Photocatalytic Degradation of Pendimethalin in the Presence of Titanium Dioxide. 1

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Photolysis of an aqueous methanolic solution of pendimethalin (I), carried out under UV light in the presence of TiO$_2$ for 7 h, led to about 50% decomposition of I in contrast with 8% without TiO$_2$. Among the six photoproducts isolated, two have been identified as 1-(1-ethylpropyl)-5,6-dimethyl-7-nitrobenzimidazole (II) and 5,6-dimethyl-7-nitrobenzimidazole (III) on the basis of spectroscopic data. Moreover, GC–MS data gave indications of two minor photoproducts, *N*-propyl-2-nitro-6-amino-3,4-xylidine (VI) and 2,3-dimethyl-5-nitro-6-(hydroxyamino)phenol (VII).

Keywords: *Pendimethalin; photodegradation; TiO$_2$*

Pendimethalin [*N*-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine (I), Figure 2] is widely used as a selective preemergent herbicide that has been demonstrated to undergo much lower conversion (9.9% in 7 days) in soil when exposed to sunlight (Parochetti and Dec, 1978) than other dinitroaniline herbicides previously studied (Leitis and Crosby, 1974). In spite of its photostability, several photoproducts of I have been identified as benzimidazoles, benzimidazole oxides, and species arising from aryl methyl oxidation, nitro group reduction and elimination, and dealkylation of the secondary amine (Dureja and Walia, 1989; Pal *et al.*, 1991). Although I's photolability at sunlight wavelengths ($\lambda \geq$ 290 nm) via indirect photolysis is less than its absorption maximum ($\lambda \geq$ 250 nm) via direct photolysis (Pal *et al.*, 1991), little is known, excepting the work of Moza *et al.* (1992), about its indirect photolysis induced by semiconductors such as titanium dioxide (TiO$_2$), which has been proposed as an important process for the degradation of xenobiotics (Ollis *et al.*, 1991). We extended the study on the photolysis of I to understand its reactivity in the presence of TiO$_2$ as well as to include the identification of additional photoproducts.

EXPERIMENTAL PROCEDURES

Chemicals. Technical grade pendimethalin (purity 90%) was obtained from Cyanamid India Ltd. (Bombay, India) and was purified by repeated crystallization from methanol, mp 56 °C (99.7% HPLC pure). All of the solvents used were of analytical reagent grade and were redistilled before use. Water used was glass-distilled (double).

Apparatus and Chromatography. The purity of I and its kinetic studies were carried out by a Hewlett-Packard (HP) Model 1050 HPLC equipped with a HP 1050 UV detector set at 240 nm and coupled to a HP Model 3392 integrator. The column used was a Nucleosil reversed-phase column (C$_{18}$, 25 × 0.4 cm); mobile phase was MeOH–H$_2$O (4:1 v/v) at a flow rate of 1.0 mL/min; volume injected was 20 μL; and retention time (RT) was 5.24 min.

Mass spectra (electron impact, 70 eV, direct insertion) were recorded on a JEOL JMS-DX 300 mass spectrometer. NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer (100 MHz) using TMS as an internal standard. IR spectra were taken of KBr pellets by using a Perkin-Elmer Model 1310 spectrophotometer. GC–MS spectra were obtained on a Shimadzu QP 2000 instrument (70 eV). The GC conditions were as follows: an ULBON HR-1 equivalent to OV-1, fused silica capillary (0.25 mm × 50 M) with film thickness 0.25 μm; temperature program 150–250 °C for 6 min, 10 °C/min.

TLC was performed on 20 × 20 cm glass plates coated with 0.5 mm silica gel G using iodine as chromogenic reagent. Column chromatography was conducted using glass columns of various sizes packed with a slurry of silica gel (60–120 mesh) in petroleum ether (bp 60–80 °C). All melting points are uncorrected.

Irradiation Experiment. I (250 mg, 500 ppm) was dissolved in 400 mL of methanol by continuous stirring. To it were added 100 mL of distilled water and 50 mg of TiO$_2$ and mixed thoroughly. The above mixture was irradiated in a photoreactor (capacity 500 mL) with a high-pressure mercury lamp (HPK 125W, Philips) jacketed with a water-cooled Pyrex filter to achieve maximum intensity of UV light at $\lambda \geq$ 290 nm under continuous stirring. The temperature of the photolysis solution in the borosilicate glass photoreactor did not exceed 25 °C. The rate of disappearance of I was directly measured at various intervals of time with an analytical HPLC. To obtain enough of the photoproducts for structure elucidation, 2 g of I was irradiated in eight batches (250 mg in 500 mL for 7 h each time).

Isolation of Photoproducts. The irradiated solutions were combined and filtered through Whatman No. 1 filter paper under normal pressure to remove the suspended TiO$_2$. Methanol was removed by a vacuum rotary evaporator (~45 °C). The remaining aqueous fraction was then partitioned successively with (i) *n*-hexane, (ii) *n*-hexane–ethyl acetate (1:1), and (iii) ethyl acetate. Each of these fractions was concentrated with a rotary vacuum evaporator and was subjected to column chromatography over silica gel as summarized in Figure 1.

(i) n-Hexane Fraction: Two crystalline compounds, M$^+$ 218 (mp 125–127 °C, white needle) and M$^+$ 261 (mp 90–92 °C, yellow needle) were isolated along with unreacted I.

(ii) n-Hexane–Ethyl Acetate Fraction: As outlined in Figure 1, this fraction afforded, besides I and M$^+$ 218, four additional compounds having M$^+$ 192 (mp 248–250 °C, light yellow crystal), M$^+$ 428 (red liquid), M$^+$ 429 (mp 256–258 °C, dark red crystal), and M$^+$ 191 (red solid).

(iii) Ethyl Acetate Fraction: The compound with M$^+$ 192 was also isolated from this fraction along with another compound, M$^+$ 198, which was characterized by GC–MS analysis.

Identification of Photoproducts. The *n*-hexane fraction yielded a yellow needle, II, mp 90–92 °C (Figure 2). Upon mass analysis, the compound gave a molecular ion at *m/e* 261 (the major mass fragments are recorded in Table 1). The IR spectrum of II indicated the presence of an aromatic nitro group appearing at 1525 and 1315 cm^{-1} in addition to grouping C=N at 1640 cm^{-1}. The NMR spectrum of II disclosed the presence of an *N*-(1-ethylpropyl) group as in I [δ 0.78 (t, 6H), 1.84 (m, 4H), and 3.8 (m, 1H)] and two aromatic methyl groups
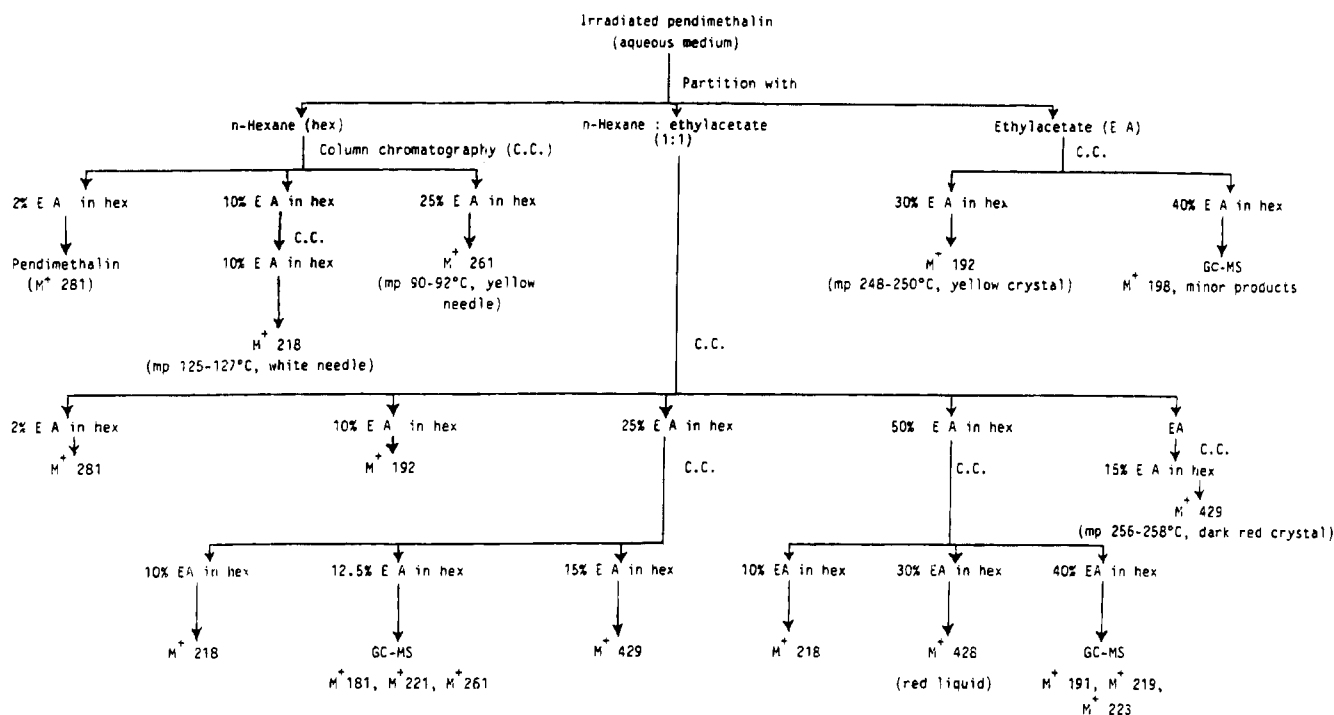
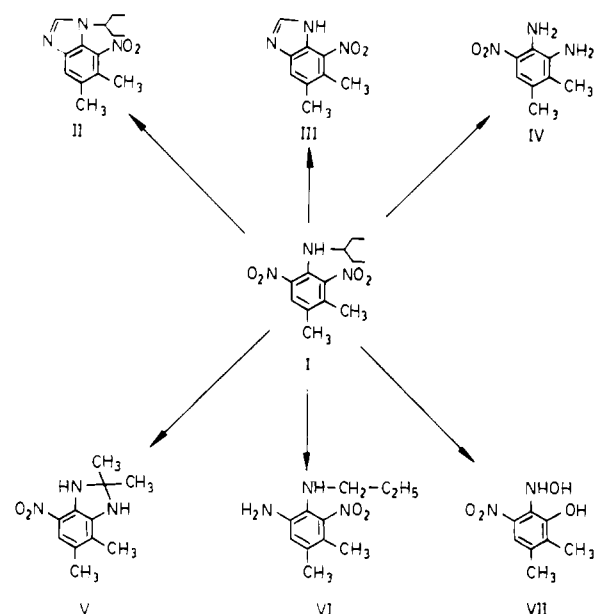**Figure 1.** Extraction scheme for pendimethalin photodegradation products.

Figure 2. Photoproducts isolated following irradiation of pendimethalin (**I**) in methanol–water (4:1 v/v) with TiO_2, $\lambda \geqslant$ 290 nm.

at δ 2.28 (s, 3H) and 2.40 (s, 3H). Besides these, the NMR spectrum also signaled two protons at δ 7.72 (s, 1H) and 7.96 (s, 1H), which could be attributed to benzene and imidazole ring protons, respectively. Moreover, MS and NMR were comparable with those reported for 1-(1-ethylpropyl)-5,6-dimethyl-7-nitrobenzimidazole (Smith et al., 1979).

A red solid, **III** (Figure 2), isolated from the n-hexane–ethyl acetate fraction (Figure 1) showed molecular ion at m/e 191, which was 70 mass units less than **II** corresponding to the loss of an ethylpropyl side chain. The remaining mass fragments were found to be similar to those of **II** (Table 1). Consequently, **III** could be assigned as 5,6-dimethyl-7-nitrobenzimidazole. The identity of this compound was further corroborated by the NMR spectrum [δ 2.71 (s, 3H), 2.52 (s, 3H), 8.10 (s, 1H), and 7.92 (s, 1H)], which was identical with that of **II** except that the resonance for the 1-ethylpropyl group had disappeared.

Table 1. Preparative HPLC Retention Time and Mass Spectral Data of Photoproducts of I

product	retention time, min	mass found	% abundance	structure
II	23.45	261	79.3	M⁺
		232	35.1	M⁺ − C₂H₅
		176	26.1	M⁺ − C₅H₁₁ − CH₃ + 1
		174	100.0	M⁺ − C₅H₁₁ − O
		160	13.7	M⁺ − C₆H₅ − NO
		159	14.3	M⁺ − C₆H₅ − O − CH₃
		146	60.4	M⁺ − C₅H₁₁ − CH₃ − NO + 1
		145	32.8	M⁺ − C₆H₅ − O − 2CH₃ + 1
		144	19.2	M⁺ − C₆H₅ − O − 2CH₃
III	20.85	191	68.3	M⁺
		174	100.0	M⁺ − OH
		146	43.5	M⁺ − NO₂ + 1
		131	6.9	M⁺ − NO₂ − CH₃ + 1
		119	24.7	M⁺ − NO₂ − 26
IV	16.00	181	38.7	M⁺
		123	11.8	M⁺ − NO − CO
		122	100.0	M⁺ − NO − CO − 1
		94	15.6	M⁺ − NO − CO − HCN − 2
		67	29.0	M⁺ − NO − CO − 2HCN − 2
V	17.50	221	72.0	M⁺
		207	38.7	M⁺ − CH₃ + 1
		205	22.6	M⁺ − O
		193	54.3	M⁺ − 2CH₃ + 2
		179	56.9	M⁺ − 2CH₃ − CH₂ + 2
		151	15.0	M⁺ − 2CH₃ − CH₂ − HCN + 2
		123	9.6	M⁺ − 2CH₃ − CH₂ − 2HCN + 2
VI	20.15	223	25.8	M⁺
		205	11.3	M⁺ − OH − 1
		193	2.7	M⁺ − NO
		167	13.9	M⁺ − NO − HCN + 1
		149	100.0	M⁺ − NO₂ − HCNH
		121	6.4	M⁺ − NO₂ − HCNH − C₂H₅ + 1
VII	15.25	198	62.4	M⁺
		183	3.8	M⁺ − CH₃
		169	72.0	M⁺ − 2CH₃ + 1
		167	29.0	M⁺ − CH₃ − O
		151	5.9	M⁺ − CH₃ − NO
		138	50.5	M⁺ − CH₃ − NO₂ + 1
		110	9.6	M⁺ − CH₃ − NO₂ − CO + 1
		96	13.9	M⁺ − 2CH₃ − NO₂ − CO + 1

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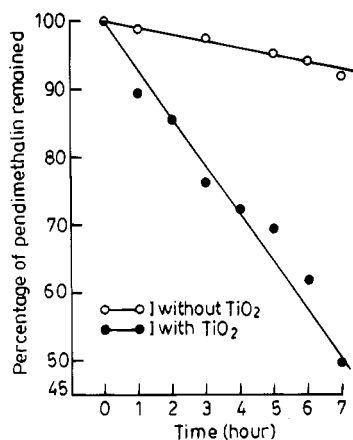

Figure 3. Percent loss of pendimethalin (**I**) during irradiation in methanol—water (4:1 v/v) at $\lambda \geqslant 290$ nm.

The fractions which were subjected to GC—MS analysis gave indications of the compounds having molecular ion peaks at m/e 181, 221, 223, and 198, and on the basis of the MS data (Table 1) the compounds were identified as 2-amino-6-nitro-3,4-xylidine (**IV**), 2,2,4,5-tetramethyl-7-nitrodihydrobenzimidazole (**V**), N-propyl-2-nitro-6-amino-3,4-xylidine (**VI**), and 2,3-dimethyl-5-nitro-6-(hydroxyamino)phenol (**VII**), respectively.

RESULTS AND DISCUSSION

As pendimethalin (**I**) is insoluble in water, the photocatalytic reaction was carried out in methanol—water (4:1 v/v). UV irradiation at $\lambda \geqslant 290$ nm of a 500 ppm (1.8 mM) solution of **I** in the presence of TiO_2 (Figure 3) resulted in rapid decomposition (50% in 7 h), whereas the compound decomposed slowly (8% in 7 h) when irradiated at the same λ without TiO_2. The higher rate of degradation of **I** in the presence of TiO_2 is attributed to the hydroxyl radical, which is generated by absorption of light at $\lambda < 400$ nm by the metal oxide in the presence of water (Oliver and Carey, 1986). Although Moza *et al.* (1992) reported $t_{1/2}$ of 2.88 h for **I** in the presence of TiO_2, the slow conversion in the present investigation might possibly be due to the inner filter effects and geometrical factors of the concentrated solution (Pal *et al.*, 1991). Column chromatographic fractionation of the irradiated solution on silica gel afforded six major compounds in crystalline form (M^+ 261, M^+ 192, M^+ 191, M^+ 429, and M^+ 428). Among the photoproducts isolated, only two (M^+ 261 and M^+ 191) have been identified, while the structure of the other four compounds could not be arrived at from mass and NMR data. Further studies on structure elucidation of these products are underway.

1-(1-Ethylpropyl)-5,6-dimethyl-7-nitrobenzimidazole, **II** (Figure 2), obtained in highest yield, is being reported for the first time as a photoproduct. Although formation of benzimidazole involves initial abstraction of an H atom (Leitis and Crosby, 1974; Plimmer and Klingebiel, 1974), which appears to be less facile from —NCHRR′ compounds than from those with —NCH₂R groups, a different plausible route (Figure 4) of benzimidazole formation has been demonstrated in the present investigation. Irradiation of TiO_2 with light of energy higher than the bandgap results in the creation of holes in the valence band and electrons in the conduction band of TiO_2 (Oliver and Carey, 1986). Both of these reactive species can recombine or the holes can be scavenged by the oxidizable species (such as H_2O, H_2O_2, or organic substrates) and electrons by reducing

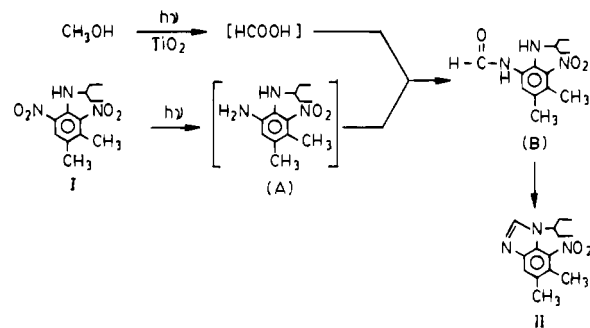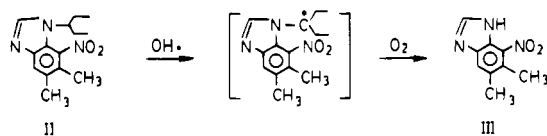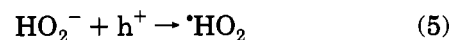**Figure 4.** Plausible pathway for the formation of benzimidazole.

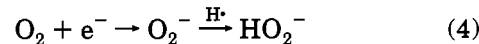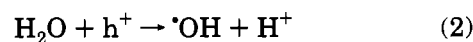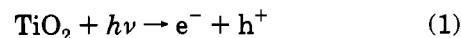
Figure 5. Proposed reaction mechanism of heteroatom dealkylation.

species (such as O_2 or H^+) in the solution yielding OH radicals (eqs 1—5), a strong oxidizing species which

$$TiO_2 + h\nu \rightarrow e^- + h^+ \qquad (1)$$

$$H_2O + h^+ \rightarrow \text{·OH} + H^+ \qquad (2)$$

$$H^+ + e^- \rightarrow H\text{·} \qquad (3)$$

$$O_2 + e^- \rightarrow O_2^- \xrightarrow{H\text{·}} HO_2^- \qquad (4)$$

$$HO_2^- + h^+ \rightarrow \text{·}HO_2 \qquad (5)$$

probably effects oxidation of methanol to formic acid. Oxidation of methanol to formic acid (Nakagawa and Crosby, 1974) has been demonstrated by positive KI + KIO_3 reaction when only aqueous methanol was irradiated in the presence of TiO_2. On the other hand, simple photoreduction of the less hindered nitro group of **I** would give the intermediate **A** (Figure 4), which involves well-known abstraction of H atoms from the methanol—water (Plimmer, 1970). Formylation of **A**, not an uncommon photochemical reaction (Nakagawa and Crosby, 1974), would give the intermediate **B**, which on cyclodehydration (Smith *et al.*, 1979) gave **II**. Interestingly, the work of Smith *et al.* (1979) indicated the formation of **II** from **I** in soil under anaerobic condition, though it left unanswered the question as to whether **II** was formed via biological or abiological pathways. This work demonstrated that **II** could be formed by a purely photochemical mechanism.

5,6-Dimethyl-7-nitrobenzimidazole, **III** (Figure 2), a new photometabolite obtained in poor yield, is expected to be formed from **II** by oxidative N-dealkylation (Figure 5). Hydroxyl radical reactions in water are also known to include hydrogen abstraction (Dorfman and Adams, 1973), and evidence for this process was obtained in the identification of photooxidation product **II**. Heteroatom dealkylation, a minor reaction of **I**, was rationalized by H abstraction in the favored α-position and might involve the detected photoproduct **III**.

Among the minor compounds identified from GC—MS analysis, **IV** and **V** were previously reported as a photoproduct of **I** (Dureja and Walia, 1989), while **VI** and **VII** appear to be new photoproducts derived from

I. VII was formed by elimination of one ethyl group from the ethylpropyl side chain (Halder *et al.*, 1989) and simultaneous reduction of the less hindered nitro group. The formation of VII could be rationalized by oxidative N-dealkylation followed by oxidation of the resulting amino group and displacement of one of the nitro groups by OH (Letzinger *et al.*, 1965).

In the environment, pesticides suffer photodegradation by hydroxyl radicals (Draper and Crosby, 1984) that have been shown to be present in sunlight-irradiated natural waters (Mill *et al.*, 1980). TiO_2 in water with UV light also produces hydroxyl free radicals. Accordingly, the reactivity of I toward hydroxyl radicals generated from TiO_2 and the nature of the products formed would be the same to what may be expected in natural waters. Thus, it seems that a potential exists for the application of photocatalysis in the removal of traces of dinitroaniline herbicides.

ACKNOWLEDGMENT

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