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Photolysis of TCDD and Trifluralin on Silica and Soil

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INTRODUCTION

Thorough investigation of the fate of environmental contaminants entails a photochemical study to elucidate the action of sunlight on these substances. A variety of conditions have been used for photochemical experiments, but there remain many uncertainties in extrapolating laboratory-derived information to environmental conditions. This communication reports some experiments to compare the photolysis of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and trifluralin (α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) on silica-coated plates with that on soil.

TCDD, the most toxic of the known chlorodioxins (HIGGINBOTHAM et al. 1968), has been found as an occasional contaminant in 2,4,5-T [(2,4,5-trichlorophenoxy)acetic acid] and other trichlorophenol derivatives. Although the amount of TCDD entering the environment is likely to be extremely small, it can produce pathological changes at very low dose levels and a daily dosage of 10 μg/kg fed to rats caused 94% mortality within 15-31 days (GUPTA et al. 1973). Small quantities of TCDD are potentially capable of being destroyed by sunlight. Earlier studies indicated that solutions in methanol underwent rapid photodecomposition when exposed to sunlight (CROSBY et al. 1971). The course of photolysis in hydrogen donor solvents involved reductive dechlorination accompanied by disruption of the ring system. However, on soil layers or glass plates, photodecomposition of TCDD appeared to be slow and was difficult to detect (PLIMMER et al. 1973); some refinement of the techniques employed was needed to determine the extent of photolysis.

Trifluralin, the second compound investigated in this study, is used as a herbicide. The observed shift of absorption maximum from 375 nm in cyclohexane to 435 nm with silica added (PLIMMER 1971) might be expected to increase the probability of photochemical reaction on silica.

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EXPERIMENTAL

1) Photolysis of TCDD on Silica:

A benzene solution of uniformly ^{14}C-labeled TCDD (0.46 μCi/mg) was spotted onto a line drawn 3 cm from the bottom edge of a pre-coated silica plate (Brinkman Silplate F-22, 20 x 20 cm, 0.25 mm coating thickness). Seven spots, each containing ca. 32 ng TCDD, were applied 2 cm apart. A 2 x 2 cm grid was lightly ruled on the plate above the origin, with the spots positioned half-way along the bottom edges of the squares. Three of the spots were covered with aluminum foil, and the plate was then exposed to summer sunlight outdoors at Beltsville, Maryland for 20 hr.

After exposure the plate was developed in hexane/chloroform (80:20) until the solvent had moved 10 cm above the origin. Silica from each square of the grid was scraped off into a scintillation vial, and 1 ml ethyl ether and 1 ml of scintillation solution was added to each vial. Radioactivity was measured using a Nuclear Mark 1 Liquid Scintillation Counter.

Typical results are shown in Table 1.

TABLE 1

Photolysis of ^{14}C-TCDD on silica and soil: Percentage of radioactivity[a] in each zone of tlc plate after development

	Experiment 1		Experiment 2			
	Silica		Silica		Soil	
Exposure Time	20 hr.	0[b]	8 hr.	0[b]	8 hr.	0[b]
Distance from Origin						
0-2 cm	29.8	3.9	11.3	2.8	6.3	6.0
2-4 cm	0.9	1.0	0	0	4.0	3.3
4-6 cm	34.1	88.0	72.3	94.7	84.2	83.5
6-8 cm	3.0	6.0	0	0	0	0
8-10 cm	0.3	0.6	0	0	0	0
Total	68.1	99.5	83.6	97.5	94.5	92.8

[a] Compared with pre-exposure control sample.

[b] From foil-covered unexposed area of plate.

2) Photolysis of TCDD on Silica and Soil:

A precoated silica plate was divided into halves by removing a strip of silica coating (0.4 mm) from the middle of the plate from top to bottom. On the right-hand half of the plate a strip of coating 1 cm wide was removed 3 cm above the bottom edge and parallel to it. Hagerstown silty clay loam soil (*ca*. 0.25 g, sieved through 280 mesh) was pressed into the gap to form an even layer that adhered after wetting and drying.

Seven spots of ^{14}C-labeled TCDD solution were applied to the silica coating on the left-hand side of the plate and to the soil coating on the right-hand side. The outermost 3 spots on each side were covered with foil and the plate was exposed to sunlight outdoors for 8 hr. The plate was developed, the coating was scraped off, and the radioactivity was measured as described in 1) for TCDD. Results are shown in Table 1.

3) Photolysis of Trifluralin on Soil:

The precoated silica plate was modified by removing a strip of silica 1 cm wide and 3 cm above and parallel to the bottom edge of the plate. A 6 cm border of silica was left at the sides of the plate. Hagerstown soil (*ca*. 0.5 g) was used to replace the coating, as described in experiment 2). Uniformly ^{14}C ring-labeled trifluralin solution in benzene was spotted onto the plate; seven spots, each of 15 μl (4 μg/μl), were applied to the soil strip. Two spots were applied to the silica at the sides of the plate as controls. Half the plate was covered with aluminum foil; the plate was then covered with a quartz plate and exposed to sunlight outdoors for 7.5 hr.

The plate was developed in benzene. The orange spots corresponding to unchanged trifluralin were scraped off, and radioactivity was measured as described for TCDD. Results are given in Table 2.

4) Photolysis of Trifluralin on Silica and Soil:

A silica-soil plate was prepared as in experiment 2) and 7 spots of 15 μl ^{14}C-labeled trifluralin solution were applied to each side of the plate. The outermost 3 spots on each side were covered with aluminum foil. No quartz plate was used in this experiment. After 9 hr exposure to sunlight, the plate was developed in benzene and the radioactivity was measured. Results are shown in Table 2.

TABLE 2

Photolysis of trifluralin: Percentage recovery[a] from tlc plates after development

	A. Quartz-covered Plate				B. No Cover			
	Silica		Soil		Silica		Soil	
Exposure Time	7.5 hr	0[b]	7.5	0[b]	9 hr	0[b]	9 hr	0[b]
% Recovery of trifluralin	52	104	84	77	40	82	71	78

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[a] Compared with pre-exposure control sample.

[b] From foil-covered unexposed section of plate.

Before each experiment, control or recovery check samples were obtained by applying three spots of the solution to top of the silica-coated plate, scraping off the dried spots, and counting the radioactivity.

RESULTS AND DISCUSSION

From the data in Table 1 for TCDD, after 20 hr exposure, only 37% of the radioactivity was present in the 4 to 6 cm and 6 to 8 cm zones, compared with 94% in the dark control sample. Most photoproducts remained at the origin; 30% of the radioactivity was concentrated in the 0-2 cm zone, compared with 4% in the control. Thus, under these experimental conditions, a polar product was formed from TCDD in sunlight. Only 68% of the original radioactivity was recovered from the exposed section of the plate after 20 hr exposure, compared with 99% recovered from the covered area, suggesting that volatility may be a factor in the losses. The products of the photolysis have not yet been identified.

Photodecomposition of TCDD on silica was measurable within 8 hr; 11.3% of the radioactivity was recovered from the 0 to 2 cm zone as compared with 2.8% for the covered area. Again, the total recovery of 83.6% of the radioactivity after 8 hr exposure on silica, compared with 97.5% from the covered area, may reflect volatility losses. Although considerable photodecomposition occurred on the silica-coated plate during 20 hr exposure to sunlight, this does not contradict our earlier observations of neglibible photodecomposition with a film or suspension of TCDD (PLIMMER et al. 1973) but indicates that photochemical processes in condensed phases are limited by the amount of light actually absorbed by the reactant. For example, the transformation of 16 ng TCDD is substantial when considered as a percentage of 32 ng, whereas 16 ng would represent an insignificant percentage when several micrograms were involved. As the quantity of reactant increases, more molecules are shielded from direct interaction with quanta of radiant energy. The data in Table 2 show that trifluralin also undergoes considerable photodecomposition when irradiated on silica. Part of this loss may be ascribed to volatilization from the plate.

Our studies have shown that some changes in ultraviolet spectra occur as a result of the interaction of organic molecules with silica. In cyclohexane, dibenzo-*p*-dioxin showed maximum absorption at 294 nm; when silica was added to the adsorption cell, there was broadening of the absorption band width, with a shift of the maximum from 294 to 288 nm (PLIMMER 1971). TCDD has an absorption maximum at 307 nm in methanol; by analogy with the behavior of dibenzo-*p*-dioxin, broadening of the absorption band in the region of the maximum wavelength might be expected on silica. By contrast, trifluralin showed an increase in absorption maximum from 375 nm in cyclohexane to 435 nm on the addition of silica (PLIMMER 1971). The interactions reflected in these spectra shifts could affect the course of photochemical reactions.

Results obtained from irradiation on soil were quite different from those on silica, both with TCDD (Table 1) and trifluralin (Table 2). Recovery of TCDD from the unexposed area of soil was lower than the comparable recovery from silica (92.8% as compared with 97.5%).

The soil retained about 6% of the radioactivity at the origin, with no difference between exposed and unexposed areas. Apparently the soil exerts a protective effect against the photolysis of TCDD. Similarly, there was no evidence that significant photodecomposition of trifluralin occurred on soil during 9 hr irradiation.

Thus, soil seemed to limit the extent of photolysis, whereas silica behaved as an essentially transparent medium and photodecomposition of adsorbed molecules appeared to be limited only by masking effects due to the reactant molecules themselves. It is noteworthy that the photolysis of TCDD proceeded rapidly on silica, which supports the suggestion that nanogram quantities of TCDD directly exposed on environmental surfaces will be decomposed by the action of sunlight. This decomposition escaped detection in earlier experiments, performed with microgram quantities of TCDD (PLIMMER et al. 1973).

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