reference standards. All the degradation products listed in Table II have been reported as metabolites of terbacil in dog urine (Rhodes et al., 1969). Jordan et al. (1975) have reported that metabolite A is the major metabolite in orange seedlings, cultured in aqueous solutions of [2-^{14}C]terbacil and that 5-chlorouracil was not detected as a metabolite of terbacil.

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LITERATURE CITED

Gardiner, J. A., Rhodes, R. C., Adams, J. B., Soboczenski, E. J., *J. Agric. Food Chem.* **17**, 980 (1969).
Holt, R. F., Pease, H. L., *J. Agric. Food Chem.* **25**, 373 (1977).
Jordon, L. S., Zurqiyah, A. A., Clerx, W. A., Leasch, J. G., *Arch. Environ. Contam. Toxicol.* **3**, 268 (1975).
Pease, H. L., *J. Agric. Food Chem.* **16**, 54 (1968).
Reiser, R. W., *Org. Mass Spectrom.* **2**, 467 (1969).
Rhodes, R. C., Reiser, R. W., Gardiner, J. A., Sherman, H., *J. Agric. Food Chem.* **17**, 974 (1969).
Smith, G. N., Ludwig, P. D., Wright, K. C., Bauriedel, W. R., *J. Agric. Food Chem.* **12**, 172 (1964).
Wolf, D. C., Martin, J. P., *Soil Sci. Soc. Am. Proc.* **38**, 921 (1974).
Zimdahl, R. L., Freed, V. H., Montgomery, M. L., Furtick, W. R., *Weed Res.* **10**, 18 (1970).

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Photolysis of 3-(4-Chlorophenyl)-1,1-dimethylurea in Dilute Aqueous Solution

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Saturated aqueous solutions of 3-(4-chlorophenyl)-1,1-dimethylurea (monuron) of approximately 200 ppm concentration were photolyzed. Irradiations were performed with either a 450 W Hanovia high-pressure mercury arc or a Rayonet photochemical reactor fitted with sunlight lamps. Light from both systems was filtered through Pyrex glass to more closely resemble sunlight by elimination of the shorter wavelength bands. Eleven products were identified from the photoreaction. Ring hydroxylation, methyl oxidation, N-demethylation, dechlorination, and dimerization were the main processes that occurred. The same products were obtained with both light sources, but the distributions of product yields were slightly different. Yields were measured at various exposure levels for principal photoproducts, and the quantum efficiency for monuron loss (Φ = 0.1) and photoproduct formation were estimated.

The first indication that substituted phenylurea herbicides were affected by ultraviolet radiation was the observed decrease in the herbicidal activity of these compounds with exposure to sunlight (Hill et al., 1955; Weldon and Timmons, 1961; Comes and Timmons, 1965). Since this initial observation, interest has developed in the photolysis of substituted phenylureas with particular emphasis on the photodegradation of 3-(4-chlorophenyl)-1,1-dimethylurea (monuron, cf. structure I, Table I). Preliminary studies were carried out by Jordan and coworkers (1964) who investigated the change in absorption spectra of monuron with increased dosage of ultraviolet light. A more extensive study was performed by Crosby and Tang (1969) in which saturated aqueous solutions of monuron were irradiated by natural sunlight and by blacklight fluorescence. Four photoproducts (II, III, IV, VII) were clearly identified, and the partial characterization of four additional photoproducts was given. Rosen et al. (1969) examined the photolysis of monuron in aqueous solution by sunlight, and the hydroxylated photoproduct (V), a previously unobserved product, was identified. Although other photoproducts were obtained in this study, identification of these products was not attempted because of the extensive work by Crosby and Tang (1969). Mazzocchi and Rao (1972) examined the photochemistry of methanolic solutions of monuron under nonoxygenated conditions employing a low-pressure mercury lamp (254 nm). A photorearrangement similar to the photo-Fries reaction of aryl esters and the analogous rearrangement of anilides was observed. The identified rearrangement products were the 2-amino- and 4-amino-*N*,*N*-dimethylbenzamide.

We extended the study on the photolysis of monuron to include the identification of additional photoproducts and the estimation of product yields. Although the conditions employed were not strictly those observed in the environment, the results may give some indication as to what might be expected under environmental conditions since the studies were performed in aqueous oxygenated solutions.

EXPERIMENTAL SECTION

Materials. Monuron was prepared by reaction of a chloroform solution of 4-chlorophenylisocyanate (K and K) with dimethylamine (Eastman). The product was initially recrystallized several times from chloroform and finally recrystallized from isopropanol until a homogeneous product with a melting point of 172–173 °C (uncorrected) was afforded. Spectral properties that verify the identity of the synthetic product are given in the Identification of Photoproducts section. Previously synthesized [*ring*-^{14}C]monuron (Tanaka, 1970) was repurified before use by the thin-layer chromatography (TLC).

Equipment. Spectrometric measurements for actinometry were taken on a Beckman DB spectrophotometer. Infrared (IR) spectra were recorded on a Perkin-Elmer 337 spectrophotometer equipped with beam condenser. The samples were analyzed in 1.5 mm micro KBr pellets. Mass spectra were obtained on a Varian CH-5DF spectrometer at 70 eV. The samples were introduced by means of a temperature-programmed solid sample probe. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian A-60A spectrometer equipped with Fourier transform (Digilab) capability. Tetramethylsilane was employed as the internal standard. Preparative TLC for

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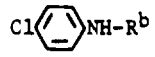
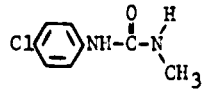
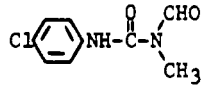
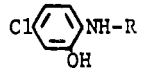
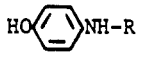
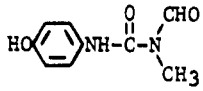
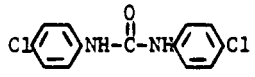
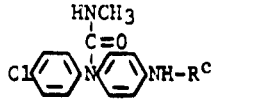
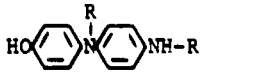
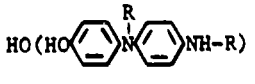
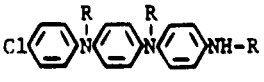
Table I. Thin-Layer Chromatographic Solvent Systems Employed to Purify Photoproducts

No.	Compd	Structure	Solvents[a]
I	3-(4-Chlorophenyl)-1,1-dimethylurea		C, A
II	3-(4-Chlorophenyl)-1-methylurea		C, A
III	3-(4-Chlorophenyl)-1-formyl-1-methylurea		C, B
IV	3-(4-Chloro-2-hydroxyphenyl)-1,1-dimethylurea		C, A
V	3-(4-Hydroxyphenyl)-1,1-dimethylurea		C, A, D
VI	3-(4-Hydroxyphenyl)-1-formyl-1-methylurea		C, E
VII	4,4'-Dichlorocarbanilide		C, B
VIII	3-{4-[*N*-(*N'*,*N'*-dimethylaminocarbonyl)-4'-chloroanilino]-phenyl}-1,1-dimethylurea (dimer)		C, A, D
IX	Monodemethylated dimer		C, A, D
X	Hydroxylated dimer		C, A, D, C,[d] D[e]
XI	Dihydroxylated dimer		C, A, D, C,[d] D[e]
XII	Trimer		C, A, D, C,[d] D[e]

[a] TLC solvent systems: A, ethyl ether-*n*-pentane-*n*-hexane-acetic acid (40:5:5:2); B, benzene-*n*-hexane-acetone (3:6:2); C, benzene-acetone (2:1); D, isopropyl ether-acetone (7:3); E, ethyl acetate-*n*-hexane (5:1). [b] R = $C(=O)N(CH_3)_2$. [c] One of two possible isomeric structures. [d] Plate was developed two times in the same solvent. [e] Methylated X and XI was separated from X by four repetitive developments in D.

the isolation and characterization of the photoproducts was accomplished on 0.5 mm thick silica gel HF plates. Two-dimensional TLC to separate the photoproducts for quantitation of yields was performed on precoated plates of Anasil HF of 0.25 mm thickness. Autoradiograms were taken on blue-sensitive Kodak x-ray film. Radioactivity was assayed in a Packard 3375 liquid scintillation spectrometer using Instagel (Packard) as the counting solution. The external standard method was employed for determination of counter efficiency.

Two light sources were utilized for the photochemical experiments. One source was the Rayonet RPR-204 reactor (The Southern New England Ultraviolet Co.) equipped with four sunlight RUL-3000 lamps with peak spectral energy distribution at 300 nm. Samples in the Rayonet system were held in standard taper Pyrex tubes with the dimensions of 15 mm o.d. by 20 cm. Each sample tube was sealed with a glass stopper held in place by a wire clamp. The other light source was a 450 W Hanovia high-pressure immersion lamp housed in a photochemical reaction system (Ace Glass Inc.). The light from this system was filtered with a Pyrex (7740) glass filter which had a minimum UV-cutoff at approximately 280 nm.

Chemical Actinometry. Actinometry of the Rayonet photoreactor was accomplished with a 0.006 M solution of potassium ferrioxalate according to the method developed by Parker and Hatchard (Calvert and Pitts, 1966). The molar extinction coefficient, measured at 510 nm for Fe^{2+}–phenanthroline complex, was determined to be 1.105 × 10^4 L/mol-cm. Two sets containing quadruplicate samples of freshly prepared ferrioxalate actinometer were employed to measure the light intensity entering into the reaction vessel. An estimation of light absorption by the aqueous monuron solutions was then made by taking the following factors into consideration: (a) spectrum of the sunlight lamps, (b) transmission spectrum of 2 mm thick Pyrex glass, (c) absorption spectrum of the ferrioxalate actinometer, (d) absorption spectrum of aqueous monuron, and (e) light intensity measured with the ferrioxalate actinometer. Employing these factors, it was estimated that only 11% of the radiation measured by the chemical actinometer was absorbed by the monuron solution.

Experimental Procedure. Saturated aqueous solutions were prepared by continuously stirring solid monuron

in distilled water for 24 h. Following equilibration, the aqueous solutions were filtered to remove the undissolved material. The concentration of monuron dissolved into water was measured gravimetrically and by gas–liquid chromatography (Tanaka and Wien, 1973). Both methods were in general agreement and indicated that 200 to 210 ppm were in solution.

In a typical experiment employing the Rayonet photoreactor, 15-mL aqueous samples of monuron (ca. 200 ppm) were heated, prior to irradiation, in a water bath to 50 °C which was the approximate operating temperature of the photoreactor. Samples were then photolyzed for 135 min to obtain a maximum distribution of photoproducts. In preparative experiments using the Hanovia lamp, 500 mL of saturated aqueous monuron was irradiated for 24 h. Temperature of the reaction during photolysis in the Hanovia system was maintained at approximately 23 °C with flowing water.

The photolyzed solutions were extracted with ethyl acetate, dried over anhydrous magnesium sulfate, filtered, and concentrated. The concentrated extracts were streaked onto preparative TLC plates, and the chromatograms were developed in solvent C (Table I). The separated bands were visualized by fluorescence quenching of ultraviolet light. The material in each band was isolated and further purified by rechromatographing in additional solvent systems as given in Table I. Mobilities exhibited by the dimeric and trimeric products were similar in all the solvent systems employed and were in the order of R_f 0.3 or lower.

For the labeled experiments, monuron solutions were prepared in distilled water at 175 ppm concentration to ensure complete dissolution of the radioactive material. [*ring*-^{14}C]Monuron with a sp act. of 1 mCi/mmol was utilized for the estimation of product yields at the various exposure levels. In the Rayonet reactor, 2-mL samples were irradiated in the manner previously described for the nonradioactive samples. Solutions were photolyzed for periods of 45, 90, 135, and 180 min. When the Hanovia lamp was employed, sample tubes with the dimensions of 6 mm o.d. × 19 cm were used. These tubes were held in a circular configuration by means of a wire support around the immersion well. Monuron solutions of 1.5-mL were photolyzed for periods of 3, 5, 15, 25, and 35 h. The radioactive samples were spotted directly onto TLC plates, allowed to dry, and then developed in two dimensions using solvents C and A. The separated compounds on the TLC plates were located by autoradiography, and each spot was removed and then assayed by liquid scintillation counting.

Identification of Photoproducts. The spectral and chemical data given below were employed for the characterization of the photoproducts. Authentic standards of I, II, III, and VII were prepared in the laboratory for verification of their identity. The chemical structures for compounds I thru XII are given in Table I.

I. IR, 3300 (NH), 1645 (C=O), 1250, 1192, 1092, 835 (doublet) cm^{-1}; mass spectrum, *m/e* (rel intensity) 198 (molecular ion, 77), 153 (26), 72 (100), 45 (69), 44 (60); NMR, (acetone-d_6) 2.90 (H, singlet, NH, exchangeable with D_2O treatment), 3.00 (6 H, singlet, $N(CH_3)_2$), 7.17 and 7.57 ppm (4 H, 2 doublets, J = 9 Hz, para-substituted aromatic ring).

II. IR, 3290 (NH), 1645 (C=O), 1243, 1090, 833 cm^{-1}; mass spectrum, *m/e* (rel intensity) 184 (molecular ion, 17), 153 (3), 127 (100), 58 (38).

III. IR, 3290 (NH), 1720 (C=O, formyl), 1595 (C=O), 1222, 1090, 1065, 832 (doublet), 710, 510 cm^{-1}; mass spectrum, *m/e* (rel intensity) 212 (molecular ion, 23), 153 (100), 127 (15). Base peak in the standard was at *m/e* 28; however, in the unknown material impurities present in the low mass region obscured this peak. Color reaction with N_2O_3 and *N*-(1-naphthyl)ethylenediamine dihydrochloride gave a positve test for the -NHCHO group (Crosby and Tang, 1969).

IV. IR, 3430 (OH), 3030 (NH), 1640 (C=O), 1260, 1115, 905, 846, 545 cm^{-1}; mass spectrum, *m/e* (rel intensity) 214 (molecular ion, 24), 169 (45), 72 (96), 45 (100), 44 (83); NMR, (acetone-d_6) 2.95 (1 H, singlet, NH), 3.04 (6 H, singlet, $N(CH_3)_2$), 3.42 (1 H, singlet, diffuse peak, OH), 6.73 (1 H, doublet of doublets, J = 9 and 3 Hz, meta proton), 6.83 (1 H, doublet, J = 3 Hz, meta proton), 7.25 ppm (1 H, doublet, J = 9 Hz, ortho proton). After methylation with diazomethane, the mass spectrum afforded a molecular ion at *m/e* 228. The NMR spectrum showed a very diffuse peak for the hydroxyl group, indicating hydrogen bonding with the carbonyl of urea; thus, hydrogen bonding of this nature is only possible if the hydroxyl group on the aromatic ring is substituted in the ortho position.

V. IR, 3350 (OH), 3240 (NH), 1635 (C=O), 1245 (broad), 1070, 850, 830, 515 cm^{-1}; mass spectrum, *m/e* (rel intensity) 180 (molecular ion, 32), 135 (12), 72 (100), 45 (11), 44 (20); NMR, (acetone-d_6) 2.82 (2 H, singlet, broad diffuse peak, OH and NH), 2.95 (6 H singlet, $N(CH_3)_2$), 6.66 and 7.26 ppm (4 H, 2 doublets, J = 9 Hz, para-disubstituted ring). In the mass spectrum the characteristic isotopic distribution for chlorine was absent; upon methylation with diazomethane (at 32 °C for 48 h in methanol–diethyl ether), the molecular ion of the derivatized product was observed at *m/e* 194.

VI. Mass spectrum, *m/e* (rel intensity) 194 (molecular ion, 4), 135 (39), 107 (18), 28 (100). Isotopic distribution for chlorine was absent.

VII. IR, 3280 (NH), 1630 (C=O), 1240, 1105, 1086, 1015, 825, 640 (broad), 505 cm^{-1}; mass spectrum, *m/e* (rel intensity) 280 (molecular ion, 55), 153 (21), 127 (100). The isotopic cluster of the molecular ion was characteristic for the presence of two chlorine atoms.

VIII. IR, 3330 (NH), 1660 (C=O, doublet), 1240, 1185, 840, 820, 756 cm^{-1}; mass spectrum, *m/e* (rel intensity) 360 (molecular ion, 33), 315 (33), 270 (33), 72 (100); NMR (dimethyl sulfoxide-d_6) 2.76 (6 H, singlet, $N(CH_3)_2$), 2.94 (6 H, singlet, $N(CH_3)_2$), 7.00 to 7.70 (8 H, multiplet, aromatic protons), 8.32 ppm (H, singlet, NH).

IX. IR, 3430 (NH), 1640 (C=O, multiplet), 1246 (1100 (broad), 830 cm^{-1}; mass spectrum, *m/e* (rel intensity) 346 (molecular ion, 1), 301 (28), 244 (100), 72 (24), 58 (16). The carbonyl absorption in the IR spectrum at 1640 cm^{-1} was a multiplet, indicating the possible presence of more than one carbonyl group; on the other hand, this multiplet may be due to impurities since the amount of this material available was very limited. Additional evidence is required to determine if this is a single product or a mixture of two isomers.

X. Derivatization of the hydroxyl group by methylation was accomplished by the same procedure employed for V. IR, (methylated) 3325 (NH), 1640 (C=O, doublet), 1214, 1180, 840, 758 cm^{-1}; mass spectrum (methylated), *m/e* (rel intensity) 356 (molecular ion, 11), 311 (58), 266 (45), 72 (100). In the IR spectrum of VIII, the underivatized hydroxyl group of X was observed as an impurity; the absorption of the OH group was at 3440 cm^{-1}.

XI. IR, (monomethylated) 3450–3250 (broad, NH and OH), 1645 (C=O, doublet), 1500 (doublet), 1210, 1122, 1025, 830, 758 cm^{-1}; mass spectrum (monomethylated), *m/e* (rel intensity) 372 (molecular ion, 3), 327 (33), 282 (28),

72 (100). Methylation was performed by the same procedure employed for V. Attempts were made to derivatize the second hydroxyl function by increasing time and temperature of reaction without success.

XII. Mass spectrum, m/e 522 (molecular ion), 477, 387, 342, 72, 45. The chlorine isotopic cluster indicated the presence of only one chlorine atom. The limited amount of material, unfortunately, made it impossible to obtain the relative intensities of the fragment ions. In the spectrum, the low mass fragments were completely off-scale at the amplification required to demonstrate the presence of the molecular ion.

DISCUSSION

The structures of the identified photoproducts are given in Table I. Products II, III, IV, and VII were previously characterized (Crosby and Tang, 1969), and the position of hydroxylation on IV was verified to be ortho by comparison with an authentic standard. Identification of V was reported by Rosen et al. (1969), and the position of hydroxylation was also verified.

Several isolated fractions of III were pooled for further purification, and during purification VI was observed as a trace impurity. Owing to the limited amount of material isolated, only mass spectral analysis could be performed. However, the mass spectrum of VI did show the expected molecular ion, base peak, and fragmentation pattern in comparison with spectral data of III and V.

Structures for VIII and XII are given in Table I with ring coupling tentatively at the para position. The chlorine isotopic distribution in the mass spectra clearly indicated the presence of only one chlorine atom in each molecular structure. Therefore, the site of ring coupling appeared to be at the para position because chlorine was eliminated from that position during formation of the dimeric and trimeric products. A coupling reaction of similar nature was observed by Rosen et al. (1970) in which 4-(3,4-dichloroanilino)-3,3′,4′-trichloroazobenzene was identified from a FMN-sensitized photoreaction of 3,4-dichloroaniline in aqueous solution. In this reaction a 3,4-dichloroanilino group was substituted for chlorine in the para position of tetrachloroazobenzene, and the position of anilino substitution was verified by synthesis of authentic material (Rosen and Siewierski, 1971). Therefore, precedence for this type of substitution with retention of position was reported. However, additional evidence must be obtained to ensure that a NIH-type shift did not occur to allow coupling at the meta position.

Product IX was characterized as a monodemethylated dimer and was depicted in Table I by one of the isomeric structures. A methyl group can be removed from either side chain, but due to the limited quantity of product available, it was not possible to determine whether IX was a mixture of the two isomeric structures or that one of the demethylated forms was preferred.

Compound X was identified as a hydroxylated dimer resulting from photohydrolysis of chlorine from the aromatic ring. Hydroxyl substitution on V, which was also formed by chlorine photohydrolysis, was verified to be at the para position by NMR spectrometry (characteristic pair of doublets at 6.66 and 7.26 ppm, J = 9 Hz) and by comparison with an authentic standard (Rosen et al., 1969). Therefore, by analogy hydroxyl substitution on X would also be expected to be at the para position.

During the separation of X from XII after treatment with diazomethane, a small quantity of XI was observed. Mass spectral analysis of XI indicated the presence of two hydroxyl groups, but only one hydroxyl function appeared to be methylated after diazomethane treatment. Further attempts to methylate the second hydroxyl group failed. The IR spectrum of XI showed a broad band for the underivatized hydroxyl, suggesting that hydrogen bonding was occurring. Hydrogen bonding, however, appeared to be weak because a definite shift in the absorption band toward longer wavelengths was not observed. Therefore, the cumulative evidence suggested that the underivatized hydroxyl group was probably highly hindered. To examine this hypothesis further, a molecular model of XI was prepared employing Courtauld atomic models (The Ealing Corp., Cambridge, Mass.) with a hydroxyl group placed ortho to the position of ring juncture. When the ortho hydroxyl was replaced by methoxyl, the molecular model became restricted to such an extent that all groups were pressed against one another and molecular motion was completely restricted. With the nonmethylated hydroxyl, motion was still restricted but to a lesser degree, and the groups were no longer pressed against each other as in the case of the methoxylated model. Therefore, it appears reasonable that XI contained a hydroxyl group situated ortho to the position of ring juncture on one of the phenyl rings, and this hydroxyl function was apparently hindered to such an extent that methylation was not possible.

Table II. Percent Yields Derived from Photolysis in the Rayonet Photoreactor

Compd	Exposure time, min			
	45	90	135	180
I[a]	71	57	44	34
II	0.5	0.6	0.7	0.6
III	T[b]	T	T	T
V	3.8	4.7	6.0	7.1
VIII	2.0	1.5	1.5	1.5
X	1.1	2.0	1.4	1.6
XII	0.7	0.7	1.3	1.5
Polymer[c]	6	12	21	31

[a] Monuron recovered. [b] Less than 0.05%; detected as trace by autoradiography. [c] Percent of monuron incorporated into polymeric material (TLC origin).

Table III. Percent Yields Derived from Photolysis with the 450 W Hanovia Lamp

Compd	Exposure time, h				
	3	5	15	25	35
I[a]	89	84	63	45	37
II	0.3	0.4	0.7	1	1
III	T[b]	0.5	0.5	1	0.4
V	0.3	3	2.5	2	1
VIII	0.3	1	1.6	1.6	1
X	0	0.2	0.2	0.4	0.4
XII	0	0.2	0.3	0.3	0.5
Polymer[c]	2	4	14	20	29

[a] Monuron recovered. [b] Less than 0.05%; detected as trace by autoradiography. [c] Percent of monuron incorporated into polymeric material (TLC origin).

In Tables II and III are given the percent product yields obtained from monuron photolysis with increased cumulative dosage in the Rayonet and Hanovia light systems. For comparison purposes, the periods of irradiation were selected so that during the time course study there was a period when approximately the same fraction of monuron was altered by both systems. All identified photoproducts could not be detected at the different exposure levels. Consequently, only those detected at several exposure levels were measured for yield determination. The same products were obtained with both light sources; however, the distribution of product yields was slightly different. A very noticeable difference was observed in the formation of V which was approximately three times as great in the

Table IV. Quantum Yields Measured in the Photolysis of Monuron (Rayonet Photoreactor)

Compd[a]	Φ[b]
I	0.1[c]
II	0.001
V	0.01
VIII	0.006
X	0.003
XII	0.002
Polymer[d]	0.02

[a] Not all products were observed at this exposure level. [b] Irradiation time was 45 min. [c] This value represents Φ loss. [d] Yield is based on the amount of monuron incorporated.

Rayonet reactor at 56% monuron loss. In the Rayonet system, the concentration of V increased steadily with increased exposure time. With the Hanovia lamp, on the other hand, the peak concentration of V was reached at approximately 5 to 10 h and then steadily decreased with continued radiation. The peak spectral energy of the Rayonet system was at 300 nm which apparently afforded a greater activation of the aromatic ring (larger formation of V, VIII, X, and XII). The Hanovia lamp, with its main spectral lines above 300 nm, yielded a greater abundance of product where the side chain was altered as evidenced by the yields of II and III. The polymer yields in Tables II and III were based on the fraction of monuron incorporated into the polymeric material, and the polymeric material, in turn, was defined as that material which remained on the TLC origin after two-dimensional chromatography. In the material balance studies when replicate samples were used, fluctuations observed in the hydroxylated product yields were also reflected in the polymer yields. Therefore, polymer formation appears to be derived mainly from oxidation and condensation of the hydroxylated by-products. As expected, the quantity of polymer increased steadily with increased exposure time.

Material balance at the different exposure levels (Tables II and III) indicated a radiocarbon loss of approximately 10 to 30%. If monuron samples were assayed for radioactivity immediately after photolysis, essentially a quantitative recovery of radiocarbon was obtained. Sparging the photolyzed samples with nitrogen into CO_2 traps demonstrated that carbon dioxide formation from ring-labeled material was negligible. When aqueous photolyzed samples were reduced to dryness under high vacuum, only a 1 to 2% transfer of radiocarbon was observed. Therefore, the direct formation of volatile photoproducts was not significant with respect to radiocarbon loss. The accumulated evidence suggested that one or more unstable nonvolatile photoproducts were formed, and the unstable material decomposed during handling into volatile by-products. With this in mind, the radiocarbon loss would appear to be occurring during spotting, developing, and drying of the TLC plates. This would then account for the significant material loss observed in the analysis of the photolyzed samples. Identification of an unstable nonvolatile photoproduct(s) appears rather uncertain, but further information regarding the character of the unstable material may possibly be obtained by identification of the volatile decomposition products.

The quantum yields estimated for monuron photolysis are given in Table IV. In the estimation of these yields it was necessary to consider several different factors; consequently, the quantum efficiency for monuron loss (Φ = 0.1) was only approximate. However, the important factor to consider upon examining the yields given in Table IV is the order of magnitude. These low quantum efficiencies suggest that direct photodecomposition of monuron under environmental conditions would not be expected to be a major pathway for the degradation of this material. On the other hand, it is possible that sunlight may still play an important role in the degradation of monuron because of the high intensity of sunlight and the possible participation of natural or unnatural photosensitizing agents in the environment.

LITERATURE CITED

Calvert, J. G., Pitts, J. N., "Photochemistry", Wiley, New York, N.Y., 1966, pp 783–786.
Comes, R. D., Timmons, F. L., *Weeds* **13**, 81 (1965).
Crosby, D. G., Tang, C.-S., *J. Agric. Food Chem.* **17**, 1041 (1969).
Hill, G. D., McGahen, J. W., Baker, H. M., Finnerty, D. W., Bingeman, C. W., *Agron. J.* **47**, 93 (1955).
Jordan, L. S., Coggins, C. W., Day, B. E., Clerx, W. A., *Weeds* **12**, 1 (1964).
Mazzocchi, P. H., Rao, M. P., *J. Agric. Food Chem.* **20**, 957 (1972).
Rosen, J. D., Strusz, R. F., Still, C. C., *J. Agric. Food Chem.* **17**, 206 (1969).
Rosen, J. D., Siewierski, M., Winnett, G., *J. Agric. Food Chem.* **18**, 494 (1970).
Rosen, J. D., Siewierski, M., *J. Agric. Food Chem.* **19**, 50 (1971).
Tanaka, F. S., *J. Agric. Food Chem.* **18**, 213 (1970).
Tanaka, F. S., Wien, R. G., *J. Chromatogr.* **87**, 85 (1973).
Weldon, L. W., Timmons, F. L., *Weeds* **9**, 111 (1961).

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