnetically stirred dispersion was purged with nitrogen gas at atmospheric pressure for 30 min (or 60 min) prior to UVC irradiation for reductive-type experiments; otherwise, the solution was air-equilibrated (flow rate 1.9 L min⁻¹). And air bubbling was continuing during UVC irradiation. The temperature was maintained nearly constant at ca. 25°C by air cooling. This experimental reactor was summarized in **Fig. 1**. The loading of Ga₂O₃ in the suspension (0.50 g L⁻¹) was such that insured the metal oxide absorbed all the photons of the UV light source (254 nm). All spectra and analyses were performed after separation of the metal oxide by centrifugation and ultimate filtration through an Advantec 0.2 μ m filter. Quantitative analyses of fluoride, iodide, nitrate and sulfate anions were carried out by ion chromatography using a Tosoh Ion Chromatograph Model IC-2001, together with a TSK Gel Super IC-AZ column (inner diameter 4.6 mm x 15 cm), Tosoh Corp., Tokyo, Japan; the eluent consisted of a mixed aqueous solution of 3.2 mM Na₂CO₃ and 1.9 mM NaHCO₃; the flow rate was 0.8 mL min⁻¹. The detector was a suppressed conductivity detector operating with a column maintained at 40°C. The quantity of fluoride ions was assayed using a calibration curve determined using standard solutions of NaF supplied by Merck KGaA, Darmstadt,

Fig. 2 Schematic diagram of lab scale reactor.

Germany. The quantity of NH₄⁺ ions was analyzed with a JASCO HPLC chromatograph; the standard column was IC Y-521 for cationic analysis and the eluent was an aqueous 4 mM HNO₃ solution; flow rate was 1.0 mL min⁻¹. The detector was also a suppressed conductivity detector operating with a column maintained at about 40°C. (**Fig. 2**)

Ames test inspection

The Ames mutagenicity test is an experimental method to detect a chemical substance that causes possible mutations. The test was performed on the initial substrate (0.50 mM in mixed solution of 55% acetone and 45% water) and on intermediate products subsequent to dehalogenation/ decomposition using both the *Salmonella typhimurium* TA-98 strain (of the flame-shift type), the TA-100 strain (of the base-pair substituted type) and YG-1024 strain (of the assay of an amino moieties) [18-20]. Strains were independently cultured by vigorously shaking the samples at 37°C for 10 to 11 hrs to prepare the suspended solution containing a fixed concentration of each strain. After pre-incubation of the dispersion (0.10 mL) at 37°C for 20 min, a 2-mL aliquot of a soft agar solution was added onto a minimum glucose plate, which was subsequently incubated at 37°C for more than 48 hrs. After incubation, the colony number of revertants was evaluated with a colony counter. The term S9 denotes a supernatant that consists of homogenized rat liver subsequent to centrifugation at 9,000 rpm. Various drug-metabolizing enzymes were collected in this fraction. Since the enzyme

groups needed a co-enzyme, the rat liver S9 was added to the tested aliquot (denoted S9mix); when the S9 was added the term +S9mix is used, and for the non-added one it is referred to as -S9mix. Generally, a compound having a nitro group or a compound (e.g., an epoxide) attached directly to DNA yields a positive response without the S9mix, whereas a compound having an amino or an aromatic group is usually activated by addition of the S9mix.

Gaussian calculations

Frontier electron densities and partial charges for each atom in Flubendiamide were calculated and optimized using the Gaussian 09 software (hf/3-31 g* configuration) [21]. The frontier electron densities on each atom infers the easiness with which $\bullet\text{OH}$ radicals can attack the positions bearing the highest electron density in the molecule. The calculated charges on each atom are helpful in inferring which atom would most likely adsorb onto the surface of the metal oxide.

RESULTS AND DISCUSSION

Disappearance of aromatic function

The photoassisted degradation of Flubendiamide by Ga_2O_3 was carried out under air oxygen conditions or else under an inert N_2 atmosphere. Specifically, four protocols were explored to examine the fate of this insecticide: (1) under an inert N_2 atmosphere without the metal oxide Ga_2O_3 , (2) under an air oxygen atmosphere without the Ga_2O_3 , (3) under an inert N_2 atmosphere in the presence of Ga_2O_3 , and (4) under an air-oxygen atmosphere in the presence of Ga_2O_3 . In (1) and (4), inert nitrogen gas was used only to remove oxygen in solution. And N_2 gas doesn't influence photochemical and photocatalytic reactions. The time course of the degradation by reactive oxygen species (ROS) and/or by valence band holes and conduction band electrons was examined under UVC irradiation in both aqueous media and methanolic aqueous media. The following processes are considered as possible consequences in applying the four protocols to degrade the insecticide [22–32].

In essence, the insecticide can be broken down with protocol (1) either through heterolytic or homolytic fission and/or by photoionization under suitable conditions. With protocol (2), in addition to the foregoing, the reactive oxygen species $^1\text{O}_2$ may be formed so that the substrate may undergo oxidative decomposition with this ROS. With protocol (3), $\text{Ga}_2\text{O}_3/\text{N}_2$, UVC irradiation of the metal oxide generates conduction band electrons and valence band holes, which can lead to reductive and oxidative degradation of the insecticide. Also,

to the extent that in aqueous media the valence band holes can generate $\bullet\text{OH}$ radicals, they can oxidize the substrate through hydroxylation of the aromatic functions present in the Flubendiamide structure. In addition to the above, protocol (4) also leads to formation of superoxide radical anions ($\text{O}_2\bullet^-$) and in acid media to the hydroperoxy radical $\bullet\text{OOH}$ that can oxidize the insecticide.

Time-dependent absorption UV spectra of Flubendiamide subjected to UVC irradiation following the four protocols are displayed in Fig. 3. The maximal peak of Flubendiamide in methanol solution occurs at about 231 nm, but because the Flubendiamide substrate is nearly insoluble in water, no spectral features are observed initially in aqueous media alone. However, two absorption bands {at least for protocols (1)–(3)} begin to appear at ca. 200 and 230 nm with increasing UVC irradiation time. We attribute this to increased solubilization of the water-insoluble substrate as a result of hydroxylation of the aromatic functions on the insecticide structure by photogenerated $\bullet\text{OH}$ radicals. In the case of protocol (4), only a single absorption band appears with maxima around 200 nm (Note that absorption bands of aromatic rings are usually observed in the 200–250 nm range).

Figure 4 displays the absorbance intensities at 231 nm against irradiation time for spectra recorded when the substrate was subjected to all four protocols. The absorbance increased linearly with increasing irradiation time under inert N_2 conditions, irrespective of the absence or presence of the photoactive metal oxide. After 72 hrs, the absorbance for the catalyst-free/ N_2 system (0.58) was greater than in the presence of the $\text{Ga}_2\text{O}_3/\text{N}_2$ system (0.47); likewise, for the catalyst-free/air O_2 (0.22) relative to the $\text{Ga}_2\text{O}_3/\text{air } \text{O}_2$ system (0.03).

Interestingly, under air oxygen atmospheric conditions and with and without the metal-oxide presence, the absorbance increased at first and then decreased upon further irradiation. In addition, the maximal absorbance for the catalyst-free/air O_2 system was significantly greater than for the $\text{Ga}_2\text{O}_3/\text{air } \text{O}_2$ system at all irradiation times. We infer that subsequent to solubilization of the substrate, opening of the aromatic rings occurs causing loss of the aromatic character of the insecticide. The lower band intensity at 231 nm for the $\text{Ga}_2\text{O}_3/\text{air } \text{O}_2$ protocol (4) vis-à-vis protocol (2) is indicative of a faster solubilization/degradation process owing to the presence of several ROS species that can impact the degradation process.

To assess that degradation does indeed occur under conditions wherein the insecticide is fully solubilized prior to UVC irradiation, experiments were also carried out in 50 vol.% methanolic aqueous media. The time-dependent absorption

Table 1 Photocatalytic reaction.

N₂ system (1)				
Flubendiamide	+	$h\nu_{254\text{ nm}}$	heterolysis, homolysis, photoionization	(1)
Air system (2)				
Flubendiamide	+	$h\nu_{254\text{ nm}}$	heterolysis, homolysis, photoionization	(1)
O ₂	+	$h\nu_{254\text{ nm}}$	¹ O ₂	(2)
Flubendiamide	+	¹ O ₂	oxidative intermediates	(3)
Ga₂O₃ /N₂ system (3)				
Flubendiamide	+	$h\nu_{254\text{ nm}}$	heterolysis, homolysis, photoionization	(1)
Ga ₂ O ₃	+	$h\nu_{254\text{ nm}}$	e ⁻ + h ⁺	(2)
Flubendiamide	+	e ⁻	reduced intermediates	(3)
Flubendiamide	+	h ⁺	oxidized intermediates	(4)
H ₂ O	+	h ⁺	OH + H ⁺	(5)
Flubendiamide	+	OH	hydroxylated intermediates	(6)
Ga₂O₃ /air system (4)				
Flubendiamide	+	$h\nu_{254\text{ nm}}$	heterolysis, homolysis, photoionization	(1)
O ₂	+	$h\nu_{254\text{ nm}}$	¹ O ₂	(2)
Flubendiamide	+	¹ O ₂	oxidized intermediates	(3)
Ga ₂ O ₃	+	$h\nu_{254\text{ nm}}$	e ⁻ + h ⁺	(4)
Flubendiamide	+	h ⁺	oxidized intermediates	(5)
O ₂	+	e ⁻	O ₂ ⁻	(6)
Flubendiamide	+	e ⁻	reduced intermediates	(7)
H ₂ O	+	h ⁺	OH + H ⁺	(8)
O ₂ ⁻	+	H ⁺	OOH	(9)
Flubendiamide	+	OH	hydroxylated intermediates	(10)
Flubendiamide	+	OOH	Peroxidized intermediates	(11)

spectra of the insecticide exposed to UVC irradiation for up to 72 hrs are reported in **Fig. 5**.

In methanolic aqueous media, the initially observed 231-nm absorption band decreased with irradiation time on examining the photoassisted degradation of the insecticide under the four protocols (**Fig. 6**). Under air atmospheric conditions, the degradation of the insecticide followed zero order kinetics for the catal.-free/air O₂ and Ga₂O₃/air O₂ {protocols (2) and (4)} with the latter attaining nearly 90% degradation versus ca. 75% for the former after 72 hrs of UVC irradiation. Under inert conditions, however, the extent of degradation was significantly less: about 43% for both the catal.-free/N₂ and Ga₂O₃/N₂ protocols (1) and (3).

Clearly, comparison of protocols (3) and (4) with the catalyst-free protocols (1) and (2) shows that the Ga₂O₃-photoassisted processes were overall faster than for the catalyst-free processes. Furthermore, comparison of the

process occurring under an inert nitrogen atmosphere in the presence and absence of the metal oxide, the Ga₂O₃ system exhibited faster degradation kinetics even though the extent of degradation after 72 hrs of illumination was the same; the latter infers that formation of •OH radicals was ineffective to cause the disappearance of the aromatic functions since methanol is a good scavenger of both valence band holes and •OH radicals. Consequently, the 75% drop in absorbance at 231 nm after 72 hrs of irradiation is likely due to the action of singlet oxygen on the insecticide, with this ROS as the principal oxidizing agent.

Dehalogenation, desulfonation and denitridation of Flubendiamide in aqueous media

The time-dependent chemical yields of fluoride, sulfate, nitrate, iodide, and ammonium ions from the photoassisted degradation of Fluobendiamide are illustrated in **Figs. 7a-7e**

Fig. 3 Time-dependent absorption spectral patterns of Flubendiamide (0.1 mM) in water under air and inert N_2 conditions in the presence and absence of Ga_2O_3 after 0, 1, 2, 3, 6, 24, 48 and 72 hrs of UVC illumination.

Fig. 4 Variations in absorbance intensity against irradiation time for Flubendiamide (0.1 mM) in water under air or N_2 conditions in the presence or absence of Ga_2O_3 after UVC illumination for 0, 6, 24, 48 and 72 hrs.

representing the four protocols utilized for examining the process in aqueous media. The relevant percent yields after 72 hrs of UVC irradiation are summarized in **Table 2**. Yield of ion was calculated by following equation.

(ion yield by HPLC analysis)/ (maximum theoretical ion yield) $\times 100$

Fluoride ions were generated in the absence of Ga_2O_3 even under inert nitrogen conditions, inferring that cleavage

Fig. 5 Time-dependent spectral absorbance patterns of Flubendiamide (0.05 mM) in 50 vol.% aqueous methanol solution under air or N_2 atmosphere in the presence or absence of Ga_2O_3 after UVC illumination for 0, 6, 24 and 72 hrs.

of the C–F bond was likely caused photolytically by direct UVC irradiation; the final defluorination yield was ca. 15%. The yield of fluoride ions in the catalyst-free/air system was nearly twofold greater (ca. 28%) than for the catalyst-free/ N_2 system at the end of 72 hrs of UVC irradiation. We suppose that both solubilization and benzene-ring opening were caused concomitantly by singlet oxygen species. In the presence of the metal oxide, the yield of fluoride was 13% in the Ga_2O_3/N_2 system, almost the same as for the catalyst-free/ N_2 system. It would appear, therefore, that defluorination by $\bullet OH$ radicals, valence band holes and by conduction band electrons was ineffective. Typically, when applying protocol (3) defluorination of a water-soluble fluorinated substance is effective even under an inert nitrogen atmosphere. However, since the insecticide is insoluble in water, contact of this substrate with the surface of the hydrophilic metal oxide may be such that solubilization by $\bullet OH$ radicals formed under inert conditions was insufficient. In the case of the Ga_2O_3 /air system, the defluorination yield was 37%, nearly threefold

greater than for the Ga_2O_3/N_2 system. Under air oxygen, formation of superoxide radical anions via electron scavenging by molecular oxygen and ultimately forming the reactive oxygen species $\bullet OOH$ likely enhanced both solubilization and defluorination. Since dissolved oxygen consumed the excited electrons, the Ga_2O_3 /air system did not exhibit the significant defluorination expected relative to the other three systems. Nonetheless, defluorination yield increased in the order $N_2 \sim Ga_2O_3/N_2 < air < Ga_2O_3/air$.

Relative to the quantity of sulfate ions produced in the Ga_2O_3 -photoassisted degradation of Flubendiamide, only small quantities of sulfate ions were produced in the catalyst-free systems, particularly under air-equilibrated conditions, photolytically made possible solely by UVC radiation. Interestingly, the yield of sulfate in the Ga_2O_3/N_2 system was nearly the same as that in the catalyst-free/ N_2 system. Evidently, $\bullet OH$ radicals and the valence band holes were inconsequential in converting the sulfonyl groups into sulfate ions. By contrast, compared with the yields for the

Fig. 6 Time-dependent changes of the 231-nm band during the photodegradation of Flubendiamide (0.05 mM) in 50 vol.% MeOH/water under air or N₂ atmospheres in the presence and absence of Ga₂O₃ after UVC illumination for 0, 6, 24 and 72 hrs.

other three systems after 72 hrs of UVC irradiation (**Table 2**; 9, 14 and 9%, respectively for protocols (1), (2), and (3), the Ga₂O₃/air system showed the highest yield of sulfate ions (ca. 88%). We deduce that the •OOH radicals derived from the superoxide radical anions were mostly responsible in generating sulfate ions. The final yields after 72 hrs increased in the order of N₂ ~ Ga₂O₃/N₂ < air < Ga₂O₃/air. For comparison, in the photodegradation of Fipronil (also included a sulfonyl group) carried out under otherwise identical conditions in our previous study⁸, the sulfate yield for Fipronil in the Ga₂O₃/air system was 93% after only 24 hrs of UVC irradiation, whereas the sulfate ion yield of Flubendiamide is only 57% after 24 hrs. This difference is likely due to the orientation of the sulfonyl group on the metal-oxide surface. The trifluoromethyl moiety in Fipronil adjoined to the sulfur atom was negatively charged and so was easily oriented toward the metal-oxide surface so that the sulfur atom had many opportunities in being attacked by •OOH radicals that led to its facile oxidation. On the other hand, the sulfur atom in Flubendiamide exists as R-SO₂-Me in which the adjacent group is not an electron-withdrawing group.

The maximum yields of iodide produced with irradiation time are illustrated in **Fig. 7d**. The extent of cleavage of the C–I bond was higher for both protocols involving air oxygen. In any case, the yield of iodide produced during the photoassisted degradation of Flubendiamide after 72 hrs increased in the order: Ga₂O₃/air (0%) < air (10%) < Ga₂O₃/N₂ (22%) < N₂ (39%) – see **Table 2**.

The amide groups in Flubendiamide can be transformed either into ammonium or nitrate ions. No nitrate ions formed for both the catalyst-free systems and for the Ga₂O₃/N₂

system. Clearly, even after 72 hrs of UVC light irradiation, no ROS species was able to produce nitrate ions from the amide groups in this insecticide, and any •OH radicals available were also insufficient to produce a significant enough quantity of nitrate, for which the yield after 72 hrs in the Ga₂O₃/air system was a maximal 14%. On the other hand, as regards to ammonium ion, the yield was about 10% for the catalyst-free/N₂ system. Therefore, the interaction of UVC and H₂O could be the cause of the formation of ammonium ions from the amide bond in this insecticide. The ammonium yield was 48% for the catalyst-free/air system. Since the reaction between singlet oxygen and the amide bond could not make ammonium ions, the oxidative decomposition was important in generating ammonium ions. In the Ga₂O₃/N₂ system, the ammonium ion yield was 26% after 72 hrs with UVC irradiation. The •OH radicals, the valence band holes and the conduction band electrons were not more effective in generating ammonium ions than singlet oxygen in solubilizing Flubendiamide. The yield of NH₄⁺ after 72 hrs was 86% for the Ga₂O₃/air system.

Gaussian-09 calculations of partial charges and electron densities

Partial charges and frontier electron densities of each atom in the Flubendiamide structure were calculated using the Gaussian 09 software (hf/3-31 g* configuration, optimization in aqueous media). Results are listed in **Table 3** and **Table 4**. The numbering scheme of each atomic fragment is displayed in **Fig. 8**. The speculative optimal steric illustration of electron densities is depicted in **Fig. 9**. Partial charges are typically taken to infer which atom(s) are likely

Fig. 7 Time dependent formation of (a) fluoride, (b) sulfate, (c) nitrate, (d) iodide and (e) ammonium ions in the photodegradation of Flubendiamide (0.1 mM, 100 ml) in aqueous media in the presence of Ga_2O_3 (50 mg) under a nitrogen or air atmosphere after UVC irradiation from 0 to 72 hrs.

Table 2 Percent yields of fluoride, sulfate, iodide, nitrate and ammonium ions during the photoassisted degradation of Flubendiamide in aqueous media subjected to the four protocols after 72 hrs of UVC irradiation.

Protocol	Systems	% F^-	% SO_4^{2-}	% I^-	% NO_3^-	% NH_4^+
(1)	N_2	15	9	39	0	11
(2)	Air O_2	28	14	10	0.6	49
(3)	$\text{Ga}_2\text{O}_3/\text{N}_2$	12	9	22	0	26
(4)	$\text{Ga}_2\text{O}_3/\text{air } \text{O}_2$	37	88	0	14	86

to adsorb onto the surface of the Ga_2O_3 catalyst; accordingly, the negatively charged atoms (F, N, and O) are expected to be oriented toward the hydroxylated metal-oxide surface. In particular, the highest negatively charged atoms are the two N atoms of the amide groups (N-24 and N-40) together

with the accompanying oxygens O-27 and O-38, as well as the two oxygens of the sulfonyl group O-55 and O-56. These atoms are expected to interact significantly with the partial positively charged hydrogens of the surface hydroxyl groups.

Those functions or atoms that possess the highest electron

Table 3 Partial charges of atoms in the Flubendiamide structure in aqueous media.

1 C	-0.17936	16 F	-0.37563	31 C	-0.23969	46 H	0.225608
2 C	-0.13695	17 F	-0.37229	32 H	0.299247	47 C	-0.55919
3 C	-0.22893	18 F	-0.37756	33 C	-0.43973	48 H	0.227834
4 C	-0.23342	19 F	-0.37071	34 C	-0.17876	49 H	0.218062
5 C	0.331659	20 C	-0.58638	35 H	0.293466	50 H	0.247074
6 C	-0.07044	21 H	0.237291	36 H	0.298739	51 C	-0.85515
7 H	0.296331	22 H	0.235766	37 C	0.878806	52 H	0.357143
8 H	0.297942	23 H	0.240608	38 O	-0.64677	53 H	0.330782
9 H	0.314352	24 N	-1.03285	39 I	0.317396	54 S	1.694971
10 C	-0.02914	25 H	0.404233	40 N	-0.8718	55 O	-0.75973
11 C	1.260598	26 C	0.92593	41 H	0.38567	56 O	-0.74652
12 C	1.261092	27 O	-0.64706	42 C	0.062914	57 C	-0.98809
13 F	-0.37248	28 C	-0.14805	43 C	-0.58699	58 H	0.304371
14 F	-0.37489	29 C	-0.19419	44 H	0.241315	59 H	0.302065
15 F	-0.37639	30 C	-0.06655	45 H	0.239886	60 H	0.314547

Table 4 Frontier electron densities on all atoms in the Flubendiamide structure in aqueous media.

1 C	6.17935	16 F	9.37562	31 C	6.2397	46 H	0.77439
2 C	6.13695	17 F	9.37228	32 H	0.70076	47 C	6.55919
3 C	6.22892	18 F	9.37757	33 C	6.43972	48 H	0.77217
4 C	6.23341	19 F	9.37072	34 C	6.17878	49 H	0.78194
5 C	5.66834	20 C	6.58639	35 H	0.70653	50 H	0.75293
6 C	6.07043	21 H	0.76271	36 H	0.70126	51 C	6.85515
7 H	0.70367	22 H	0.76424	37 C	5.1212	52 H	0.64286
8 H	0.70206	23 H	0.75939	38 O	8.64678	53 H	0.66922
9 H	0.68565	24 N	8.03285	39 I	52.68258	54 S	14.30503
10 C	6.02913	25 H	0.59577	40 N	7.87181	55 O	8.75972
11 C	4.73941	26 C	5.07408	41 H	0.61433	56 O	8.74652
12 C	4.73891	27 O	8.64707	42 C	5.93708	57 C	6.9881
13 F	9.37248	28 C	6.14803	43 C	6.587	58 H	0.69563
14 F	9.37490	29 C	6.19418	44 H	0.75869	59 H	0.69794
15 F	9.37639	30 C	6.06655	45 H	0.760114	60 H	0.68545

density are the most likely ones to be attacked by reactive oxygen species (ROS) and singlet oxygen. Radical species formed on the surface of the metal oxide catalyst are so short-lived (e.g., in the microsecond region for $\bullet\text{OH}$ radicals in aqueous media) that their interaction with species not on the metal-oxide surface is rather negligible. Accordingly, such short-lived electrophile species as the $\bullet\text{OH}$ or $\bullet\text{OOH}$ radicals together with $^1\text{O}_2$ interact with groups/atoms closest to the solid's surface, especially those displaying highest electron densities. In the catalyst-free/air system, singlet oxygen is the predominant oxidizing agent to cause the oxidation of the insecticide. In the $\text{Ga}_2\text{O}_3/\text{air}$ system, the percent yield of

NH_4^+ ions is greater than that of sulfate ions up to 6 hrs of UVC irradiation.

Mutagenicity ames tests

In any photoassisted process involving environmental pollutants, it is imperative that the resulting intermediates and/or final products be no more toxic or mutagenic than the initial pollutant substrate. Studies on the mutagenic activity of products from photoassisted processes have tended to be rather scarce. Accordingly, it was imperative to carry out the Ames test to verify that the intermediates were neither toxic nor mutagenic. In the present study, the Ames test was used

Fig. 8 Speculated model of Flubendiamide indicating the numbering scheme for the calculated electron densities and partial charges on each atom.

to assess the mutagenic activities of the agrochemical insecticide Flubendiamide using the three strains TA-98, TA-100 and YG-1024 without (-S9 mix) and with the S9 mix (+S9 mix). In particular, the assays for Flubendiamide (0.50 mM) were performed in a mixed solution of acetone (55%) and water (45%). Results from the Ames tests carried out on the intermediate products of the photodegradation of Flubendiamide after 1, 2, 3, 6 and 24 hrs of UVC illumination are reported in **Fig. 10**. The mutagenic activity of intermediates and products that resulted from the photodegradation of the Flubendiamide insecticide was also assayed with TA-98, TA-100 and YG-1024 strains under the conditions of -S9mix and +S9 mix; results are displayed in **Fig. 10**. Although the background level of each assay varied between 27 and 30 revertants, we confirmed that the number of revertant colonies increased linearly with increasing concentration of the positive controls 4-nitroquinoline-N-oxide and benzo[a]pyrene under identical experimental conditions. These findings indicate the validity of the assay system. The validity of the assay system was also confirmed by the dose dependency of the number of revertant colonies obtained with the positive control employed, 4-nitroquinoline-N-oxide. In the other assays, repeated colony selection resulted in reducing the background level with enhanced sensitivity. Since the background of -S9 mix for the TA-100 strain commonly showed a background level of around 104 (**Fig. 10c**), no problems were encountered under these conditions, although the mutagenicity test data were slightly lower. When the TA-98 strain was employed, the background level (+S9 mix) was 30 (**Fig. 10b**). The number of revertant colonies of 40 would then be taken

Fig. 9 Electrostatic potential view of the Flubendiamide molecule.

as being relatively small in this test. However, if the numbers were 100 to 200, then mutagenicity would undoubtedly be recognized as there being no mutagenic activity. Mutagenic activities for the TA-98 and TA-100 strains were also assessed for the photodegraded solution of Flubendiamide (0.50 mM) in the presence of β -Ga₂O₃ particles (**Fig. 10**). For each irradiation time of 0, 1, 2, 3, 6 and 24 hrs, four bars are shown to indicate the loading of 0, 0.005, 0.0125, and 0.025 mmol per plate. Experiments were carried out as follows: after incubating the strain solution (100 mL) overnight, it was mixed with a phosphate buffer (500 mL) and various solution loadings (10, 25, and 50 mL). An increase of the sample concentration showed no enhancement of mutagenic activity compared to the background level.

We also discovered that the cell toxicity of the starting reagent for the TA-100 strain was stronger at the higher concentration. The bacterial cell colonies of the TA-98 strain (background level, 27; **Fig. 10a**) increased slightly with increasing irradiation time on the standard base of the initial sample prior to irradiation. No mutagenic activity of the photodegraded Flubendiamide solutions was evidenced, regardless of the 10, 25 and 50 mL loadings. When the TA-100 strain was employed, the background level (+S9 mix) was 100 (**Fig. 10d**). The number of bacterial cell colonies for the initial solution hovered around this value in the case of the 25-mL loading. After various UV illumination times, the number of colonies was relatively low in comparison with the number in the initial solution. The number of colonies tended to increase gradually with increasing irradiation time. However, the illuminated solution still showed a relatively low value. The strain of YG-1024 indicates high sensitivity

Fig. 10 Mutagenic activities of TA-98, TA-100 and TA-1024 strains in the photodegraded solution of Flubendiamide (0.50 mM) in a mixed solution or acetone (55%) and water (45%) by Ga_2O_3 particles. For each irradiation time of 0, 1, 2, 3, 6 and 24 hrs, four bars are shown to indicate the loading of 0, 0.005, 0.0125 and 0.025 μmol per plate. The dotted line means the average level of each background.

for the mutagenicity of a substance containing amino moiety. The results for the YG-1024 (+S9 mix) were also negative (**Fig. 10e** and **Fig. 10f**). Consequently, we deduce that there was no mutagenic activity of the intermediates and products from the photodegradation of Flubendiamide, even after relatively long UVC illumination times.

CONCLUSION

Non-degradable Flubendiamide, a widely-employed agrochemical can be easily degraded in the presence of the metal oxide Ga_2O_3 exposed to UVC irradiation. For comparison, the degradation of Flubendiamide was also carried in an air (oxygen) atmosphere and nitrogen gas atmosphere in

the presence and absence of Ga_2O_3 . The percent yields of formation of products by Ga_2O_3 in air increased in the order: I^- (0%) < NO_3^- (14%) < F^- (37%) < NH_4^+ (86%) ~ SO_4^{2-} (88%). Deiodination with the $\text{G}_2\text{O}_3/\text{N}_2$ system (22.0%) was more effective than with $\text{G}_2\text{O}_3/\text{Air}$ (0%). The ring-opening reaction of the two aromatic groups proceeded fairly rapidly; hydroxylated aromatic products were generated in the $\text{G}_2\text{O}_3/\text{N}_2$ system. Since Flubendiamide is insoluble in aqueous media, its adsorption on the surface of Ga_2O_3 was facilitated in aqueous methanol (50%) media in which the disappearance of the aromatic functions was enhanced. Adsorption behaviors of the insecticide were evaluated by partial charge of Gaussian calculation as well as the attack position of reactive oxygen species (e.g., $\bullet\text{OH}$ radicals and singlet oxygen) were

inferred. The photodegraded products under UVC irradiation displayed no mutagenic activity.

ACKNOWLEDGMENTS

The authors appreciate the financial support by the M.Sc. collaborators H. Kubota and M. Murata to H.H., who also wishes to thank Dr. T. Oyama (Japan) and Prof. J. Zhao (CAS, China) for their kind encouragements. N.S. is grateful to Prof. Albini of the University of Pavia for his continued hospitality in his PhotoGreen Laboratory.

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