

s-Triazine Herbicide Dealkylation by Free-Radical Generating Systems

Hydroxyl radicals generated by chemical systems dealkylate *s*-triazine herbicides. Ring cleavage does not occur. Mono- and completely dealkylated products from atrazine, simazine, and propazine

were identified by mass spectrometric analysis. Identical products have been detected in several biological systems.

Pesticides may be degraded metabolically or in the soil environment by a variety of mechanisms. 3-Amino-triazole (amitrole), for example, although stable in a variety of chemical reagents, is readily degraded by free radical generating systems (Plimmer *et al.*, 1967). Extension of these studies to other pesticides may provide analogies or models for reaction pathways of importance in the environment. Fenton's reagent (ferrous sulfate-hydrogen peroxide) is a simple system for the generation of hydroxyl radicals. The objective of our work was to investigate the nature of the products formed by Fenton's reagent with the herbicide, 2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine (atrazine) and related *s*-triazine herbicides.

METHODS AND MATERIALS

Purified *s*-triazine herbicides and ¹⁴C-ring and side-chain labeled 2-hydroxy-4-ethylamino-6-isopropylamino-*s*-triazine (hydroxyatrazine) were synthesized and supplied by the Geigy Company, Ardsley, N.Y.

¹⁴CO₂ from labeled atrazine was measured by trapping in 2-methoxymethanol (7 ml) and monoethanolamine (10 ml). This solution was added to a scintillation solution (10 ml) containing PPO (5 g) and POPOP (0.15 g) in toluene (1 l.). Determinations of radioactivity were carried out in a Nuclear Chicago Mark 1 liquid scintillation counter.

Preparative thin-layer chromatography was carried out on plates coated with a 2 mm layer of silica gel (Merck GF 254) with petroleum ether (60–110° C), ethyl acetate, acetic acid (3:5:0.1, v/v) as the developing solvent. Mass spectra were determined on a Perkin-Elmer Model GC 270 combined gas chromatograph/mass spectrometer by using the solids inlet.

In a typical experiment 100 mg purified atrazine was reacted with 105 ml 0.285 *M* ferrous sulfate solution in 0.071 *M* sulfuric acid containing 2.3% hydrogen peroxide. Oxygen was bubbled through the solution for 3 hr. The reaction mixture was then exhaustively extracted with ethyl acetate in a continuous liquid-liquid extractor. The ethyl acetate

was concentrated and examined by thin-layer chromatography. Products were revealed by ultraviolet light and isolated by extraction of bands scraped from a preparative plate with ethyl acetate for 16 hr in a Soxhlet thimble. Solvent was removed and the fractions were subjected to mass spectrometric analysis.

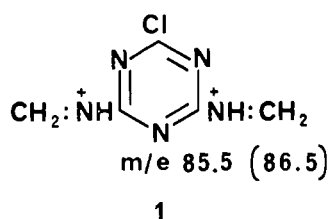
RESULTS AND DISCUSSION

Fenton's reagent and related systems, such as the cupric ion-ascorbic acid reagent, effect oxidation by generation of hydroxyl radicals or metal-complexed radicals. The products of reaction of some *s*-triazine herbicides with these systems are similar to those isolated from *in vivo* metabolism (Bakke *et al.*, 1967; Kearney *et al.*, 1965; Shimabukuro, 1967). Fenton's reagent removes the *N*-alkyl groups from the herbicidal triazines, and the ring remains intact. This could be demonstrated by examining the radioactive volatile products from ¹⁴C-ring-labeled and ¹⁴C-ethyl-labeled hydroxyatrazine trapped in methanolamine during oxidation with Fenton's reagent or cupric ion-ascorbic acid. No volatile radioactive products were obtained from ring-labeled hydroxyatrazine, whereas up to 40% of the radioactivity of *N*-ethyl labeled hydroxyatrazine was trapped by methanolamine. We conclude that only the *N*-alkyl group is attacked by the model systems.

A study of the products of oxidation of atrazine, propazine [2-chloro-4,6-bis(isopropylamino)-*s*-triazine], and simazine [2-chloro-4,6-bis(ethylamino)-*s*-triazine] confirmed these conclusions. The structures of the products were elucidated by mass spectrometric analysis.

The mass spectrum of simazine [2-chloro-4,6-bis(ethylamino)-*s*-triazine] is typical of the alkylamino-*s*-triazines. A strong molecular ion at *m/e* 201 is accompanied by an ion *m/e* 203 due to the presence of the chlorine isotope of mass 37. Fragments due to loss of alkyl groups occur at *m/e* 186, 175, 158, and 145, accompanied in some cases by McLafferty rearrangements. Fragments are observed at *m/e* 85.5 and

86.5, due to the stable doubly charged ion (1). Principal



features of *s*-triazine herbicide spectra have been discussed by Jörg *et al.* (1966). Similar pathways are available for the fragmentation of propazine and atrazine. Characteristic losses of alkyl groups predominate. Losses of olefin by McLafferty rearrangements were common. The spectrum of authentic 4,6-diamino-2-chloro-*s*-triazine had an intense molecular ion at *m/e* 145 (147), and loss of chlorine afforded an abundant fragment at *m/e* 110.

Propazine, simazine, and atrazine yielded 4,6-diamino-2-chloro-*s*-triazine when reacted with Fenton's reagent. Dealkylation probably took place in two stages: as 4-amino-2-chloro-6-ethylamino-*s*-triazine was obtained from simazine, and 4-amino-2-chloro-6-isopropylamino-*s*-triazine was obtained from atrazine (Figure 1).

Thin-layer chromatography of the simazine oxidation mixture separated six components with *m/e* 167, 187, 145, 173, 201, and 167 in increasing order of *R_f* values. All products were chlorinated except for *m/e* 167. Compounds *m/e* 201, 173, and 145 correspond to simazine, 4-amino-2-chloro-6-ethylamino-*s*-triazine, and 4,6-diamino-2-chloro-*s*-triazine, respectively. The compound *m/e* 187 is a chlorinated *s*-triazine, and an abundant fragment ion at *m/e* 159 indicates loss of an ethylene molecule by a McLafferty rearrangement. Hence, one *N*-ethyl group remains intact. The remaining substituent may be *N*-methyl, resulting from oxidation of the terminal carbon atom of the *N*-ethyl group to a carboxylic acid, followed by decarboxylation. The two compounds of *m/e* 167 are not chlorinated and both show fragment ions at *m/e* 149 (M-18).

N-Dealkylation of the *s*-triazine herbicides is an important mode of biological degradation in soil fungi, plants, and animals (Bakke *et al.*, 1967; Kearney *et al.*, 1965; Shimabukuro, 1967).

The fact that similar products are obtained by the action of Fenton's reagent does not imply that the same mechanism is operative, but our study indicates that useful model com-

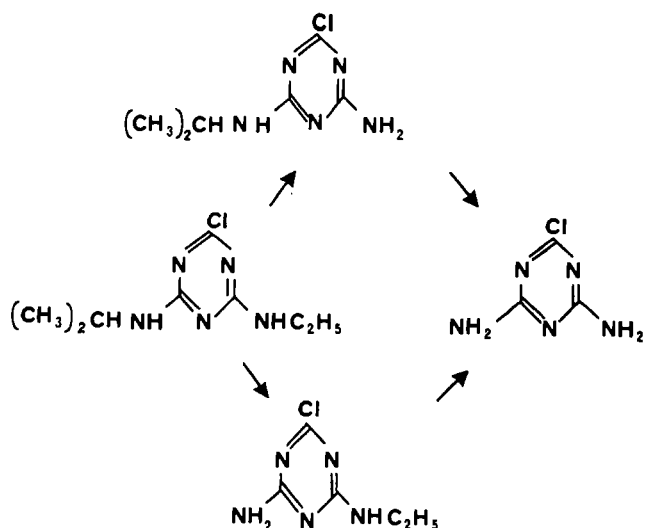


Figure 1. Free-radical oxidation of atrazine

pounds may result by the reaction of radical hydroxylating systems with pesticides.

ACKNOWLEDGMENT

Purified triazine herbicides and hydroxyatrazine-¹⁴C were generously supplied by the Geigy Co., Ardsley, N. Y.

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Received for review November 30, 1970. Accepted January 2, 1971.
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