

Photostabilization of Trifluralin Adsorbed on a Clay Matrix

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The photochemical behavior of trifluralin (TF) adsorbed on montmorillonite (Mont), with and without the organic cation thioflavin T (TFT) coadsorbed, is reported. The effect of complexation on the photostability of TF was studied by measuring the reaction rates and photoproduct yields in photolysis experiments and the herbicidal activity of TF in soil samples following exposure to UV light, using oat roots bioassays. In the two complexes (Mont-TF and Mont-TFT-TF) considerable photostabilization of TF was observed, as compared with the herbicide in its free form. The interactions between TF and the clay were studied by Fourier-transform infrared spectroscopy. It is suggested that photostabilization is due to steric hindrance imposed by the clay surface to the cyclization step of the photochemical reaction.

INTRODUCTION

Photodecomposition is characteristic of substituted aromatic nitro groups, such as dinitroaniline herbicides (Probst et al., 1975). The widely used herbicide trifluralin (TF, Figure 1) photodecomposes readily in aqueous solutions (Crosby, 1976; Crosby and Leitis, 1973; Leitis and Crosby, 1974; Probst et al., 1975), on soil (Golab and Occolowitz, 1979) and glass surfaces (Wright and Warren, 1965), and in the vapor phase (Soderquist et al., 1975). These studies identified a variety of photoproducts, many of which are not active as herbicides. The sequence of reactions involving cyclization and oxidative dealkylation steps has been found for several herbicides of this group (Crosby, 1976).

The photolability of the dinitroaniline herbicides in general, and that of TF in particular, is a serious drawback for field applications since both frequency of application and amounts used must be increased to ensure its effectiveness as a herbicide. Moreover, the sensitivity to photodecomposition determines the method of application, the persistence of the applied herbicide, and the spectrum of weeds controlled (Hurle and Walker, 1980).

Our major goal in the current work has been to find procedures for retarding TF photolysis. We have followed an approach for photostabilizing pesticides that involves adsorbing the photolabile pesticide to clays together with specially selected organic chromophores (Margulies et al., 1985). As a result of specific intermolecular interactions on the clay surface, substantial extension of the pesticidal activity can be achieved. The method was proven to be successful with the pyrethroid bioresmethrin (Margulies et al., 1985, 1987) and with an unstable nitromethylene heterocycle insecticide (Margulies et al., 1988; Rozen and Margulies, 1991; Kleier et al., 1985). We have also studied the details of the photolysis reaction and the modes of intermolecular interactions between TF and montmorillonite.

MATERIALS AND METHODS

Analysis. TF and its photoproducts (I and II, Figure 1) were quantitated, following irradiation with UV light, by gas chromatography (GC) with a Varian 3700 instrument using flame ionization detection. A J&W column (30 m, 0.53 mm i.d.) operated at 160 °C with helium carrier gas at 1 mL/min was used for separations. For characterization, the photoproducts I and II were isolated by high-performance liquid chromatography (HPLC) in a LKB 2152 instrument with a Tracor 970A detector and a Hibar Lichrochart 250-4 (25 cm) column, using methanol/water 1:1 as carrier at 1 mL/min.

Compounds were characterized by GC-mass spectrometry (GC-MS) with a Finnegan 4610 mass spectrometer operated in the electron impact (EI) mode (70 eV). The column (J&W SF-54, 30 m, 0.25 mm i.d.) was operated with temperature programming (80-250 °C, 15 °C/min). Under these conditions the retention times (R_t) for TF and its photoproducts, I and II, were 4.6, 5.1, and 4.8 min, respectively. Alternatively, GC-MS was accomplished with a Hewlett-Packard 5985B instrument (EI) equipped with a 10-m HP methyl silicone column operated at 80-250 °C, 20 °C/min. Retention times were as follows: TF, 8.2 min; I, 10.1 min; and II, 8.6 min.

Ultraviolet spectra were recorded in a Uvikon 810 spectrophotometer. Infrared spectra were obtained using KBr pellets with a Nicolet MX-S FTIR spectrophotometer interfaced to an Elite Star 16-bit PC and a Goerz SE 284 digital plotter.

Preparation of Clay Complexes. The clay used was sodium montmorillonite SWy-1 obtained from the Source Clay Repository of the Clay Minerals Society. Trifluralin (analytical) was obtained from Agan Chemical Co. (Ashdod, Israel). Thioflavin T (TFT) was obtained from Fluka. The clay-dye complex (Mont-TFT) was prepared by dropwise addition of aliquots of a 1 mM aqueous solution of TFT to a 0.5% (w/v) aqueous suspension of the clay under continuous stirring. After 30 min of centrifugation (16000g), the precipitate was washed three times with distilled water, freeze-dried, and ground to <50 μ m. Attempts to measure the concentration of the cationic dye in the supernatant by ultraviolet spectroscopy failed because absorption could not be detected. This indicates that the complete adsorption to the clay had occurred.

The montmorillonite-TFT-trifluralin (Mont-TFT-TF) and montmorillonite-trifluralin (Mont-TF) complexes were prepared by adding the appropriate amount of TF in hexane to the powdered clay or Mont-TFT respectively, and evaporating the solvent under gentle reduced pressure. These procedures have been described previously (Margulies et al., 1988).

Irradiation Procedures. Photolyses were carried out within a Rayonet photoreactor (The New England Ultraviolet Co.) equipped with 14 RPR 3500 lamps, having a peak output at 350 nm. The reactor was placed horizontally, and samples in sealed borosilicate tubes (16 \times 100mm) containing TF, Mont-TF, or

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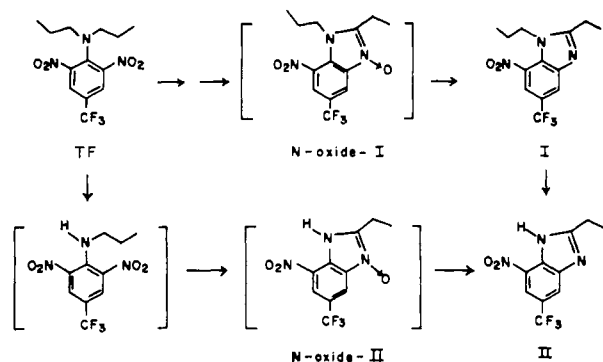


Figure 1. Photodecomposition of trifluralin (TF) adsorbed on montmorillonite to benzimidazoles (I and II) arising from oxidation and subsequent dealkylation/cyclization reactions [after Soderquist et al. (1975)].

Mont-TFT-TF (0.4 mmol of TF/g of clay) were also held in a horizontal position in a merry-go-round arrangement and secured at both ends, rotating to ensure equal exposure of the samples. Photolysis runs were carried out in duplicate or quadruplicate. Dark controls were kept within the reactor, over the irradiation periods (3, 6, and 9 h). No degradation of TF was detected in the dark. To isolate sufficient amounts of products I and II for characterization, TF was irradiated under the same conditions in eight tubes for 24 h, which resulted in approximately 50% conversion.

Photoproducts and remaining TF were extracted from the clay matrix with methylene chloride (2 mL) followed by methanol (2 mL). The extracts were concentrated, filtered and analysed (GC, GC-MS, and HPLC). Methylene chloride recovered trifluralin predominantly and methanol photoproducts I and II.

Bioassay. The herbicidal activities of irradiated and non-irradiated samples of TF, Mont-TF and Mont-TFT-TF were tested in bioassays using oat (*Avena sativa* var. Saya-3) seeds. Plastic petri dishes (5-cm diameter) were filled with 32 g of sandy soil and were sprayed with aqueous suspensions of the herbicide. The clay-containing dispersions were sonicated before spraying, and their concentrations were calculated so that, after spraying, the concentration of TF in the soil would be 0.4 ppm. The dishes were placed on the bottom of the photoreactor (where two lamps were removed) kept in horizontal position, covered with Pyrex glass to filter the 254-nm radiation, and irradiated at 350 nm for periods of 9, 18, and 48 h. Control samples were protected from irradiation by covering the Petri dishes with aluminum foil. Two sets of controls were used: one was kept inside the reactor (where the temperature rises to 57 °C) and the other at room temperature. No significant differences were observed between the two sets of controls, and therefore the possibility of thermal degradation effects could be neglected. After irradiation, the soil was carefully mixed to incorporate the material exposed to the radiation and irrigated to field capacity (10% w/w). Seven oat seeds were seeded in each Petri dish, and the dishes were sealed with parafilm and then incubated at 30 °C. The experiment was carried out in five replicates. Root length was determined 7 days after planting.

RESULTS AND DISCUSSION

Bioassays. The dose-response curves of oats to TF, alone and adsorbed to montmorillonite, are shown in Figure 2. It is evident that adsorption to the clay does not significantly affect the herbicidal activity of TF. Furthermore, the same response was observed in bioassays carried out using a clay-organic sample in which TF was adsorbed to a montmorillonite whose surface area had been completely covered by a large organic cation (methyl green, at loads beyond the cation-exchange capacity: 0.8 mmol/g of clay). In all cases a TF concentration of 0.4 ppm in soil was sufficient for complete inhibition of root development. This concentration was selected for all bioassays using irradiated samples.

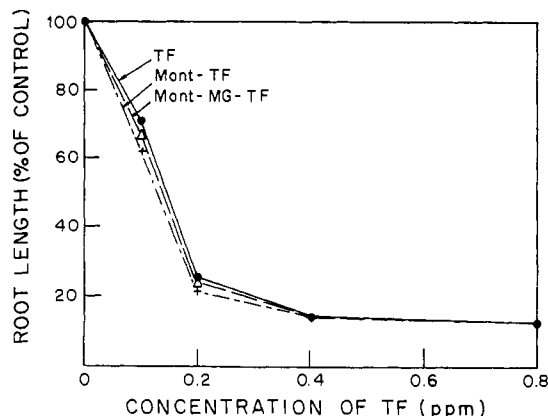


Figure 2. Dose-response of oat roots to trifluralin incorporated in soil. TF, trifluralin alone; Mont-TF, trifluralin adsorbed on montmorillonite (0.4 mmol of TF/g of clay); Mont-TFT-TF, trifluralin coadsorbed with methyl green on montmorillonite (0.4 mmol of TF/g of clay; 0.8 mmol of methyl green/g of clay). Root length of untreated control: 55 ± 7 mm.

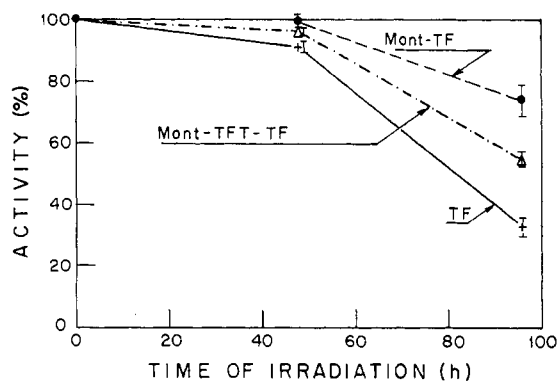


Figure 3. Herbicidal activity of UV-irradiated samples of trifluralin applied on soil as determined by oats bioassay. TF, trifluralin alone; Mont-TF, trifluralin adsorbed on montmorillonite (0.4 mmol of TF/g of clay); Mont-TFT-TF, trifluralin coadsorbed with thioflavin T (TFT) on montmorillonite (0.4 mmol of TF/g of clay; 0.5 mmol of TFT/g of clay). The percent activity was calculated by assigning 100% and 0% to the root lengths of nonirradiated (8 ± 1 mm) and control (without TF) (56 ± 7 mm) samples, respectively.

In Figure 3 results are presented of an experiment aimed to estimate the biological activity of TF incorporated in the soil, following irradiation with UV light (350 nm). The percent activity was calculated by assigning 100% and 0% to the root lengths of nonirradiated and control (without TF) samples, respectively. It can be seen that samples in which TF was adsorbed to montmorillonite retained about 75% of their herbicidal activity after 96 h of irradiation, whereas for TF in its free form the activity dropped to ~30%. Coadsorption of TFT (tested in this study as potential stabilizer of TF) did not improve the photostabilization. On the contrary, in samples containing 0.5 mmol/g TFT coadsorbed, only 55% of the initial activity was preserved. This suggests that the interactions responsible for the photostabilization are those between the molecules of TF and the clay surface rather than those between TF and TFT. The presence of TFT molecules adsorbed probably reduces the clay-TF interactions.

Reaction Rate. Experiments using analytical techniques (irradiation → extraction → chromatography) also demonstrated significant differences between the extent of conversion of trifluralin alone and complexed with montmorillonite. As shown in Figure 4, Mont-TF and Mont-TFT-TF exhibit approximately twice the amount of trifluralin at each of the sampling intervals. Considerable

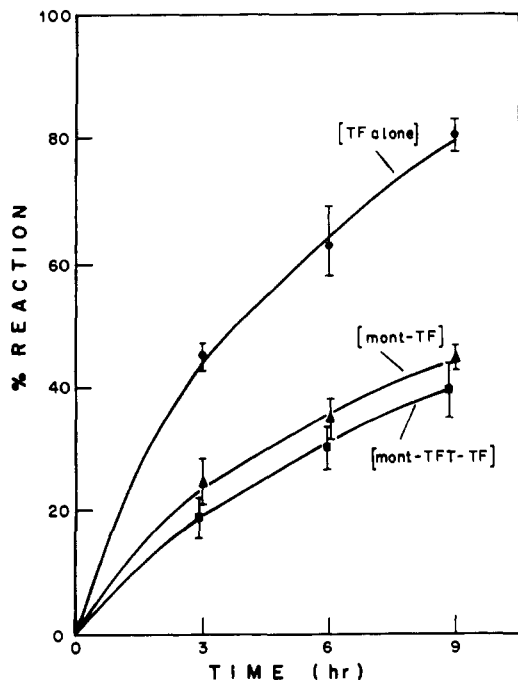


Figure 4. Photolysis of trifluralin (TF), alone and adsorbed on montmorillonite with and without thioflavin T (TFT). Percent conversion is plotted against time over a 9-h period. Points are obtained from experiments with at least duplicate samples.

variability is evident in the values used in Figure 4, probably due to the inherent difficulties in obtaining uniform irradiation of the clay samples. It is of interest to note that the inclusion of the organic cation TFT does not appreciably alter the photostability of TF in comparison with the use of clay alone, in contrast with our results with other pesticides (Margulies et al., 1988). Simple mixing of TF with montmorillonite gave results comparable to those obtained on irradiation of unprotected trifluralin, thus ruling out the possibility of photostabilization resulting from light shielding.

Effect of Complexation on Photoproduct Yields.

In addition to recovered TF, two other products (I and II) were recovered, constituting between 5% and 100% of the reacted trifluralin depending on the reaction conditions (Figure 5). The ratios of I and II vary over a wide range, with I predominating throughout. Previous results describing trifluralin photodecomposition in the solid phase showed I and II forming from the corresponding *N*-oxides (Leitis and Crosby, 1974) in approximately the same yields (Soderquist et al., 1975). This study consistently detects I as the major component (Figure 5). While irradiation of clay preparations gives ratios of I:II of 2:1 to 3:1, trifluralin alone decomposes to yield I:II in ratios of approximately 10:1. Since the overall effect of clay complexation is a reduction in the reaction rate, it must be concluded that the stabilization operates on the cyclization step leading to I, rather than on further reaction to II. It is also worth noting that the reaction proceeds exclusively to I and II when Mont-TF is used, i.e., nearly 100% recovery, while irradiation of both TF alone and Mont-TFT-TF gives lower accountability of reacted TF (Figure 5).

The absence of photoproducts in the Mont-TF preparation, which have been previously observed on soils (Golab and Occolowitz, 1979), is probably due to complexation of the *N*-oxide progenitors of I and II with the charged surface of the clay. In the photolyses of TF alone a variety of products are observed in small yields (GC-MS); these include the aniline and diazo dimers previously reported.

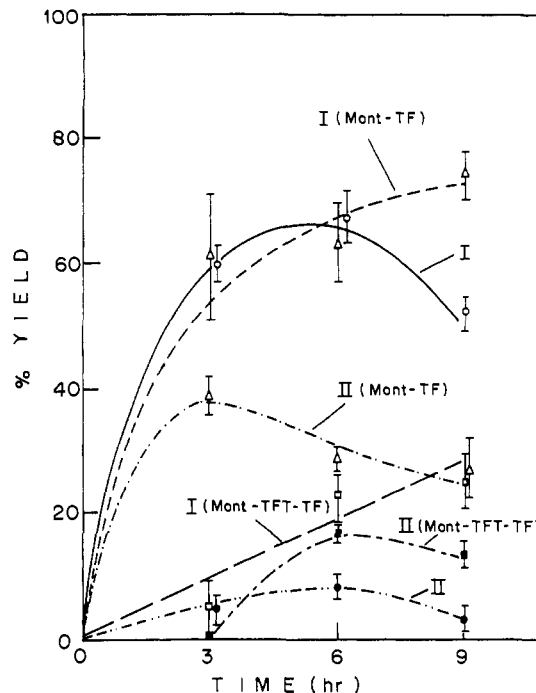


Figure 5. Formation of photoproducts I and II as a function of time. Values are from duplicate samples. Yields are calculated as percent of TF reacted.

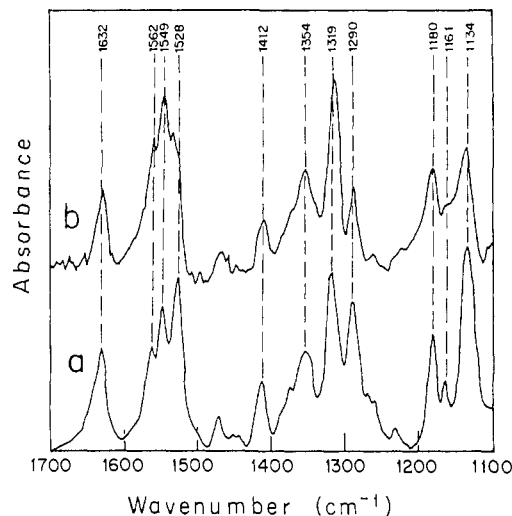


Figure 6. Fourier-transform infrared absorption spectra of trifluralin (TF): (a) alone; (b) adsorbed on montmorillonite (after the spectrum of montmorillonite was subtracted).

Intermolecular Interactions and Photostabilization Mechanism. Information regarding intermolecular interactions and the mechanism of photostabilization of TF on the surface of montmorillonite can be obtained using infrared spectroscopy. In Figure 6 the FTIR spectra of TF in its free form (a) and adsorbed to the clay (b) are shown. The two peaks at 1528 and 1549 cm^{-1} in the spectrum of TF can be assigned to the antisymmetric stretching vibrations of each of the two NO_2 groups (Sullivan et al., 1980), which are not identical due to steric reasons (nonplanarity with aromatic ring). The fact that the main difference between the two spectra is a shift of the 1528- cm^{-1} peak toward higher wavenumbers indicates that TF molecules interact with the clay through one of these groups. Other vibrations are much less affected by adsorption.

The change in the FTIR spectrum upon irradiation of TF on the surface of montmorillonite is shown in Figure

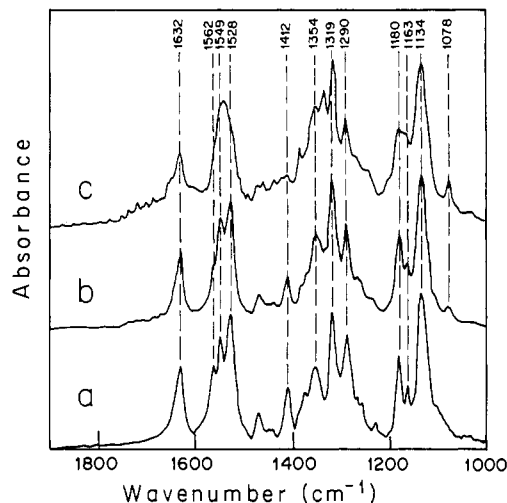


Figure 7. Fourier-transform infrared absorption spectra of trifluralin (TF) irradiated with UV light when adsorbed to montmorillonite: (a) nonirradiated; (b) after 2 h of irradiation; (c) after 8 h of irradiation. The spectra were measured after TF and its photoproducts were extracted from the clay.

7. Spectra b and c were recorded after extraction of the unreacted herbicide and photoproducts from the clay. The disappearance of the peaks at 1528 (NO_2 stretching) and 1412 cm^{-1} (C-H bending) after 8 h of irradiation is consistent with the suggested reaction mechanism (Figure 1). One nitro group is transformed during the cyclization reaction, and the propyl chain (responsible for the 1412- cm^{-1} absorption) is lost in the dealkylation reaction leading to photoproduct II. The same changes in the FTIR spectrum are observed when free TF (not adsorbed on the clay) is irradiated but in much shorter irradiation times. It is worth noting that the nitro group involved in the cyclization reaction is the one through which the TF molecules are adsorbed to the clay (absorption at 1528 cm^{-1}). It is suggested that photostabilization is due to steric hindrance imposed by the clay surface to the cyclization step of the photochemical reaction. The proximity to the clay surface inhibits the conformational change required for cyclization of the propyl chain (Figure 1), resulting in reduction in the overall reaction rate. On the other hand, once photoproduct I is formed, the dealkylation reaction leading to photoproduct II is favored because the smaller and more planar structure of II favors the adsorption interactions with the clay surface.

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