Photodecomposition of 3-(p-Chlorophenyl)-1,1-dimethylurea (Monuron)

D. G. Crosby and C.-S. Tang[1]

The effect of sunlight on dilute aqueous solutions of 3-(p-chlorophenyl)-1,1-dimethylurea (monuron) was examined, and a special photoreactor was utilized to simulate the outdoor exposure. Photoproducts were separated by thin-layer chromatography; 3 - (p - chlorophenyl) - 1 - formyl - 1 - methylurea, 1 - (p - chlorophenyl) - 3 - methylurea, 4,4' - dichlorocarbanilide, and 3 - (4 - chloro - 2 - hydroxyphenyl)-1,1-dimethylurea were verified by the identities of their infrared and mass spectra with those of the synthesized standards. 1-(p-Chlorophenyl)-3-formylurea, 4'-chloroformanilide, and p-chloroaniline were tentatively identified by co-chromatography with the authentic compounds in several solvent systems. The principal pathways of monuron photodecomposition were found to be stepwise photooxidation and demethylation of the N-methyl groups, hydroxylation of the aromatic nucleus, and polymerization.

The substituted urea herbicide 3-(p-chlorophenyl)-1,1-dimethylurea (monuron, I) is used for selective control of germinating broadleaf and grassy weeds in crops such as cotton, sugar cane, pineapple, asparagus, and citrus. The effect of sunlight and (or) ultraviolet (UV) irradiation on monuron was examined by Comes and Timmons (1965), Jordan et al. (1963, 1964, 1965), Weldon and Timmons (1961), Rosen et al. (1969), and Sheets and Danielson (1960); each of these studies demonstrated the photodecomposition of the herbicide. Geissbühler, et al. (1963), found that 3-[p-(p-chlorophenoxy)phenyl]-1,1-dimethylurea (chloroxuron) likewise decomposed rapidly under UV irradiation; thin-layer chromatography (TLC) revealed the presence of monomethylated and demethylated derivatives among the photoproducts. Rosen and Strusz (1968) determined that the principal photolytic transformation of aqueous 3-(p-bromophenyl)-1-methoxy-1-methylurea (metabromuron) was substitution of an hydroxyl group for the bromine on the aromatic nucleus; 3-(p-bromophenyl)-1-methylurea and p-bromophenylurea also were identified as minor products.

Although the photodecomposition of monuron long has been a subject of interest, few products or transformation processes have been described. The purpose of the present investigation was to identify the products of monuron photodecomposition in aqueous solution and to propose a possible scheme for the decomposition process.

EXPERIMENTAL

Materials. 3 - (p - Chlorophenyl) - 1,1 - dimethylurea (monuron) was received as a 96% crude product (m.p. 168° to 172° C., E. I. du Pont de Nemours and Company). It was recrystallized twice from aqueous methanol to a melting point of 170 to 171° C. and was homogeneous on TLC.

3-(p-Chlorophenyl)-1-formyl-1-methylurea was prepared by boiling under reflux equimolar amounts of N-methylformamide and p-chlorophenyl isocyanate (J. T. Baker Chemical Company) as a 30% acetone solution. White needles were obtained after recrystallization from ethanol, m.p. 93° to 94° C. (Gerjovitch and Johnson, 1956, report 98° to 100° C.). Elemental analysis: calculated for $C_8H_9ClN_2O_2$, C 50.84, H 4.27; found C 51.21, H 4.19. Infrared (IR) spectrum: 1720 (CO), 1684 (CO) cm.$^{-1}$. Nuclear magnetic resonance (NMR) spectrum: 3.23 δ (N-CH$_3$) and 8.30 δ (N-CHO). Mass spectrum; parent peak m/e 212 (parent), 153 (base, ClPhNCO).

1-(p-Chlorophenyl)-3-methylurea was prepared by passing dried methylamine gas into a 30% ether solution of p-chlorophenyl isocyanate. Recrystallization from aqueous methanol gave a m.p. of 199° to 201° C. IR spectrum: 3344 (NH), 1639 (CO) cm.$^{-1}$. Mass spectrum: m/e 184 (parent), 127 (base, ClPhNH), 153 (ClPhNCO).

4,4'-Dichlorocarbanilide was obtained by stirring p-chlorophenyl isocyanate in water (Smith, 1965), m.p. >275° C. (dec). The IR spectrum of the purified material agreed with that published in Sadtler Standard Spectra (1966).

1-(p-Chlorophenyl)-3-formylurea was prepared by adding a 30% solution of p-chlorophenyl isocyanate in acetone dropwise to a 30% solution of formamide in acetone with constant stirring. The desired product was separated by TLC in solvent A (vide infra), m.p. 166° to 169° C. IR spectrum: 1720 (CO), and 1695 (CO) cm.$^{-1}$. Mass spectrum: m/e 198 (parent), 153 (base, ClPhNCO).

p-Chloroformanilide was prepared by boiling under reflux equimolar amounts of formic acid and p-chloroaniline. The recrystallized product had a m.p. of 100° to 101° C. [Lit. 102° C. (Pollock et al. 1965)].

3-(4-Chloro-2-methoxyphenyl)-1,1-dimethylurea was synthesized from 5-chloro-2-nitroanisole (K and K Laboratories, Inc.). The nitro compound was reduced as a 5% solution in absolute ethanol at room temperature and one atmosphere pressure of hydrogen in the presence of platinum oxide as catalyst. The residue was immediately dissolved in tetra-

---

Department of Environmental Toxicology, University of California, Davis, Calif. 95616

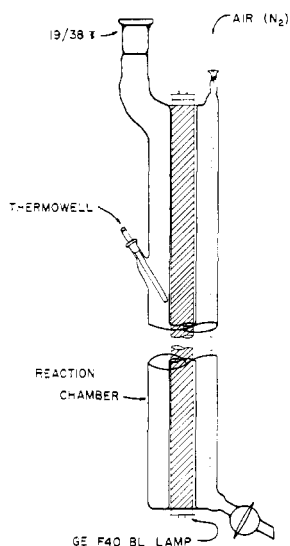[1] Present address, Department of Agricultural Biochemistry, University of Hawaii, Honolulu 96822

Figure 1. Preparative photo-reactor

Figure 2. Thin-layer chromatogram from monuron irradiated in (a) sunlight and (b) preparative photoreactor

hydrofuran, and excess dimethylcarbamoyl chloride (Matheson, Coleman and Bell) was added. After standing overnight, the reaction mixture was diluted with ether and washed several times with water. The ether solution was dried, concentrated, and subjected to TLC (solvent A); the oily 3-(4-chloro-2-methoxyphenyl)-1-,1-dimethylurea exhibited an R_f of 0.51. IR spectrum: 3430 (NH) and 1675 (CO) cm.$^{-1}$. Mass spectrum: m/e 228 (parent and base).

Methods. IR spectra were measured with a Perkin Elmer Model 337 Infrared Spectrophotometer; mass spectra were recorded on a Varian M-66 instrument; and NMR spectra were measured in carbon tetrachloride or deuterated dimethylsulfoxide with a Varian Model A-60 Spectrometer.

Standard solutions for irradiation were prepared by dissolving 200 mg. of monuron in one liter of deionized water. The suspension was stirred overnight and filtered to provide a solution containing about 200 p.p.m. of monuron. Irradiation in sunlight was carried out in 34 by 22 by 4.5 cm. borosilicate glass baking dishes covered with perforated clear plastic wrap which did not absorb light above 200 mμ. Water was added daily to compensate for evaporation losses. The solution gradually developed a pale pink color and was extracted after 14 days of exposure.

A preparative photoreactor (Figure 1) was designed to simulate sunlight irradiation. It was constructed of borosilicate glass and equipped with a 40-watt G. E. F40BL Blacklight fluorescent lamp. Air was conducted to the bottom of the reaction chamber (flowrate 6 ml. per min.) to provide an aerobic environment and stirring; in the case of anaerobic irradiation, nitrogen gas was used instead of air. Seven days' irradiation under aerobic conditions was required to obtain results closely resembling those of sunlight exposure. Samples for isolation and identification usually were prepared in this equipment.

Separation and Identification. The irradiated solution was extracted three times with ether and the combined extracts were dried over anhydrous magnesium sulfate. The aqueous phase remained pink; the pigments were extracted into methylene chloride, and the extract was dried. The dark brown, nonextractable material which remained at the interface during extractions was collected by filtration. The volume of each extract was reduced to about 10 ml. on a rotary evaporator, and further concentration was carried out in a centrifuge
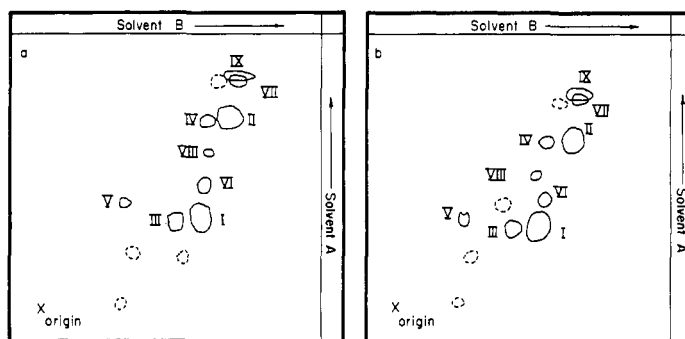
tube under a stream of nitrogen. Unchanged monuron precipitated from the extract during the evaporation and the ether concentrate was decanted to another centrifuge tube before TLC separation.

Thin-layer chromatography was carried out on Brinkmann Silica Gel G (0.5-mm. thickness) containing 1% zinc orthosilicate:manganese phosphor in the following solvents:

Solvent A. Ethyl ether:petroleum ether:acetic acid (20:5:1)

Solvent B. Hexane:acetone:toluene (2:2:1)

Solvent C. Ethyl ether:hexane:ethanol (15:4:1)

Solvent D. Benzene:ethyl acetate:methylene chloride (9:5:3)

The concentrated ether extract was applied to the plates as a band. After development with solvent A, the fluorescence-quenching bands were removed, extracted several times with redistilled acetone, and the concentrated extracts were rechromatographed with solvent B. Repeated purification in this manner was required before a purity suitable for physical identification was achieved. Minor photoproducts were tentatively identified by cochromatography with the authentic compounds. Two-dimensional chromatography used solvent A in the first direction and solvent B in the second.

Detection of phenolic compounds employed 1% p-nitrobenzenediazonium fluoborate in 20% aqueous sodium acetate solution. Compounds containing —NH$_2$ or —NHCHO groups were detected by exposing the developed plates to dinitrogen trioxide (generated from sodium nitrite and hydrochloric acid) and then spraying with 1% aqueous N-(1-naphthyl)ethylenediamine dihydrochloride; a positive reaction was indicated by formation of a purple color.

RESULTS AND DISCUSSION

Under summer sunlight in Davis, Calif., the decomposition of monuron in dilute aqueous solution amounted to less than 6% in 14 days. The breakdown pattern was not particularly dependent upon the initial monuron concentration; solutions containing either 200 p.p.m. or 20 p.p.m. produced the same decomposition products. Two-dimensional TLC (Figures 2a and 2b) demonstrated the close similarity between monuron photodecomposition in sunlight and under controlled laboratory conditions. However, prolonged irradiation (e.g., 10 days) or a fast flow of air in the preparative photoreactor resulted in a brownish solution, and the red pigments which contributed the pink tone to the sunlight-irradiated solutions were not observed. Irradiation with an immersion-type low-pressure mercury arc lamp (Henderson and Crosby, 1967) also failed to yield the red pigments, although several unidentified compounds were formed in addition to those produced in sunlight.

Table I. Photodecomposition Products of Monuron

Compound	Structure	Solvent			
		A	B	C	D
		R_f			
Monuron	I	0.34	0.57	0.17	0.25
3-(p-Chlorophenyl)-1-formyl-1-methylurea	II	0.70	0.70	0.44	0.48
1-(p-Chlorophenyl)-3-methylurea	III	0.32	0.52	0.11	0.23
1-(p-Chlorophenyl)-3-formylurea[a]	IV	0.68	0.61	0.27	0.45
p-Chlorophenylurea[a]	V	0.37	0.30	0.07	0.13
3-(p-Chloro-o-hydroxyphenyl)-1,1-dimethylurea	VI	0.44	0.57	—	—
4,4'-Dichlorocarbanilide	VII	0.84	0.71	0.52	0.54
p-Chloroformanilide[a]	VIII	0.60	0.59	0.24	0.40
p-Chloroaniline[a]	IX	0.84	0.69	0.51	0.58

[a] Chromatographic and chromogenic identification only.

Figure 3. Photodecomposition of monuron in aqueous solution under aerobic conditions

Photoproducts (Table I) were identified by comparison of their spectral and/or chromatographic properties with those of authentic standards, and a scheme for the photodecomposition of monuron in aqueous solution is proposed in Figure 3. The monodemethylated compound 3-(p-chlorophenyl)-1-methylurea (III) was the principal product. Photodecomposition of the formylureas II and IV proceeded smoothly under both aerobic and anaerobic conditions in aqueous solutions to provide the deformylated products III and V. However, when they were irradiated for the same length of time on a dry chromatoplate, no deformylation took place; it appears that the decomposition is hydrolytic but very slow in the absence of light.

4'-Chloroformanilide (VIII) and p-chloroaniline (IX) also were present in the photolysate but not necessarily because of stepwise degradation. 4,4'-Dichlorocarbanilide (VII) and p-chloroaniline could be formed via p-chlorophenyl isocyanate (Smith, 1965); probably because of the demonstrated instability of isocyanates in water; the authors were unable to obtain direct evidence for this intermediate.

3-(4-Chloro-2-hydroxyphenyl)-1,1-dimethylurea (VI) had an R_f of 0.44 on TLC with solvent A and gave a positive phenol reaction. Upon standing, the chromatograms darkened gradually. The white crystals melted at 176° to 177° C., and their IR spectrum contained a broad band at 3030 cm.$^{-1}$ suggesting intramolecular bonding of the phenolic hydrogen and the carbonyl oxygen (Nakanishi, 1962). In the mass spectrum, m/e 214 (parent) and m/e 169 [base, parent less $NH(CH_3)_2$] supported the proposed structure. Methylation with diazomethane gave a light brown oil whose IR and mass spectra matched those of synthesized 3-(4-chloro-2-methoxyphenyl)-1,1-dimethylurea. Although γ-irradiation of substituted aromatic compounds in dilute aqueous solution also has yielded hydroxylated products (Fendler and Gasowski, 1968), substitution of aromatic hydrogen by the hydroxyl group in a sunlight-induced photoreaction has not been reported previously in the study of pesticide photodecomposition.

Under the influence of sunlight or UV irradiation, aromatic halogen substituents were replaced by hydroxyl groups during the photodecomposition of 2,4-dichlorophenoxyacetic acid (Crosby and Tutass, 1966) and 3-(p-bromophenyl)-1-methoxy-1-methylurea (Rosen and Strusz, 1968). Replacement of the aromatic chlorine of monuron represented a minor reaction in the present experiments, if indeed it occurred at all, although Rosen et al. (1969) indicated that the hydroxy
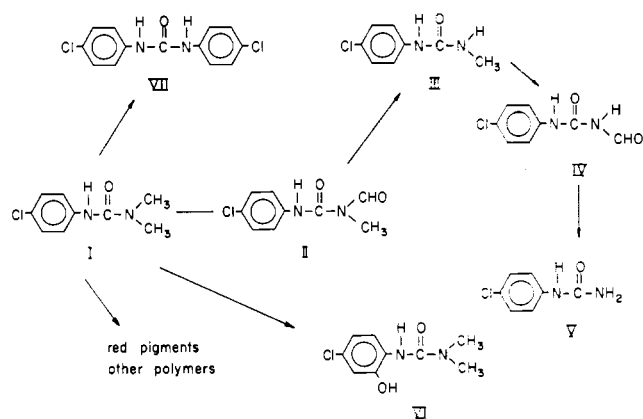
compound was formed under similar conditions. The pH of monuron solutions was approximately the same (ca. pH 8) before and after sunlight irradiation indicating that hydrogen chloride was not liberated in significant quantity.

Thin-layer chromatography of the methylene chloride extracts gave as a single major product a dark-red, high-melting solid soluble in dimethylsulfoxide, acetone, and methylene chloride. It was slightly soluble in ether and water, but insoluble in nonpolar solvents such as hexane. The UV spectrum of its aqueous solution showed maxima at 235, 270, 360, and 500 mµ similar to that of an oxidation product of p-chloroaniline, 2-p-chloro-anilino-5-amino-benzoquinone di-p-chloroanil (Daniels and Saunders, 1953). The mass spectrum was inconclusive, but the NMR spectrum suggested that the dimethylamido group was still intact (δ 2.88). Because of the small amount of sample, further characterization was not successful; however, it is apparent that the red compound represents yet another type of monuron oxidation product.

The dark brown nonextractable material was soluble in 5% sodium hydroxide solution and its IR spectrum was similar to that of the humic acid formed in the photolysis of dichlorophenoxyacetic acid (Crosby and Tutass, 1966). Under anaerobic conditions, the rate of photodecomposition was reduced greatly and neither red pigment nor humic acid type polymers were detected. It is apparent that photooxidation represents by far the most important route of monuron photodecomposition and may explain why 3-(p-hydroxyphenyl)-1,1-dimethylurea was not isolated from the photolysis mixture.

The analogy between the products of monuron photodecomposition and monuron metabolism is striking. Man and laboratory animals long have been known both to demethylate and to hydroxylate aromatic amine derivatives. For example, rabbits convert phenylurea to p-hydroxyphenylurea, and p-chloroaniline is oxidized primarily to 2-hydroxy-4-chloroaniline (Williams, 1959). Ernst and Böhme (1965) reported that monuron was metabolized in the rat to yield 3-(4-chlorophenyl)urea (V), 3-(4-chloro-2-hydroxyphenyl)urea, 3-(4-chloro-2-hydroxyphenyl)-1-methylurea, and related compounds. Complex red pigments analogous to the monuron photolysis product also were formed by the action of peroxidase on p-chloroaniline (Daniels and Saunders, 1953).

Higher plants (Smith and Sheets, 1967; Swanson and Swanson, 1968) and soil microorganisms (Dalton et al., 1965) similarly dealkylate monuron. Although hydroxylated products have not been reported in these instances, the capacity of higher and lower plants to hydroxylate similar compounds has been demonstrated repeatedly (Menzie, 1966),

and the large proportion of unidentified, polar monuron metabolites found in cotton and soybean plants, for instance (Smith and Sheets, 1967), well might represent phenolic compounds or their conjugates.

ACKNOWLEDGMENT

We wish to thank Kei Miyano, G. F. Mallett, Kenneth Osborne, and T. J. Schnitter for technical assistance with various aspects of this investigation.

LITERATURE CITED

Comes, R. D., Timmons, F. L., *Weeds* **13**, 81 (1965).
Crosby, D. G., Tutass, H. O., J. AGR. FOOD CHEM. **14**, 596 (1966).
Dalton, R. L., Evans, A. W., Rhodes, R. C., *Proc. S. W. Weed Control Conf.*, **18**, 72 (1965).
Daniels, D. G. H., Saunders, B. C., *J. Chem. Soc.*, **1953**, 822.
Ernst, W., Böhme, C., *Food Cosmet. Toxicol.* **3**, 789 (1965).
Fendler, J. H., Gasowski, G. L., *J. Org. Chem.* **33**, 2755 (1968).
Geissbühler, H., Haselbach, C., Aebi, H., Ebner, L., *Weed Res.* **3**, 277 (1963).
Gerjovich, H. J., Johnson, R. S., (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,762,695 (Sept. 11, 1956).
Henderson, G. L., Crosby, D. G., J. AGR. FOOD CHEM. **15**, 888 (1967).
Jordan, L. S., Coggins, C. W., Day, B. E., Clerx, W. A., *Weeds* **12**, 1 (1964).
Jordan, L. S., Day, B. E., Clerx, W. A., *Res. Progr. Rep., Western Weed Control Conf.*, 80 (1963).
Jordan, L. S., Mann, J. D., Day, B. E., *Weeds* **13**, 43 (1965).
Menzie, C. M., "Metabolism of Pesticides," Special Scientific Report: Wildlife No. 96, U. S. Dept. of Interior, Washington, D. C., 1966.
Nakanishi, K., "Infrared Absorption Spectroscopy," p. 30, Holden-Day, Inc., San Francisco, 1962.
Pollock, J. R. A., Stevens, R., Eds., "Dictionary of Organic Compounds," Vol. **2**, p. 627, Oxford University Press, New York, 1965.
Rosen, J. D., Strusz, R. F., J. AGR. FOOD CHEM. **16**, 568 (1968).
Rosen, J. D., Strusz, R. F., Still, C. C., J. AGR. FOOD CHEM. **17**, 206 (1969).
Sadtler Research Laboratories, "The Sadtler Standard Spectra. Standard Infrared," Vol. **28**, No. 28084, Philadelphia, Pa., 1966.
Sheets, T. L., Danielson, L. L., "The Nature and Fate of Chemicals Applied to Soils, Plants, and Animals, pp. 170–80, U.S.D.A., A.R.S. 20–9. Mimeo., 1960.
Smith, P. A. S., "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. **1**, p. 239, W. A. Benjamin, Inc., New York, 1965.
Smith, J. W., Sheets, T. J., J. AGR. FOOD CHEM. **15**, 577 (1967).
Swanson, C. R., Swanson, H. R., *Weed Sci.* **16**, 137 (1968).
Weldon, L. W., Timmons, F. L., *Weeds* **9**, 111 (1961).
Williams, R. T., "Detoxication Mechanisms," 2nd ed., John Wiley and Sons, Inc., New York, 1959.