

Photodegradation of Bentazon, Clopyralid, and Triclopyr on Model Leaves: Importance of a Systematic Evaluation of Pesticide Photostability on Crops

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Photolyses of three herbicides, bentazon, clopyralid, and triclopyr, were studied on plant leaves after crop treatment. The experiments were carried out on cuticular wax films, which are good models for leaf surfaces. The pure compounds and their commercial formulations were investigated under simulated solar light. At the recommended agricultural application rates, the three formulated herbicides photolyzed more rapidly on films than on soil or in water. Their photolysis is likely to be an important dissipation path from crops after treatment. The effects induced by the adjuvants in formulations were varied. Adjuvants slowed the photodegradation of bentazon slightly. In Garlon, in which triclopyr and clopyralid are combined, the adjuvants did not affect the photolysis of clopyralid even though they accelerated the rate of photolysis of triclopyr by a factor of 7. The kinetics were also affected by the application rates. This work also underscores the importance of assessing the photoreactivity of active ingredients in conditions similar to those of their application.

KEYWORDS: Bentazon; clopyralid; triclopyr; photolysis; cuticular wax; adjuvants; pesticides

INTRODUCTION

Photolysis is an important degradation process influencing the fate of pesticides in the environment. The abundant literature on pesticide photodegradation reports various reactions pathways (1). The mechanisms can differ according to the nature of the compound, the environmental segment studied (soil, water, plant, vegetation), and the experimental conditions (pH, incident photon flux) (2). However, there is relatively little information on the photochemical decomposition of the active ingredient (AI) once it is deposited on the leaf surface. Most pesticides are sprayed onto cultures. Once the droplets are dried, the AI remains sorbed on the leaf surface, where it is subjected to different environmental variables. Information about the photodegradation on leaves under various environmental conditions is essential to estimating the importance of this dissipation path in the field. The photolability of pesticides on crops has some important consequences. First, photolability is sometimes counterbalanced with an increase in application frequencies or with higher application rates (3). Second, the photoproducts can accumulate on the crops, making the evaluation of their potential side effects imperative. In the present climate of reduction in pesticide use and Good Plant Protection Practice, a systematic evaluation of the photostability of ingredient on crops is warranted.

Pesticide photolysis on vegetation occurs mainly on the leaf surface (4–7). Once the compound is inside the leaf, photochemical reactions are slowed due to light attenuation and plant metabolism. Systems such as isolated cuticles or thin cuticular wax films are often used to model the leaf surfaces (5, 7–11). In the field, agrochemicals are used as formulated. Adjuvants are employed to improve the performance of the active ingredients (12). They enhance herbicidal activity and characteristics of the application (better distribution, drift reduction) but must be used with caution to avoid volatility or shelf-life alteration (13). Very few studies have considered the effect of additives on the transformation rate of the AI on leaves. Nevertheless, it has been shown that the herbicide formulation could significantly promote photoreactions (10, 14, 15).

In the present study, three herbicides were selected due to their widespread application in agriculture for broadleaf weed control (figure 1). Bentazon is a member of the thiadiazine group, acting as a photosynthetic electron transfer inhibitor (16). Triclopyr and clopyralid are from the chemical class of pyridine; they affect both plant cell respiration and growth (17–19). Triclopyr and clopyralid are sometimes used in combination, as in the case of the commercial formulation Garlon.

The three molecules show distinct spectral absorption properties in water (Figure 1). They all absorb in the sunlight spectral region and are all likely to be phototransformed under outdoor conditions. However, their spectra overlap with sunlight very differently. Bentazon has the broadest absorption spectrum, up to 375 nm, whereas clopyralid absorbs only slightly above 290

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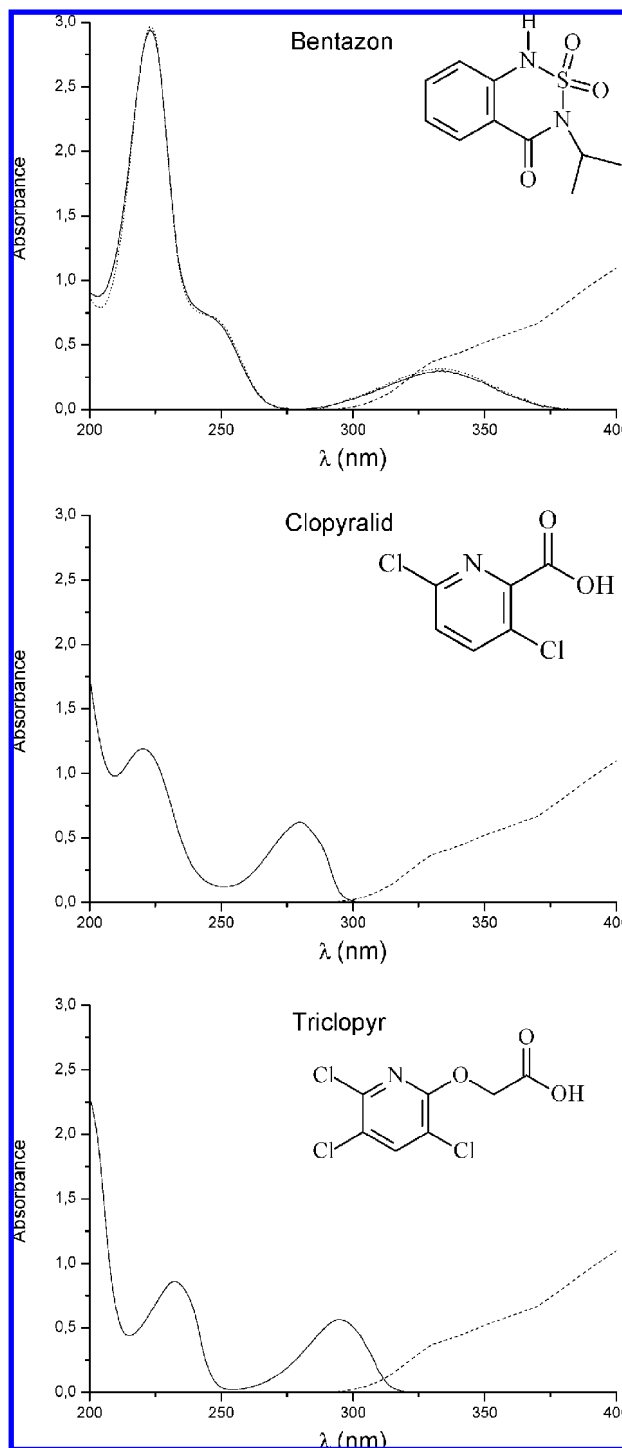


Figure 1. Absorption spectra at pH 6.5 of bentazon (—, pure; ···, formulated), clopyralid, and triclopyr (10^{-4} M). The summer incident solar light on Earth is represented in dashed lines.

nm. Photochemical studies have already been undertaken (in water or on soil) for each chemical, but their photolysis on vegetation has never been considered. The aim of the present work is to characterize the photoreactivity of the three herbicides on a commercial cuticular wax (carnauba gray wax). AIs were tested both as pure compounds and in their commercial formulations (to be representative of field conditions). A series of experiments was conducted to determine and quantify the influence of adjuvants and application rates on the rate of photolysis.

Table 1. Physicochemical Properties of Bentazon, Clopyralid, and Triclopyr^a

herbicide	mol wt	solubility in water (mg/L)	vapor pressure (mPa)	pK _a	agricultural rate (g/ha)
bentazon	240.28	570	0.17	3.3	1200 (2.5 L/ha) ^b
clopyralid	192.00	7800	1.33	2.3	60 (1 L/ha) ^c
triclopyr	256.48	408	0.2	3.97	240 (1 L/ha) ^c

^a Values measured between 20 and 25 °C. ^b The recommended rate for use of Basamais on maize. ^c The recommended rate for use of Garlon.

MATERIALS AND METHODS

Chemicals and Reagents. Bentazon [3-isopropyl-(1*H*)-2,1,3-benzothiadiazin-4(3*H*)-one-2,2-dioxide], clopyralid (3,6-dichloro-2-pyridinecarboxylic acid), and triclopyr (3,5,6-trichloro-2-pyridyloxyacetic acid) used in this study were high-purity compounds (>99%) purchased from Riedel-de Haën (Saint-Quentin Fallavier, France). The physicochemical properties of the herbicides are summarized in **Table 1**, and their structural formulas are given in **Figure 1**. Commercial formulations were purchased in a regular agricultural shop. Basamais (480 g/L) was the bentazon commercial formulation chosen here. The formulation named Garlon combines both clopyralid and triclopyr (60 and 240 g/L, respectively). Solutions of the pure and formulated pesticides were prepared by accurately weighing and dissolving the pesticides in deionized water purified by a Millipore Milli-Q device. All solutions were stored in the dark at 4 °C. All solvents obtained from Merck (Fontenay-sous-bois, France) were of HPLC grade. Water and acetonitrile (of LC-MS grade) for HPLC-MS analysis were obtained from J. T. Baker Laboratories (Paris, France). Formic acid (of LC-MS grade) was purchased from Fluka (Saint-Quentin Fallavier, France).

Experimental Procedures. Irradiation of herbicides was carried out on thin cuticular wax films that mimic the leaf surface, as described by ter Halle et al. (10). One gram of carnauba wax was deposited in a dish (40 mm internal diameter, 25 mm high) and placed in an oven at 100 °C for 5 min to uniformly distribute the melting wax. Herbicide solutions (3 mL) were added on top of the wax film, and water was evaporated under a fan system at room temperature, in the dark overnight. Experiments were conducted with both analytical grade and commercially formulated compounds at the recommended field rate, resulting in surface concentrations of herbicides that were comparable to their concentrations on crop after spraying. The aqueous concentration of bentazon was 2.1×10^{-4} M, with a resulting surface concentration after water evaporation from wax film of 1.2×10^{-5} g/cm² (equivalent to 1200 g/ha). The aqueous concentration of clopyralid was 1.3×10^{-5} M, with a resulting surface concentration after water evaporation of 6×10^{-7} g/cm² (60 g/ha). The aqueous concentration of triclopyr was 3.9×10^{-5} M with a resulting surface concentration after water evaporation of 2.4×10^{-5} g/cm² (or 240 g/ha). Irradiations were carried out using a Suntest CPS photosimulator from Atlas equipped with a xenon arc lamp and a special glass filter that restricted the transmission of wavelengths below 290 nm. Irradiance was set at 550 W/m², whereas the emitted wavelengths ranged from 290 to 800 nm. This satisfactorily simulates the sunlight irradiance in western Europe in June. The dishes were placed in the photoreactor and covered by a quartz plate to avoid pesticide sublimation. The irradiation times were 4, 8, 16, 24, and 48 h. The temperature within the reactor was kept at 35 °C by a flow of cold water. After each exposure, the films were rinsed with 3 mL of buffered water (pH 6.5) and analyzed by HPLC-DAD. Two samples were prepared for each irradiation time, and HPLC-DAD analysis was made in triplicates. Samples were stored at 4 °C in the dark prior to analysis. Results are reported in mean values, whereas error bars represent the standard deviation. We have verified immediately after water evaporation that the rinsing procedure enables recovery of $95 \pm 5\%$ of the initially deposited ingredient. Dark control experiments were carried out in parallel at room temperature. The lack of significant losses excludes thermal degradation, volatilization, or wax penetration as alternative dissipation paths in the time scale of the experiment.

The three herbicides tested (pure and formulated) all followed pseudo-first-order kinetics upon irradiation with correlation values r^2 of >0.96. To estimate the efficiency of the rinsing procedure,

Table 2. Rate of Photolysis and Half-Lives on Wax Films and Comparison with Literature Data Obtained in Soils and Water^a

herbicide	dose applied	cuticular wax films		$t_{1/2}$	
		k (s ⁻¹)	$t_{1/2}$ (h)	water	soils
bentazon	RAR	P: ND F: $6.3 \times 10^{-6} \pm 6\%$	~ 20 30 ± 2	65–96 h (16)	>940 h (16)
	RAR $\times 2$	P: F: $1.47 \times 10^{-5} \pm 5\%$	13 ± 1		
clopyralid	RAR	P: $7.5 \times 10^{-6} \pm 14\%$ F: $6.4 \times 10^{-6} \pm 14\%$	26 ± 4 30 ± 4	261 days (19)	no degradation (19)
	RAR $\times 5$	P: F: $9.2 \times 10^{-6} \pm 27\%$	21 ± 5.7		
triclopyr	RAR	P: $2.6 \times 10^{-6} \pm 16\%$ F: $1.8 \times 10^{-5} \pm 11\%$	75 ± 12 11 ± 1	12–31.2 h (20)	minor degradation (19)
	RAR $\times 5$	P: F: $1.5 \times 10^{-5} \pm 11\%$	13 ± 1		

^a P, pure; F, formulated.

immediately after evaporation, wax films were rinsed with buffered water. Rate constants and half-lives are expressed with errors representing the 95% confidence level. Comparison between the two rates was established using a statistical hypothesis test and a critical region of 5%. In addition, the p value was reported if the rates were stated to be different by the test.

HPLC-DAD Analysis. Changes in the concentration of bentazon, triclopyr, and clopyralid were determined using a HPLC-DAD system under the following conditions. A 25 μ L aliquot was injected in a Agilent Zorbax SB-CN column of 250 mm length and 4.6 mm i.d.; flow rate, 1 mL/min; eluent system, 60:40 water/acetonitrile mixture. The detection wavelength was set to 310 nm for bentazone, 293 nm for triclopyr, and 280 nm for clopyralid. Differences between initial concentration (C_0) and the concentration at the time of analysis (C) were assumed to be the amounts of degradation observed in the kinetic experiments.

Photoproduct Identification. Due to the complexity of the formulation mixture, analytical studies were performed on only the pure molecule. The concentration of the solutions of clopyralid and triclopyr deposited was higher than that used for the kinetic study and was set to 10^{-4} M for better signals. The solution of bentazon used for the kinetic study and the corresponding agricultural application rate was concentrated enough for the HPLC-MS analysis. An LC/QTOF equipped with an orthogonal geometry Z-spray ion source was used (Waters/Micromass, Manchester, U.K.). A photodiode array detector Waters Alliance 2695 system was used for UV detection. A volume of 25.0 μ L was injected on a reversed-phase column (X terra, Waters, C₁₈, 3.5 μ m, 100 mm \times 2.1 mm). A flow rate of 0.3 mL/min was set with a mobile phase composed of acetonitrile (solvent A) and acidified water (solvent B, formic acid 0.1% v/v; pH 2.6) for separation. The gradient was 5% A between 0 and 5 min, 5–95% A (linear) between 5 and 15 min, and 95% A between 15 and 25 min. For clopyralid and triclopyr no photoproducts were detected, for bentazon the photoproducts were well separated under these conditions. The desolvation chamber and ion source block temperatures were set at 350 and 100 $^{\circ}$ C, respectively. The source temperature as well as the sample cone position allowed the formation of a stable spray and minimized the formation of droplets and water clusters. Gaseous N₂ was used as the nebulizer gas (50 L/h) and the desolvation gas (500 L/h). The optimum voltages found for the probe and ion source components (to produce maximum intensity) were 2.1 kV for the stainless steel capillary, 35 V for the sample cone, and 2 V for the extractor cone. In the negative mode, voltages were switched. The presence of sulfur atoms was confirmed by comparing the measured and simulated isotopic ratios. Scanning was performed from m/z 100 to 1000. Tandem mass spectrometric (MS/MS) experiments were conducted in a collision cell with an argon pressure of 1 bar. A collision energy gradient (15–35 eV) was used for preliminary fingerprints, and specific energies of 15–45 eV were used to unambiguously assign the MS/MS fragments. Scanning was performed from m/z 50 to 300 in the “high-resolution” mode.

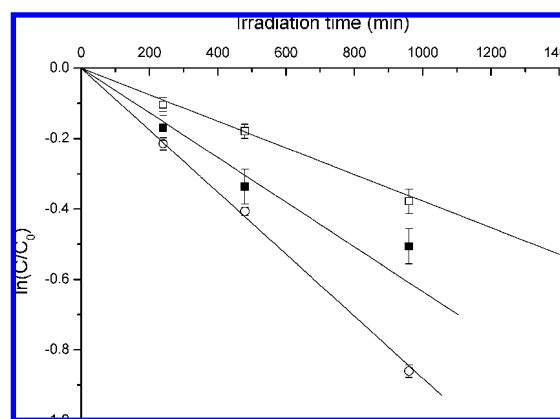


Figure 2. Photolysis on wax film at an intensity of 500 W/m²: (■) pure bentazon at recommended agricultural application rate⁻²; (□) formulated bentazon at the same concentration; (○) formulated bentazon at twice the recommended agricultural application rate.

RESULTS AND DISCUSSION

The herbicide surface concentration at the wax films after water evaporation was close to that encountered on crops after treatment. We have also applied slightly higher rates (2 or 5 times higher) to estimate the effects of excessive doses on the photochemical dissipation path and to underscore the importance of tailoring experimental conditions to mirror real (field) conditions to validate further discussions on an environmental scale.

Photodegradation of Bentazon. Dark control showed no bentazon decay on the time scale of the experiment, leading to the exclusion of other phenomena such as volatilization, thermal degradation, or penetration into the wax. Pure bentazon underwent fast photolysis on wax films at the recommended agricultural rate (20). Due to important standard deviation of the replicates, the half-life of photolysis was estimated to be around 20 h. The kinetic curve of formulated bentazon photolysis presented a more homogeneous distribution of points, probably due to the presence of adjuvants that enabled a homogeneous spreading of the active ingredient at the film surface. Photolysis of formulated bentazon was retarded (**Figure 2**), with a half-life of photolysis of 30 h 20 min \pm 1 h 50 min. The comparison of absorption spectra between pure and formulated bentazon did not exhibit clear differences (**Figure 1**). Thus, the adjuvants did not limit bentazon photolysis by the sunscreen effect; instead, deactivation of the excited state of bentazon is more likely.

At twice the RAR, there is a marked increase in the photolysis of formulated bentazon by a factor 2.3 (**Figure 2**).

Table 3. Elemental Composition, Retention Time, and Mass Spectra of Bentazon and Four Identified Photoproducts

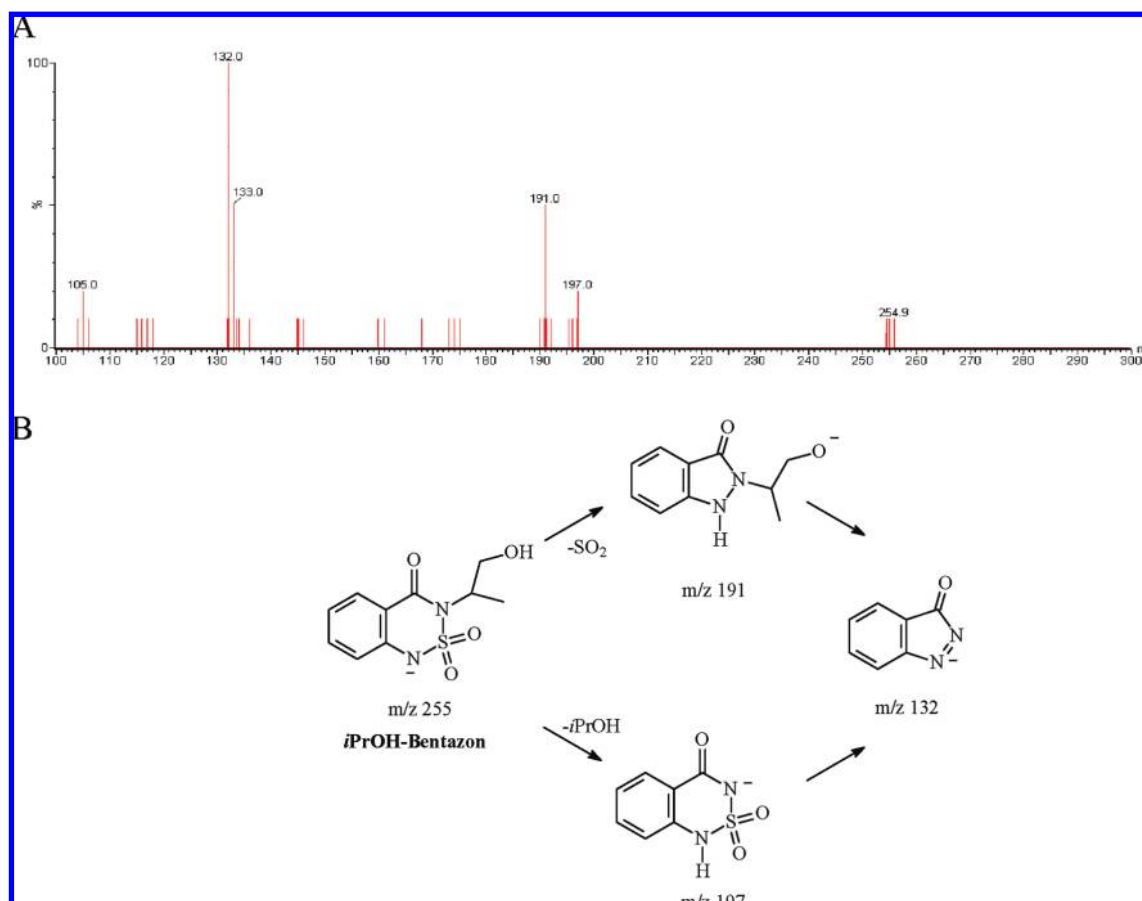
compound	elemental composition	t_R (min)	mass (m/z) ES ⁻	mass (m/z) ES ⁺	MS/MS in ES ⁻
SO ₃ -bentazon	C ₁₀ H ₁₄ N ₂ O ₄ S	9.09	257 [M - H] ⁻		at 257: 257 [M - H] ⁻ ; 177 [M - SO ₃ - H] ⁻
iPrOH-bentazon	C ₁₀ H ₁₂ N ₂ O ₄ S	9.9	277 [M + Na - 2H] ⁻ ; 255 [M - H] ⁻ ; 209; 187		at 255: 255 [M - H] ⁻ ; 197 [M - iPrOH - H] ⁻ ; 191 [M - SO ₂ - H] ⁻ ; 132 [M - iPrOH - SO ₂ - H] ⁻
ring-OH-bentazon	C ₁₀ H ₁₂ N ₂ O ₄ S	11.7	255 [M - H] ⁻ ; 215		at 255: 255 [M - H] ⁻ ; 231; 191 [M - SO ₂ -H] ⁻ ; 148 [M - iPr - SO ₂ - H] ⁻ ; 108
bentazon	C ₁₀ H ₁₂ N ₂ O ₃ S	12.7	239 [M - H] ⁻		at 239: 239 [M - H] ⁻ ; 197 [M - iPr - H] ⁻ ; 175 [M - SO ₂ - H] ⁻ ; 132 [M - iPr - SO ₂ - H] ⁻
dimer	C ₂₀ H ₂₂ N ₄ O ₇ S ₂	14.3	493 [M - H] ⁻	495 [M + H] ⁺ ; 453 [M - iPr + H] ⁻	

Bentazon photolysis in water and on soils was already described. The half-life of photolysis of bentazon ranged between 65 and 96 h (16) in water. In contrast, bentazon was photochemically stable ($t_{1/2} > 940$ h) on soil (16). Bentazon photolysis was much faster on wax films than in water or on soil on the basis of the obtained results.

In the literature, the results from the analyses of photoproducts in water were partly contradictory. Benzamide derivatives resulting from the loss of sulfur dioxide were detected by GC-MS (amino, nitro, and nitroso *N*-isopropyl benzamide derivatives) (21). On the other hand, a sulfamic acid derivative (SO₃-bentazon) and a hydroxylated bentazon have been identified more recently using quadrupole time-of-flight mass spectrometry (22). The sulfonate bentazon (SO₃-bentazon) results from sulfur–nitrogen bond cleavage, although there is no clear evidence of the cleavage position. Because of steric effects, the authors assumed that a cleavage at the N position (labeled 1a in Figure 5) seemed more likely. The fragmentation pattern of

the hydroxylated bentazon shows evidence of hydroxylation of the isopropyl moiety (iPrOH-bentazon in Figure 5) (22).

Four photoproducts were identified by UV detection at 250 nm on wax films, two major products at 9.1 and 14.3 min and two minor products at 9.9 and 11.7 min. The first product (at 9.1 min) was identified as a sulfamic acid derivative (SO₃-bentazon) by ESI-TOF-HPLC in the negative mode. This product responded in only the negative mode; the [M - H]⁻ quasi molecular ion at m/z 257 was identified. This product showed the same fragmentation pattern as described by Peschka et al. (22) (see Table 3, line 1). The second major photoproduct was detected at 250 nm at 14.3 min. Comparison of positive and negative modes in LC-ESI-MS allowed us to identify m/z 493 and 495 as the [M - H]⁻ and [M + H]⁺ quasi molecular ions, respectively. This compound, which had a higher molecular weight than bentazon, was attributed to a dimer. Nilles et al. had also observed the oxidative dimerization of bentazon on soils (21). Two minor photoproducts that responded mostly in

**Figure 3.** (A) MS/MS spectrum of iPrOH-bentazon; (B) proposed fragmentation pathway in MS/MS mode in ES⁻.

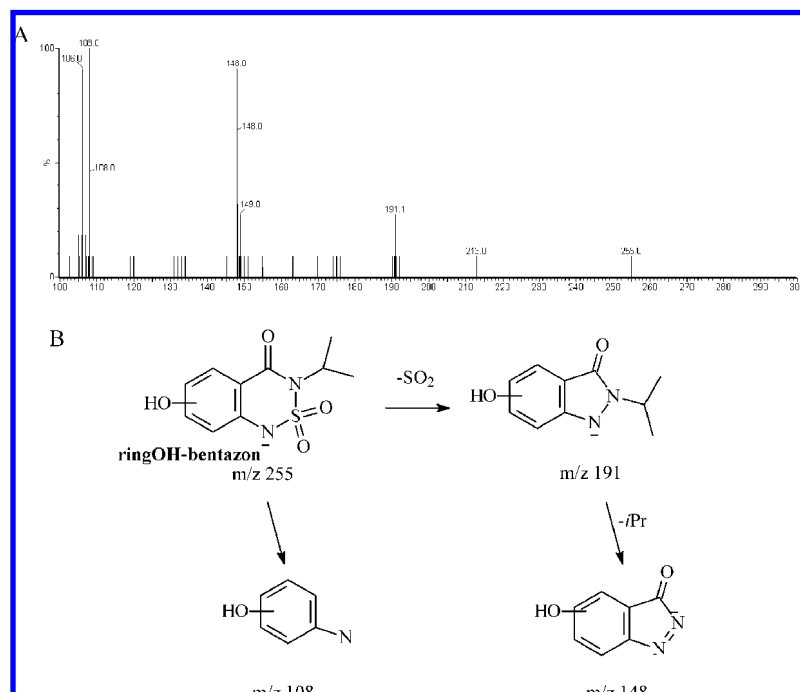


Figure 4. (A) MS/MS spectrum of ring-OH-bentazon; (B) proposed fragmentation pathway in MS/MS mode in ES^- .

negative mode were detected by ESI-TOF-HPLC. The quasi molecular ion $[M - H]^-$ was found at m/z 255 for both molecules, and these two compounds could be isomers of hydroxylated bentazon. At higher collisional energies, the fragmentation pattern of these two photoproducts allowed us to pinpoint the hydroxyl group position. Fragmentation at m/z 255 for the peak at 9.9 min in LC(-)ESI-MS/MS led to the formation of fragments at m/z 197, 191, and 132 (**Figure 3A**). The fragment at m/z 197 resulted from the loss of the hydroxylated isopropyl. Likewise, the fragment at m/z 191 is the result of the loss of sulfur dioxide and the subsequent ring closure. This product is thus attributed to the hydroxylated bentazon in the isopropyl group. The same fragmentation pattern was described in ref 22 and similarly attributed to this isomer.

The second isomer has a fragmentation pattern consisting of fragments at m/z 191, 148, and 108 (**Figure 4A**). The fragment at m/z 191 corresponded to the loss of $[SO_2]$, identical to the other isomer (**Figures 3B** and **4B**). The fragments at m/z 148 and 108 were characteristic of the hydroxylation of the ring moiety. For example, the fragment at m/z 148 corresponded to the subsequent loss of the isopropyl and sulfur dioxide groups. Even though the ring-OH-bentazon and its fragmentation pattern have already been described by HPLC-MS/MS due to its being a well-known metabolite of bentazon (23), this is the first report of it as a photolytic product.

In summary, bentazon sorbed on wax films followed different degradation paths under simulated solar light. We have identified photoproducts resulting from either oxidation or dimerization and oxidation (**Figure 5**). In addition, bentazon also seemed likely to undergo photohydrolysis even if the irradiations were performed after the evaporation of water. It is interesting to note that while some photoproducts are in common with those observed in the previously studied media (water and soils), there exist other photoproducts that are specifically formed on wax films (such as ring-OH-bentazon).

Photodegradation of Clopyralid. The fate of clopyralid in the environment has been documented. In particular, clopyralid is notorious for its ability to persist in dead plants and compost (17). Furthermore, it is described as stable in soil with no

significant photodegradation. A slow photochemical degradation can occur in water with a half-life of 261 days (19). It is thus stated that the photodegradation of clopyralid is not an environmentally significant degradation pathway either in water or on soils.

The photodegradation of clopyralid on wax films was rapid under simulated solar light (**Figure 6**). The half-life of pure clopyralid was 26 h (\pm 4 h). Clopyralid photoreactivity on wax films was comparable to that measured by Abramamovic et al. on glass plates (24). When the commercial formulation (in combination with triclopyr) was tested, there was no marked effect of the adjuvants on the reaction rate ($t_{1/2} = 30 \pm 4$ h). Formulated clopyralid tested at 5 times the recommended rate was transformed slightly more rapidly (p value < 0.003).

Clopyralid offers an illustration of the strong influence of the media on photoreactivity. Finally, because clopyralid is rather photolabile on wax films, photolysis should thus be a major dissipation path of clopyralid from crops after treatment.

Attempts to identify the photoproduct of clopyralid were unsuccessful, as clopyralid probably broke down into volatile low molecular weight molecules.

Photodegradation of Triclopyr. The photolysis of triclopyr was a minor route of dissipation in soil (25), whereas its photolysis decay in water was fast (12–31.2 h) (26, 27). Triclopyr on wax film had a half-life of 75 ± 12 h upon irradiation. Formulated triclopyr (Garlon, in combination with clopyralid) was transformed 7 times more rapidly with a photolysis half-life of 11 ± 1 h. The adjuvants of this commercial formulation were observed to have distinct effects on the two active ingredients used in combination. Even though the photolysis of clopyralid was not altered (above paragraph), the photolysis of triclopyr was strongly accelerated.

No clear effect on the rate of photolysis of formulated triclopyr was observed at 5 times the RAR (**Figure 7**). We could not detect triclopyr photoproduct, as it probably breaks down into volatile low molecular weight molecules.

Role of Adjuvants. Adjuvants may influence phototransformations in several ways. We assume adjuvants to first have a physical effect on the photochemical processes. They allow a

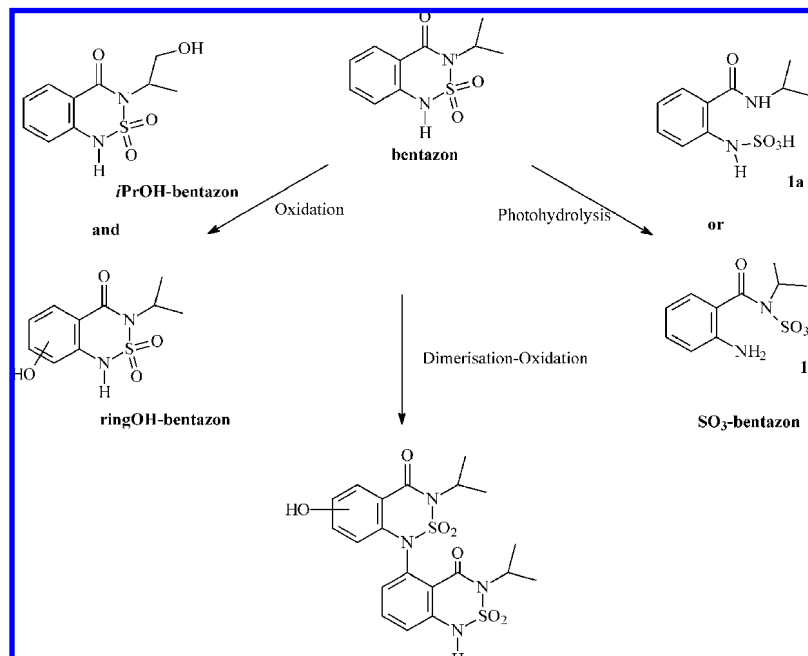


Figure 5. Proposed bentazon photolytic pathway on carnauba wax films.

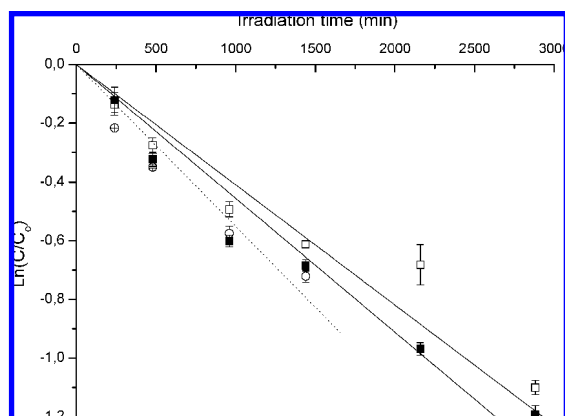


Figure 6. Photolysis of clopyralid on wax films at an intensity of 500 W/m^2 : (■) pure clopyralid applied at the recommended agricultural rate; (□) formulated clopyralid applied at recommended agricultural rate; (○) formulated clopyralid applied at 5 times the recommended agricultural rate.

better spreading of the active ingredient at the surface and consequently facilitate its interaction with light. Adjuvants may also interact chemically to either accelerate or slow the reaction, depending on the structure of the adjuvants and the photochemical reactivity of the active ingredients. For instance, adjuvants may interact with excited states and deactivate them, thereby decreasing the reaction rate. Only a detailed mechanistic study and knowledge of the structure and composition of adjuvants could help to elucidate this chemical interaction.

In this work, we observed the contrasting effects of adjuvants. The slowing of the photolysis of bentazon despite a better spreading of bentazon on the wax film, which in turn favors light absorption, indicates the presence of compounds in the adjuvants, which inhibits the photochemical reaction very efficiently. The additives present in Garlon do not absorb above 290 nm (the difference between the absorption spectra of the commercial formulation and the pure molecules weighed in their concentration in the formulation is <1%). In Garlon the same adjuvants accelerated the rate of photolysis in triclopyr while

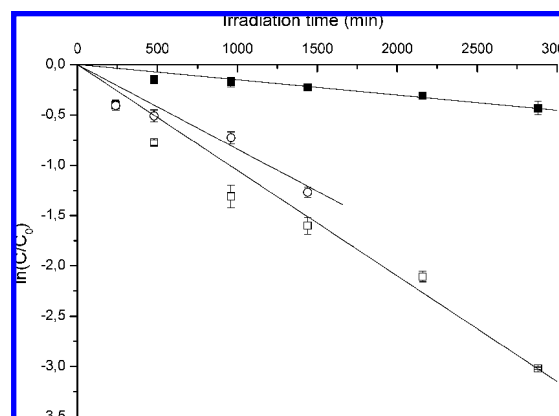


Figure 7. Photolysis of triclopyr on wax film at an intensity of 500 W/m^2 : (■) pure triclopyr applied at recommended agricultural rate; (□) formulated triclopyr at the same concentration; (○) formulated triclopyr at 5 times the recommended agricultural rate.

leaving the photolysis of clopyralid unaffected. The accelerating effect might be due to the better spreading of triclopyr; the overall lack of effect on clopyralid is probably due to the presence of constituents that inhibit the photolysis of clopyralid. These compounds paradoxically do not affect the photolysis of triclopyr, illustrating the complexity inherent in these reactions. A systematic study that includes commercial formulations is thus required to elucidate the photochemical fate of pesticides sprayed on crops.

Bentazon, clopyralid, and triclopyr adsorbed on wax films are sensitive to simulated sunlight. The half-lives of photolysis on cuticular wax are globally lower than those reported in water and soil. The rates of photolysis are affected both by the presence of adjuvants and by the applied rates of the chemicals. No generalizations of the effect of formulation on the rate of photolysis could be made because all three possible cases were observed (no effect, accelerating, and moderating). There is a lack of a general trend concerning the effect of the initially applied dose. Photolysis on crops should thus be systematically considered, and the experimental conditions should therefore

be designed to be as close as possible to field conditions. The results of this investigation clearly demonstrate the importance of photolysis among the dissipation processes from crops after treatments with herbicides.

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Received for review October 28, 2008. Revised manuscript received December 17, 2008. Accepted December 17, 2008. We thank the Région Auvergne for financial support.

JF803282F