Photolysis of Phenylurea Herbicides

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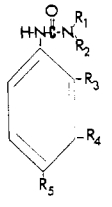
The photolytic conversions of the widely used herbicides linuron and monuron have been studied. After exposure to sunlight for 2 months, an aqueous solution of linuron yielded 13% 3-(3-chloro-4-hydroxyphenyl)-1-methoxy-1-methylurea, 10% 3,4-dichlorophenylurea, and 2% 3-(3,4-dichlorophenyl)-1-methylurea. One of the products of monuron photolysis was 3-(*p*-hydroxyphenyl)-1,1-dimethylurea. Some of the properties of the phenolic materials are presented.

Metobromuron (I), 3-(*p*-bromophenyl)-1-methoxy-1-methylurea can be converted by sunlight to a number of compounds, the major product being 3-(*p*-hydroxyphenyl)-1-methoxy-1-methylurea (II) (Rosen and Strusz, 1968). One would therefore predict that one of the photolytic products of 3-(*p*-chlorophenyl)-1,-1-dimethylurea (monuron, III) would be 3-(*p*-hydroxyphenyl)-1,1-dimethylurea (IV). Tang and Crosby (1968), however, in addition to finding several oxidation and polymerization products of monuron, found only one phenolic material, 3-(4-chloro-2-hydroxyphenyl)-1,1-dimethylurea (V). To extend these studies, the photolyses of monuron and 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea (linuron, VI) were investigated and the effect of several hydroxyphenylureas on photosynthetic oxygen evolution was determined. Table I shows the structures.

Table I. Structures of Compounds in Text



	R_1	R_2	R_3	R_4	R_5
I	Me	OMe	H	H	Br
II	Me	OMe	H	H	OH
III	Me	Me	H	H	Cl
IV	Me	Me	H	H	OH
V	Me	Me	OH	H	Cl
VI	Me	OMe	H	Cl	Cl
VII	Me	OMe	H	Cl	OH
VIII	H	OMe	H	Cl	Cl
IX	Me	H	H	Cl	Cl
X	H	H	H	Cl	Cl
XI	Me	OMe	H	OH	OH
XII	Me	OMe	H	OH	Cl

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EXPERIMENTAL

Irradiation Conditions. Aqueous solutions of VI (55 p.p.m.) were exposed to sunlight during the same 17-day period in late summer 1967 in the same manner as the solutions of I previously described (Rosen and Strusz, 1968). Another 55-p.p.m. solution of VI was exposed between mid-May and mid-July 1968. An aqueous solution (178 p.p.m.) of III was exposed for the entire month of September 1968.

Isolation of Reaction Products. At the end of the exposure periods, the aqueous solutions were saturated with sodium chloride and extracted twice with an equal volume of ethyl acetate. In the case of VI, half of the combined ethyl acetate extracts was extracted with an equal volume of 1*M* sodium hydroxide. The basic solution was then acidified with dilute hydrochloric acid before re-extraction with ethyl acetate. The ethyl acetate layers were washed with water, dried over anhydrous sodium sulfate, filtered, and concentrated for separation by GLC and TLC.

Gas-Liquid Chromatography. GLC procedures were reported earlier (Rosen and Strusz, 1968). Programming between 100° and 200°C. at 5° per minute, the retention times for VI, 3-(3-chloro-4-hydroxyphenyl)-1-methoxy-1-methylurea (VII), 3-(3,4-dichlorophenyl)-1-methoxyurea (VIII), 3-(3,4-dichlorophenyl)-1-methylurea (IX), and 3,4-dichlorophenylurea (X) were 7.6, 8.4, 10.2, 14.7, and 15.6 minutes, respectively. Compounds III and IV could not be quantitated.

Thin-Layer Chromatography. The ethyl acetate extracts (50 mg. per ml.) of the reaction product mixtures of III and VI were streaked on 500-micron silica gel G plates and eluted with chloroform-pyridine-methanol (100:10:1). The materials which cochromatographed with synthesized IV ($R_f = 0.34$) and VII ($R_f = 0.68$) were scraped from the plate, eluted with ethyl acetate, and subjected to infrared analysis. The R_f values of III and VI in this system were 0.54 and 0.77, respectively. The system developed by Katz and Nieh (1967) was used to confirm the presence of IX and X.

Synthesis of Materials. Phenols IV, VII, and XI, respectively, were obtained by converting the ethyl esters of *p*-hydroxybenzoic acid, 3-chloro-4-hydroxybenzoic acid, and 3,4-dihydroxybenzoic acid to their corresponding benzazides (Curtius *et al.*, 1895) and subsequently converting these benzazides to the desired

materials with either *O,N*-dimethylhydroxylamine or dimethylamine (Rosen and Strusz, 1968). After recrystallization from ethyl acetate, IV had a melting point of 203–04°C.; recrystallization from ethyl ether afforded VII (m.p. 134–35°C.). Recrystallization of 3-(3,4-dihydroxyphenyl)-1-methoxy-1-methylurea (XI) was not performed. All three materials gave mass and infrared spectra in accord with their assigned structure.

Photosynthesis Inhibition. Photosynthesis was monitored polarographically with an oxygen electrode (Yellow Springs Instrument Co.) in an atmosphere of 5% carbon dioxide in nitrogen. The test materials were dissolved in ethanol (10 mg. per ml.). Phytotoxicity was measured by injecting 10-μl. volumes into 5 ml. of rapidly photosynthesizing *Euglena gracilis* suspended in water. Output of the polarograph was measured with a 100-mv. potentiometric recorder.

RESULTS AND DISCUSSION

The reaction mixture obtained by exposing linuron to sunlight for 2 months contained approximately 69% unchanged material, 12% VII, 8% X, and 2% IX. The yields were approximately 13, 10, and 2%, respectively. Compound VII was confirmed by infrared spectroscopy. Materials IX and X were identified by GLC and TLC only, but were expected on the basis of previous results. In similarity with metobromuron photolysis, no methoxy derivative (VIII) was found. A previous exposure, conducted concurrently with that of metobromuron for 17 days, resulted in a 4.3% yield of VII and unmeasurable quantities of other irradiation products. During this period, I was converted to its corresponding phenol (II) in approximately 20% yield.

Plimmer and Hummer (1968) found that chlorine atoms were selectively removed from polyhalogenated aromatic compounds during photolysis in methanol, the rates being dependent on the ring positions of the chlorines and the nature of other ring substituents. They concluded that the path of dechlorination could not be easily predicted. The photolysis of linuron, therefore, could have resulted in the formation of three phenolic 1-methoxy-1-methylureas—VII, XI, and 3-(4-chloro-3-hydroxyphenyl)-1-methoxy-1-methylurea (XII). Since the directing influence of the methoxymethylurea group has not been established, attempts were made to find XI and XII among the reaction products. Unfortunately, XII could not be synthesized because of our failure to synthesize its precursor, 4-chloro-3-hydroxybenzoic acid; XI did not come through our GLC column. However, examination of the phenolic fraction of the irradiated solution by GLC indicated only one material, having a retention time equal to that of synthesized VII. The thin-layer chromatogram of this phenolic fraction indicated only one intense spot, R_f value equal to that of VII. One very faint spot cochromatographed with XI. These results strongly suggested that the methoxymethylurea group directed the photolytic dechlorination para in preference to meta.

The ratio of phenol VII to oxidation products in the reaction mixture of linuron was much smaller than the phenol–oxidation products ratio in the reaction mixture of metobromuron. This reflects the greater ease of debromination as compared to dechlorination, thus allowing the competing oxidation reactions to become more important.

The monuron reaction mixture contained a number of compounds, all but one of which we made no attempt to identify because of the work of Tang and Crosby (1968). One compound not identified by these researchers was a material we found to cochromatograph with synthetic IV and which had an infrared spectrum identical with that of IV. Quantitation of IV could not be made because of severe tailing.

The responses of algal cells (*Euglena gracilis*) to I, III, and VI were as expected—i.e., the inhibition of photosynthetic oxygen evolution was complete and irreversible. None of the hydroxy derivatives (II, IV, and VII) evoked a measurable response. However, these cells were intact and oxygen evolution as measured was that produced from photosynthesis and not simply the "Hill reaction." Therefore, the apparent detoxification could be accounted for if there is a decrease in cell penetrability.

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LITERATURE CITED

Curtius, T., Strauve, A., Radenhausen, R., *J. Prakt. Chem.* **52** (2), 227 (1895).
Katz, S. E., Nieh, M. T., *Bull. Environ. Contam. Toxicol.* **2**, 75 (1967).
Plimmer, J. R., Hummer, B. E., Division of Agricultural and Food Chemistry, 155th Meeting, ACS, San Francisco, Calif., April 1968.
Rosen, J. D., Strusz, R. F., J. AGR. FOOD CHEM. **16**, 568 (1968).
Tang, C. S., Crosby, D. G., Division of Agricultural and Food Chemistry, 156th Meeting, ACS, Atlantic City, N. J., September 1968.

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