The Partial Photolysis of 6-Chloropicolinic Acid in Aqueous Solution

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Few of the published studies on the photochemical degradation of pesticides concern the rates at which losses occur with differing light sources.

Because intermediates in photolysis reactions may possess adsorption spectra unlike the spectrum of the parent compound, and because no light source produces uniform luminous intensity at all wavelengths, a change of light sources can result in a change in relative photolysis rates of parent compound and intermediate products.

One consequence of these differing rates is that intermediates may accumulate and appear to be of practical significance under one light source, but may never occur in significant quantities under a different light source. Such a phenomenon has been observed in the photolysis of the pesticide residue, 6-chloropicolinic acid (3), and is the subject of this communication. This compound is formed in the soil from hydrolysis of 2-chloro-6-(trichloromethyl)pyridine, known as N-SERVE® nutrient stabilizer.

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Solution Irradiation

Samples irradiated in direct sunlight were dissolved in excess 0.05N sodium bicarbonate, poured into shallow glass dishes, and placed in direct sunlight for several hours prior to analysis. Water was added at intervals to compensate for evaporation loss. The amount of compound in each dish was adjusted to provide 0.43 mmol./meter^2 of illuminated surface.

Samples irradiated with the mercury vapor lamp were placed in shallow dishes 11 cm. beneath the reflector base of a George W. Gates and Company Model 420-UI ultraviolet light source fitted with a 360-watt Uviarc burner. An electric fan provided sufficient cooling to maintain the solution temperature near 20°C. Here, too, the amount of compound was adjusted to provide 0.43 mmol./m^2 of illuminated surface.

Identification of Product

The isolation of 6-hydroxypicolinic acid from an irradiated aqueous solution of 6-chloropicolinic acid was accomplished in the following way. All evaporations were done in vacuum.

900 mg. of 6-chloropicolinic acid dissolved in 600 ml. of 0.05N sodium bicarbonate was exposed, 30 ml. at a time, in a 95-mm. diameter petri dish under the mercury vapor arc for 8 hours. The 590 ml. of solution recovered was shaken with 590 ml. ether, separated, and

evaporated to 35 ml. Dilute hydrochloric acid was added to pH 2 and the solution was shaken with 3 35-ml. portions of ether.

The solid obtained by evaporation of the aqueous phase was boiled with 3 successive 35-ml. portions of methanol. The decanted methanol extracts were filtered through paper, combined and evaporated to dryness. The solid (1.054 gram) was recrystallized from boiling water with the aid of decolorizing carbon to obtain colorless needles melting at 260 to 265°C. with decomposition. 6-Hydroxypicolinic acid is reported to melt at 282°C. (dec.) (1).

A comparison between the infrared absorption spectrum of this product and that of a reference sample of 6-hydroxypicolinic acid is shown in Figure 1. The excellent agreement demonstrates that this main photolysis product of 6-chloropicolinic acid must be 6-hydroxypicolinic acid.

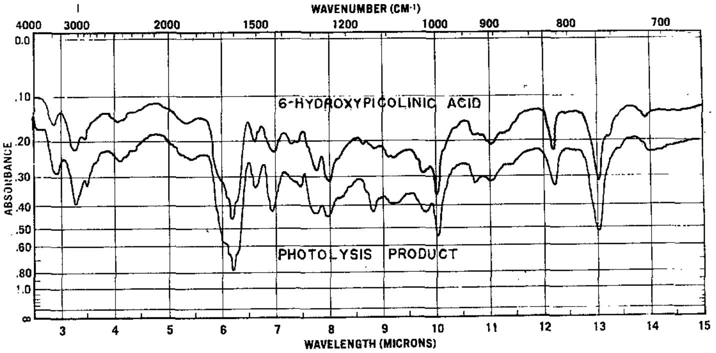

Figure 1. Infrared absorption spectra of 6-hydroxypicolinic acid and of photolysis product. Samples in potassium bromide windows.

The identity of the product was confirmed by mass spectrometry, which showed a molecular ion peak at m/c = 139 and a fragmentation pattern identical with that of a reference sample of 6-hydroxypicolinic acid.

Estimation of 6-Chloropicolinic Acid

The concentration of 6-chloropicolinic acid was estimated spectroscopically. The sample (less than 20 ml.) was diluted to 25.0 ml. with 1.5N ammonia, an aliquot was placed in a 1-cm. quartz cell, and the ultraviolet absorption spectrum measured on a Beckman DB spectrophotometer. A "base line" was subsequently constructed between 253 and 284 mu. on the recorded spectrum, and the vertical distance between this base line and the spectral curve at 273 mu. read. This distance bore a linear relationship to concentration of 6-chloropicolinic acid in the 25-ml. volume, as one may see from Figure 2.

Estimation of 6-Hydroxypicolinic Acid

6-Hydroxypicolinic acid was estimated spectroscopically. The sample (less than 20 ml.) was diluted to 25.0 ml. with 1.5N ammonia, an aliquot was placed in the 1-cm. quartz cell, and the ultraviolet absorption spectrum recorded. Here, the "base line" was constructed between the spectral curves at 290 mu. and at 328 mu., and the peak height from this base line to the spectral curve at 305 mu. was read. This height also bore a linear relationship to concentration of 6-hydroxypicolinic acid in the 25-ml. volume, as may be seen from Figure 2.

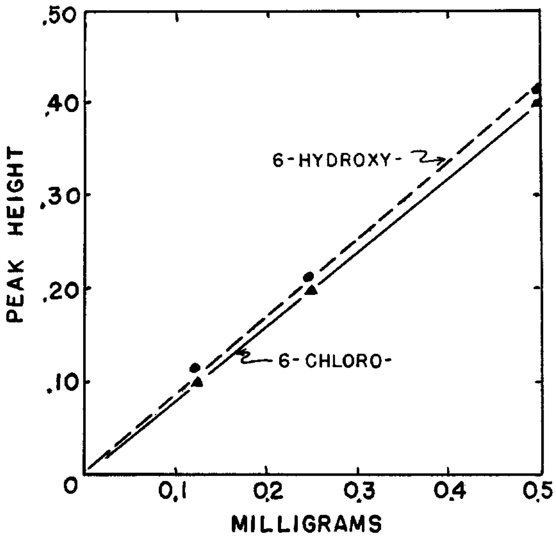

Figure 2. Calibration curves for analysis of 6-chloropicolinic acid and of 6-hydroxypicolinic acid

Degradation by Direct Sunlight

Replicate samples of solutions containing identical molar concentrations of 6-chloropicolinic acid were exposed to direct summer sunlight at Walnut Creek, California. Concurrently, a similar set of solutions containing the identical molar concentrations of 6-hydroxypicolinic acid, in identical containers were also exposed to direct sunshine. Samples were removed at intervals and analyzed for 6-chloropicolinic acid and for 6-hydroxypicolinic acid.

The loss rates for these 2 compounds are compared in Figure 3. When irradiated in direct sunlight, a buffered aqueous solution of the sodium salt of 6-hydroxypicolinic acid degrades much more rapidly than the sodium salt of 6-chloropicolinic acid.

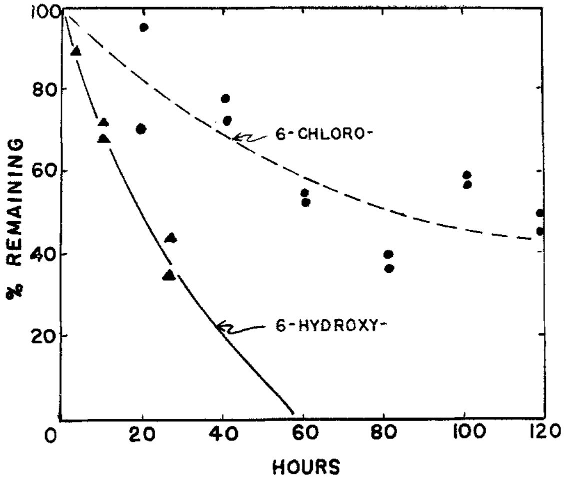

Figure 3. Photolysis rates in direct sunlight. All samples irradiated at 0.43 mml./m^2. Illuminated area in 0.05M sodium bicarbonate

Degradation by Mercury Arc

The experiment described for solar irradiation was repeated under the light of a mercury vapor arc. The loss rates are compared in Figure 4. Under the high-intensity mercury arc and in buffered aqueous solution, the sodium salt of 6-chloropicolinic acid photodegrades much more rapidly than the sodium salt of 6-hydroxypicolinic acid.

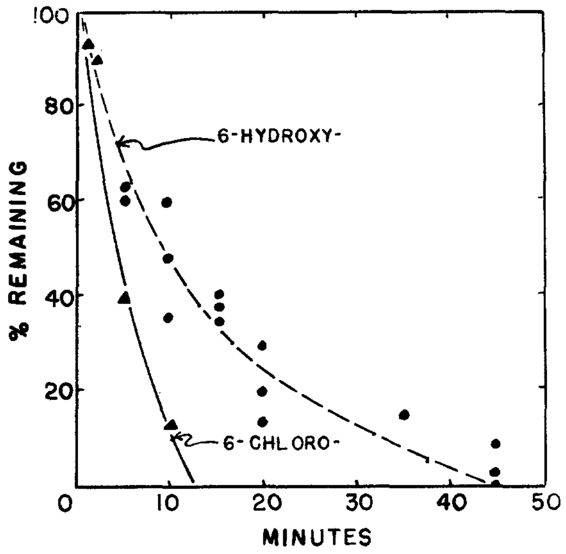

Figure 4. Photolysis rates in light from 360-watt mercury vapor arc. Samples irradiated 11 cm. beneath reflector at 0.43 mmol./m^2 illuminated area in 0.05M sodium bicarbonate

Rate of Production of 6-Hydroxypicolinic Acid

When the rate of formation of 6-hydroxypicolinic acid from 6-chloropicolinic acid was measured, it was found that under illumination with the mercury vapor arc, the concentration started at zero, rose through an early maximum, and then fell off again to zero. Under illumination with direct sunlight, no 6-hydroxypicolinic acid could be detected as a photolysis product of 6-chloropicolinic acid. These effects may be seen in Figure 5.

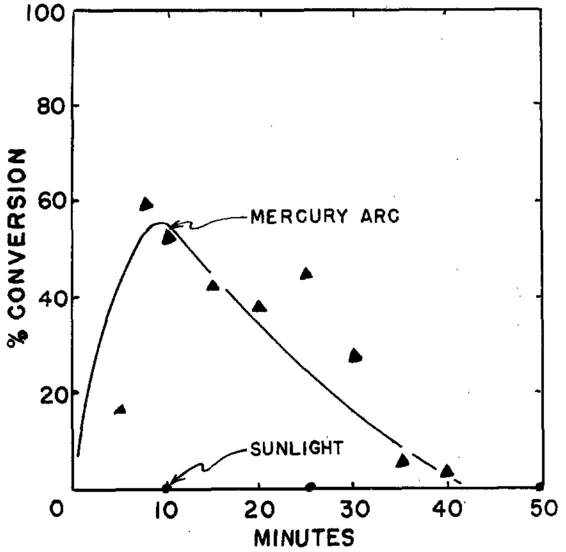

Figure 5. Rates of appearance of 6-hydroxypicolinic acid in irradiated aqueous sodium bicarbonate solutions of 6-chloropicolinic acid. Initial compound present at 0.43 mmol./m^2 illuminated area.

Discussion

The failure to observe the formation of 6-hydroxypicolinic acid from 6-chloropicolinic acid by solar irradiation is probably attributable to at least 2 factors. First, the absorption spectrum of the sodium salt of 6-hydroxypicolinic acid is such that the molar absorptivity is far greater in the 300 to 400-m$\underline{u}$. range than is the molar absorptivity of the sodium salt of 6-chloropicolinic acid. Second, direct sunlight at the earth's surface is considerably more intense at wavelengths between 300 and 400 m$\underline{u}$. than at wavelengths shorter than 300 m$\underline{u}$. (2).

The authors feel that 6-hydroxypicolinic acid really is an intermediate in the solar photolysis of 6-chloropicolinic acid, but that it is degraded further before it reaches a detectable concentration.

These results emphasize one of the pitfalls of using light sources other than natural sunlight for the study of pesticide degradation. The practical importance of photolysis products can be evaluated only by experiments which utilize solar illumination.

References

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