

Figure 2. Effects of: (I) amounts of root materials, (II) incubation time, (III) pH, and (IV) root age on the production of water-soluble radiocarbon from [¹⁴C]diazinon by the 10000g supernatant prepared from corn roots. Plants were grown in complete nutrient solutions.

amounts of water-soluble radiocarbon. An optimum activity was observed at pH 5 (Figure 2,III) after subtraction of the amounts of water-soluble radiocarbon produced by boiled plant material (controls) from that produced by the nonboiled incubation mixtures. Incubation mixtures prepared from 5-day-old roots were more active than those

prepared from younger ones (Figure 2,IV).

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Effect of Nonionic Surfactants on the Photochemistry of 3-(4-Chlorophenyl)-1,1-dimethylurea in Aqueous Solution

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Solutions of 3-(4-chlorophenyl)-1,1-dimethylurea (monuron) at approximately 200-ppm concentration were photolyzed in aqueous media containing nonionic surface-active agents. The Triton X and the Tergitol TMN series of nonionic surfactants were employed to observe the difference in effects provided by aryl- and alkyl-substituted polyoxyethylene glycols. X-100, X-405, TMN-6, and TMN-10 were used at 0.2, 0.4, 1, and 2% concentrations. All surfactant solutions were at concentrations in excess of the critical micelle concentration. Samples were examined under oxygenated and nonoxygenated conditions. The identified photoproducts were obtained from demethylation, coupling, and reductive dechlorination reactions. Surfactants increase the rate of monuron degradation, eliminate ring hydroxylation reactions, and enhance the reductive dechlorination reaction. The results indicate that the photochemical reactions occurred in the organic phase of the micelles rather than in the aqueous phase of the solvent.

The photolysis of 3-(4-chlorophenyl)-1,1-dimethylurea (monuron, I) has been studied in aqueous solution (Crosby and Tang, 1969; Rosen et al., 1969; Tanaka et al., 1977) and in methanolic solution (Mazzocchi and Rao, 1972). In these studies, pure materials were placed into solution and photolyzed. Under normal environmental conditions, however, pesticides are generally applied as formulations

which include surface-active agents. The amount of surfactant applied with a given pesticide depends on the formulation. In some instances, approximately as much surfactant (on a weight-to-weight basis) is applied as active ingredient. Therefore, there appears to be a need to determine the effect of surface-active agents on the photolytic degradation of pesticides.

Although there are three main classes of surfactants available (cationic, anionic, and nonionic), this investigation was conducted with the nonionic surfactants because of the widespread usage of these materials in pesticidal formulations. The nonionic surfactants usually contain the polyoxyethylene glycol moiety and are gen-

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Table I. Surfactants Employed in the Photochemical Study

surfactant	hydrophobe	hydrophile no. of EO ^a	cloud pt., °C	M_r , av	CMC, ^d % ^e	HLB ^g	active ingredient, % ^e
Tergitol TMN-6	2,6,8-trimethyl-4-nonanol	6	36 ^b	451	0.084	11.7	90
Tergitol TMN-10	2,6,8-trimethyl-4-nonanol	10	76	<i>f</i>	<i>f</i>	14.0	90
Triton X-100	<i>p</i> -(1,1,3,3-tetramethylbutyl)phenol	9.5	65 ^c	625	0.02	13.5	100
Triton X-405	<i>p</i> -(1,1,3,3-tetramethylbutyl)phenol	40	>100	1969	0.16	17.9	70

^a Average number of ethylene oxide (EO) units by natural distribution. ^b Tergitol series measured in 0.5% aqueous solution (Union Carbide Technical Bulletin, F-5900H). ^c Triton series measured in 1% aqueous solution (Rohm and Haas Technical Bulletin, CS-16 G/cd). ^d Critical micelle concentration measured at 25 °C (Mukerjee and Mysels, 1971). ^e Percent by weight. ^f Data unavailable. ^g Hydrophile-lipophile balance. The HLB of a nonionic surfactant is the approximate weight percent of ethylene oxide in the surfactant divided by 5. Data taken from the above cited technical bulletins.

erally prepared by the base-catalyzed addition of ethylene oxide to long-chain alcohols or alkyl phenols. Consequently, these materials are not of the same molecular weight and are classified as heterogeneous surfactants. The Triton X (Rohm and Haas) and the Tergitol TMN (Union Carbide) series of nonionic surfactants were employed in this investigation to observe the difference in effects provided by aryl- and alkyl-substituted polyoxyethylene glycols.

EXPERIMENTAL SECTION

Materials and Equipment. The Tergitol TMN and Triton X series of nonionic surface active agents (Table I) were purchased from Sigma Chemical Co., St. Louis, MO. TMN-6 and TMN-10 were obtained as 90% aqueous solutions. X-405 was received as a 70% aqueous solution and X-100 as neat material. [*ring*-¹⁴C]Monuron with a specific activity of 1 mCi/mmol and [*methyl*-¹⁴C]monuron with a specific activity of 3.4 mCi/mmol were prepared in the laboratory (Tanaka, 1970).

Photoreactor (Rayonet with 300-nm sunlight lamps), thin-layer chromatography (TLC), autoradiography, liquid scintillation counting, infrared (IR), and mass spectral equipment and methods were as previously described (Tanaka et al., 1977). A Waters Associates high-pressure liquid chromatograph (LC) equipped with two 6000-psi, high-pressure pumps, Model 660 solvent programmer, ultraviolet light (254 nm) detector, and micro-Bondapak C₁₈ column was used to achieve separations that could not be readily accomplished by TLC. Nuclear magnetic resonance (NMR) spectra were taken on a Varian XL-100 spectrometer with tetramethylsilane as the internal standard. TLC plates developed in one dimension were monitored with a Packard Model 7201 radiochromatogram scanner.

Experimental Procedure. Sample irradiations in this investigation were conducted with the following procedure in all cases. Solutions were held in 20 cm × 13 mm i.d. × 15 mm o.d. standard taper Pyrex tubes with a volume of approximately 20 mL. Samples were warmed in a water bath at 50 °C (equilibrium temperature of the photoreactor) for 30 min and then photolyzed for 135 min.

Qualitative determination of photoproducts was conducted with X-100 at 0.2% and TMN-10 at 0.4% concentration because maximum product distribution was obtained at these levels. The aqueous surfactant solutions for these studies contained 200 mg (50 μCi) of [*ring*-¹⁴C]monuron/liter of solution. Oxygen was not excluded from these samples. Reaction vessels were filled with about 15 mL of solution, and four sample tubes were irradiated each time. The irradiation procedure was repeated until the liter of aqueous monuron was photolyzed. After

photolysis, saturated aqueous sodium chloride was added and the photoproducts were extracted with ethyl acetate. The extracts were pooled, dried over magnesium sulfate, filtered, and concentrated for purification. Photoproducts were purified by preparative TLC. In the presence of TMN-10, the products could be located on the TLC plate by fluorescence quenching of ultraviolet light. In the presence of X-100, however, photoproducts could only be located by autoradiography.

The quantitative effect of surface-active agents on the photochemistry of monuron was estimated by photolyzing solutions with 0.2, 0.4, 1, and 2% (w/w) concentration of surfactant in 170 ppm aqueous monuron. Each sample contained 340 μg (1.7 μCi) of [*ring*-¹⁴C]monuron dissolved in 2 mL of aqueous surfactant solution. Triplicate samples were warmed at 50 °C for 30 min and then placed on a rotary shaker for 16 h to allow equilibration of the dissolved monuron between the aqueous phase and the micellar phase. Solubility studies have shown that equilibration periods for solutes in aqueous micellar solutions range from hours to as long as 3 months for solid polycyclic compounds (Elsworthy et al., 1968). The samples were irradiated using the general procedure. The photolyzed samples were assayed by applying 30-μL aliquots onto precoated Anasil HF plates and developing in two dimensions with solvent systems C and A (Table II). The radioactivity of the separated products was measured by liquid scintillation counting.

TLC separation of fenuron from monuron using the above solvent systems was incomplete; therefore, LC was employed to effect the separation. Implementing LC in the solvent program mode, pump A was started with 10% acetonitrile-water and pump B with acetonitrile (neat). At a chromatographic flow rate of 1.5 mL/min, the solvent program was complete when pump A reached a solvent mixture of 30% acetonitrile-water. Standard monuron and fenuron were used to establish retention times, and after introduction of aliquots of the photolyzed samples, these materials were collected from the effluent of the LC. Activity of trapped monuron and fenuron was determined by liquid scintillation counting. It was also possible to effectively separate monuron from fenuron by two-dimensional TLC using solvent system E (Hance, 1969) in conjunction with C. Yields estimated using TLC separation with solvent E as the second dimension were the same as those obtained using LC separation.

Identification and Estimation of Formaldehyde. Aqueous monuron (500 mL, 200 ppm) containing 5 μCi of [*methyl*-¹⁴C]monuron and 0.2% X-100 was used for qualitative examination for formaldehyde. A monuron solution with 0.2% TMN-10 was also employed. Samples were handled and irradiated employing the procedure used

Table II. Thin-Layer Chromatographic Solvent Systems for Purification of Photoproducts

no.	compound	structure	solvents ^a
I	3-(4-chlorophenyl)-1,1-dimethylurea		C, D, E
II	3-(4-chlorophenyl)-1-methylurea		C, D, E
III	3-phenyl-1,1-dimethylurea		C, D, E
IV	3-phenyl-1-methylurea		C, D, E
V	3-{4-[N-(N',N'-dimethylamino-carbonyl)-4'-chloroanilino]phenyl}-1,1-dimethylurea (monuron dimer)		C, D (LC) ^b
VI	3-{4-[N-(N',N'-dimethylamino-carbonyl)anilino]phenyl}-1,1-dimethylurea (fenuron dimer)		C, D (LC) ^b
VII	formaldehyde	HCHO	C, B ^c

^a TLC solvent systems: A, diethyl ether-pentane-hexane-acetic acid (40:5:5:2); B, benzene-hexane-acetone (3:6:2); C, benzene-acetone (2:1); D, chloroform-methanol (9:1); E, nitromethane-chloroform (1:1). ^b After TLC, high-pressure liquid chromatography was used for final purification. ^c As the formaldomethone derivative. R = C(=O)N(CH₃)₂, R' = C(=O)NH(CH₃).

for qualitative studies. After photolysis, 500 mg of methone was added, and the irradiated solution was stirred at 40 °C for 20 h. The formaldomethone was separated by four successive extractions with 150-mL aliquots of diethyl ether, and the material was purified by preparative TLC. Location of products on the TLC plates was accomplished by either ultraviolet light fluorescence quenching or by radiochromatogram scanning. The identity of the formaldehyde derivative was verified by mass spectrometry and by TLC cochromatography with an authentic standard.

Samples for quantitative measurement of formaldehyde were prepared by dissolving 300 μg (5.1 μCi) of [*meth-yl-¹⁴C*]monuron in 2 mL of aqueous 0.2% X-100 or 0.2% TMN-10. Sample preparation and irradiation were conducted with the procedure used for quantitative estimation of photoproducts. Triplicate samples were photolyzed under oxygenated and nonoxygenated conditions. Oxygenated samples were equilibrated with air in the reaction vessel and nonoxygenated samples were degassed with a stream of nitrogen (Tanaka and Wien, 1973). Degassing by N₂ flushing has been confirmed to be as reliable as the more tedious freeze-pump-thaw method (Lappin and Zannucci, 1971). After irradiation, 25 mg of methone dissolved in 1 mL of ethanol was added to the photolyzed monuron and the mixture was heated at 50 °C for 1 h. The derivatized sample was allowed to stand overnight at ambient temperature; then 30-μL aliquots were applied to precoated Anasil HF plates. Standard formaldomethone was used for cochromatography, and the plates were developed in solvent system C. The separated formaldomethone was removed from the TLC plates and the radioactivity was estimated for product quantitation.

For this method of formaldomethone estimation, background activity caused by other photoproducts was verified as being negligible. Background measurements were accomplished by applying 20-μL aliquots of photo-

lyzed sample without methone treatment onto TLC plates. The chromatograms were cochromatographed with standard formaldomethone in solvent system C. The separated formaldomethone spots were analyzed as described above. Radioactivity measurements for these spots were equal to background or only 35 dpm above background at a maximum.

Identification of Photoproducts. The structures of the identified photoproducts are given in Table II. Monomethyl monuron (II) and monuron dimer (V) were observed in this investigation. The analytical data for their identification were previously reported (Tanaka et al., 1977). Authentic standards for fenuron, monomethyl fenuron, and formaldomethone were prepared in the laboratory.

Fenuron (III). IR 3360, 3320 (doublet, NH), 1650 (C=O), 1252, 1192, 885, 758, 698 cm⁻¹; mass spectrum, *m/e* (rel intensity) 164 (molecular ion, 42), 119 (7), 72 (100); NMR (acetone-*d*₆) 2.78 (1 H, singlet, NH), 2.97 (6 H, single, N(CH₃)₂), 6.93-7.51 ppm (5 H, multiplet, phenyl).

Monomethyl Fenuron (IV). IR 3350, 3310 (doublet, NH), 1640 (C=O), 1305, 1240, 1165, 905, 750, 730, 690 cm⁻¹; mass spectrum, *m/e* (rel intensity) 150 (molecular ion, 73), 93 (100).

Fenuron Dimer (VI). IR 3290 (NH), 1630 (C=O), 1237, 1180, 1100, 935, 830, 755 cm⁻¹; mass spectrum, *m/e* (rel intensity) 326 (molecular ion, 2), 281 (20), 236 (41), 72 (100).

Formaldomethone (VII). TLC cochromatography; mass spectrum, *m/e* 292 (molecular ion).

RESULTS AND DISCUSSION

The photolysis of monuron in dilute aqueous solution was previously reported (Tanaka et al., 1977) and 11 photoproducts were characterized. With this information available, some assessment of the effect of nonionic surfactants on the photochemistry of monuron became possible.

Table III. Percent Product Yield from Aqueous Monuron Irradiation with Increasing Concentrations of Triton X and Tergitol TMN Surfactants

percent (w/w) of surfactant	unreacted monuron	fenuron	mono-methyl-fenuron	monuron dimer	fenuron dimer	poly-meric ^b material	other products	total recov.
0.2% TMN-6	19	50	0.8		3.5 ^a	18	0.8	92
0.4% TMN-6	13	57	0.4		3.0	17		90
1.0% TMN-6	9	56	0.2		2.7	20	0.6	89
2.0% TMN-6	4	60	0.5		4.1	21	1.5	95
0.2% TMN-10	31	36	0.4	1.7	0.6	18	2.7	90
0.4% TMN-10	18	49	0.4	0.4	1.5	20	0.1	89
1.0% TMN-10	9	57	0.3	0.5	0.9	21		89
2.0% TMN-10	5	62	0.2	0.7	0.9	20		89
0.2% X-100	25	29	0.3	1.3	1.3	27	1.5	85
0.4% X-100	16	37	0.3	1.0	1.4	32	0.5	88
1.0% X-100	6	44	0.3	0.7	1.3	36	0.4	89
2.0% X-100	6	48	0.2	1.1	1.2	31	0.3	88
0.2% X-405	28	26	0.3	1.2	0.8	24	0.6	81
0.4% X-405	18	38	0.3	1.1	0.7	27		85
1.0% X-405	4	46	0.4		2.2	40	0.4	92
2.0% X-405	2	53	0.5		2.2	37	0.7	94

^a Monuron and fenuron dimers were not always clearly resolved by TLC. ^b Yield is based on the amount of monuron incorporated into polymeric material (TLC origin).

Generally, the assumption has been that surfactant solutions behave as singly dispersed systems up to the critical micelle concentration (CMC), and osmotic coefficient measurements clearly support this view (Shinoda et al., 1963). Hence, the photochemistry of monuron with surfactant concentrations below CMC would be expected to be like aqueous solutions with an organic solvent of equal concentration. To evaluate the effect of nonionic surfactants, the experiments in this investigation were conducted with concentrations in excess of CMC. The CMC values given in Table I are only intended to indicate their order of magnitude.

Micelles by definition are reversible aggregates of a large but not infinite number of monomers and the micelle-forming reaction must obey the laws of chemical equilibrium (Mukerjee and Mysels, 1971). Micellar size varies continuously with temperature, concentration of surfactant, or other additives. When solution temperature of a nonionic surfactant is elevated, turbidity suddenly occurs in a narrow temperature range; this temperature is called the cloud point (Shinoda et al., 1963).

Monuron solutions were preheated to 50 °C to equilibrate sample temperature with the operating temperature of the photoreactor. During temperature equilibration, all samples remained clear except for those containing TMN-6. With a cloud point of 36 °C for TMN-6, turbid solutions were obtained at 50 °C. The TMN-6 samples containing monuron, however, afforded transparent solutions after photolysis. On the other hand, samples without monuron remained cloudy after irradiation. The reduction in solution pH by hydrochloric acid generated from monuron photodechlorination had no effect on cloud point (Maclay, 1956).

The identified photoproducts from irradiation of aqueous monuron solutions containing nonionic surface-active agents are shown in Table II. Only dealkylation, coupling, and reductive dehalogenation reactions were observed in the presence of surfactants. The photooxidation products (Tanaka et al., 1977; Rosen et al., 1969) observed with aqueous oxygenated monuron were not detected.

The percent yields for the monuron photoproducts obtained at varying surfactant concentrations are shown in Table III. At lower surfactant concentrations, the large micellar aggregates in the turbid TMN-6 samples exhibited a marked effect on monuron photodegradation. The

quantity of monuron decomposed and fenuron produced at 0.2 and 0.4% TMN-6 were much higher than would be expected in comparison with TMN-10 data. The recoveries of unreacted monuron in Table III were all lower than the 44% recovery (Tanaka et al., 1977) observed for aqueous monuron alone. As surfactant concentration was increased, a greater fraction of monuron was degraded even though the irradiation period was held constant. Enhancement of degradation by both classes of surfactants appears to rest mainly in their ability to partition monuron from the aqueous phase into the organic phase of the micellar structure. Since clouding occurred with the TMN-6 samples, the results could not be directly compared with data obtained with other surfactants. The results obtained at the 1 and 2% levels of TMN-6, however, do appear to agree surprisingly well with the data obtained with other surfactants. Apparently, when surfactant levels reach 1 or 2% concentrations, the micelles can effectively partition monuron from the aqueous phase.

Total recoveries in Table III ranged from 81 to 95%, and material loss was apparently caused by formation of unstable nonvolatile products that decomposed during analysis into volatile by-products. This type of material loss was described earlier for the low recoveries in the photolysis of aqueous monuron (Tanaka et al., 1977).

Formaldehyde was identified as a photoproduct from monuron-surfactant solutions containing oxygen. The production of formaldehyde implies that an unstable hydroxymethyl or methylol (Figure 1, VIII) intermediate was involved in the demethylation reaction mechanism (Tanaka et al., 1972). Formation of the formylmethyl analogue (IX) of monuron—a photoproduct observed in aqueous oxygenated photolysis reactions—was not observed when surfactant solutions were employed. Therefore, dealkylation, in this case, appears to occur by decomposition of a methylol intermediate rather than by the proposed hydrolysis of an *N*-formyl group (Crosby and Tang, 1969) to afford the demethylated product (Figure 1). This demethylation reaction appears to take place in the polyoxyethylene portion of the micelles because water is required for the photolytic formation of formaldehyde (Cohen et al., 1973).

To observe the effects of oxygen, aqueous monuron solutions containing X-100 and TMN-10 were photolyzed under oxygenated (air equilibrated) and nonoxygenated (degassed with N₂) conditions. The results are given in

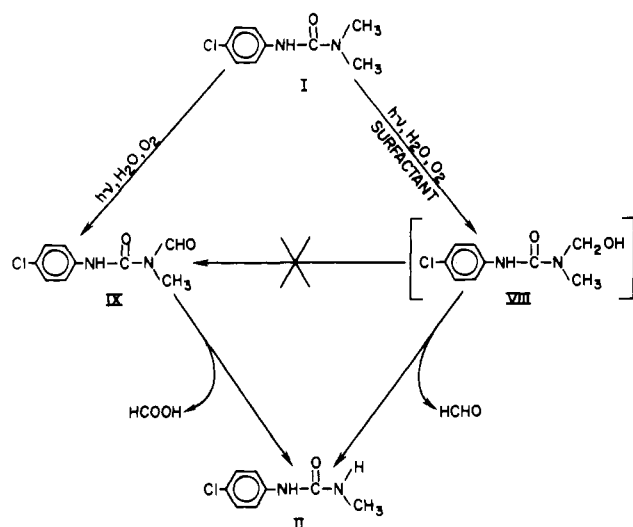


Figure 1. N-Demethylation reaction scheme.

Table IV. Percent Yield for Oxygenated and Nonoxygenated Photoreactions of Aqueous Monuron with 0.2% X-100 and 0.2% TMN-10

photoproducts	0.2% X-100		0.2% TMN-10	
	oxy- gen- ated ^a	non- oxy- gen- ated ^b	oxy- gen- ated ^a	non- oxy- gen- ated ^b
monuron	25	38	31	32.5
fenuron	29	41.5	36	33.5
monomethylfenuron	0.3	0.3	0.4	0.3
monuron dimer	1.3	1.8	1.7	1.3
fenuron dimer	1.3	0.5	0.6	0.5
formaldehyde ^c	5.1	5.1	4.6	4.0
polymer ^d	27	10	18	25

^a Equilibrated with air in the reaction vessel. ^b Degassed with nitrogen. ^c Data obtained with [methyl-¹⁴C]monuron. ^d Percent of monuron incorporated into polymeric material (TLC origin).

Table IV. With oxygen, the amount of monuron degraded was higher for both alkyl and aryl surfactant solutions. Fenuron yields were slightly higher than the quantity of unreacted monuron. The high yield of fenuron under oxygenated conditions indicates that oxygen had no effect on the reductive dechlorination reaction. Therefore, in the presence of surface-active agents, oxygen appears to be excluded from the region where reactions involving the aromatic ring take place. This is further indicated by the fact that coupling reaction products were formed, but ortho- and para-hydroxylated products were not observed. The complete elimination of the para-hydroxylated analogue of monuron (X) as a photoproduct (Figure 2) is surprising because this product was obtained in highest yield in an earlier photolysis study (Tanaka et al., 1977) with aqueous oxygenated solutions. At this time, the reason for nonparticipation of oxygen in these photoreactions is not clear. But, the addition of surfactants to aqueous monuron clearly eliminates the ring hydroxylation reactions and enhances the reductive dechlorination reaction. A scheme for the photoalteration of monuron under oxygenated conditions in the presence of a nonionic surfactant is shown in Figure 2.

In previous monuron degradation studies with ultraviolet light (Crosby and Tang, 1969; Tanaka et al., 1977), the formation of formaldehyde was not observed. With the addition of surface-active agents, however, formaldehyde was identified as a photoproduct. An exami-

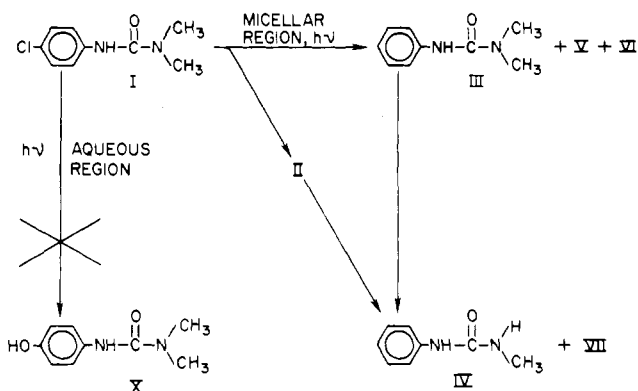


Figure 2. Photoalteration of monuron in aqueous oxygenated solution with a nonionic surface-active agent.

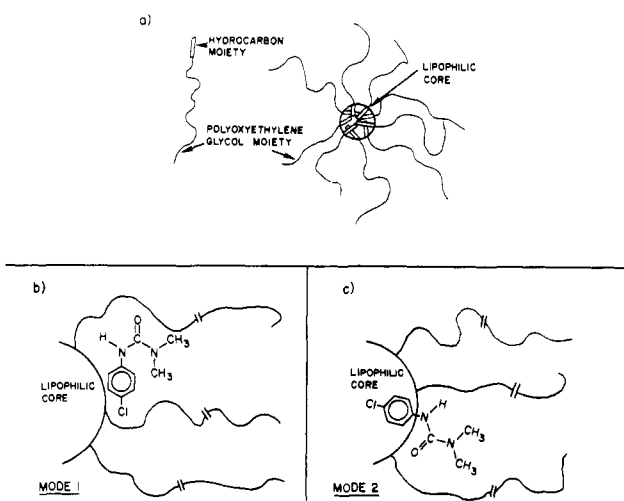


Figure 3. Schematic diagram for the illustration of two possible modes of monuron incorporation into nonionic surfactant micelles: (a) nonionic surfactant micelle, (b) adsorption onto the surface of the micellar core, (c) penetration into the lipophilic core.

nation of formaldehyde yields under oxygenated and nonoxygenated conditions revealed that with surfactants, approximately equivalent quantities of formaldehyde were produced (Table IV). Thus, the presence of oxygen was not critical with respect to formaldehyde production.

In the monograph by Shinoda et al. (1963), four possible modes for incorporation of material into micelles are given. These modes are: (a) inclusion into the micellar core; (b) penetration into the micellar core; (c) adsorption onto the surface of the micellar core; and (d) incorporation into the polyoxyethylene groups of the micelle. Of the four possible modes, two appear as possible candidates to explain the participation of nonionic surfactants in the photochemistry of aqueous monuron. Two models that could not be ruled out by our experimental data are: (mode 1) adsorption onto the micellar core and (mode 2) penetration into the micellar core. Using a schematic diagram for an individual micelle as illustrated by Shinoda et al. (1963), Figure 3 illustrates the two possible modes for monuron solubilization by surfactant micelles.

Evidence to support the two modes of micellar incorporation of monuron are given below. (a) With the presence of oxygen in the aqueous media, reductive dechlorination remains as the major reaction yielding fenuron. This indicates that the dehalogenation reaction occurs in a nonaqueous environment where oxygen is excluded. (b) The identification of formaldehyde implies an unstable methylol intermediate is involved in the N-demethylation process. To afford the methylol (VIII)

without formation of formylmethyl monuron (IX), an environment in which water is available and oxygen is essentially excluded appears to be a basic requirement. These criteria would appear to be fulfilled in the environment of the polyoxyethylene side chains adjacent to the lipophilic core of the micelle. (c) TMN-6 containing samples were photolyzed above cloud point, and sample turbidity disappeared after irradiation. If the lipophilic alkyl moiety of TMN-6 was being degraded to decrease turbidity, some interaction must take place between the surfactant and the solute which adsorbs the incident radiation. These observations therefore suggest that the aryl moiety of monuron is either dissolved into or is adsorbed onto the surface of the micellar lipophilic core.

In summary, the experimental results show nonparticipation of oxygen in the photoreactions of monuron when surface-active agents are present. Therefore, we are tentatively proposing that oxygen is being excluded from the surface and the inside of the surfactant micellar lipophilic core. Further studies must be conducted, however, to elucidate the exact cause for the nonparticipation of oxygen. In consideration of the evidence obtained, both mode 1 (adsorption onto the lipophilic core) and mode 2 (penetration into the lipophilic core) can be used to explain the observed effects. Perhaps both modes of micellar involvement are in operation or perhaps intermediate stages between these two extremes are in participation. The precise mode of micellar involvement is not critical with respect to the overall photochemical study being reported. However, employing nonionic surface-active agents in excess of CMC, the important observation revealed in this study is the fact that the photoreactions take place in the organic phase of the micelles rather than in the aqueous phase of the solvent.

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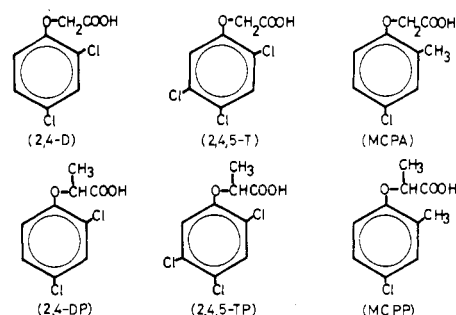
Structural and Conformational Aspects of Phenoxyalkanoic Acids as Determined in the Solid State by Diffraction Methods

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A detailed X-ray structural investigation on active phenoxyalkanoic acid plant growth compounds [(2,4-dichlorophenoxy)acetic acid, (2,5-dichlorophenoxy)acetic acid, 2,4,5-trichlorophenoxyacetic acid, and (\pm)-2-(2,4,5-trichlorophenoxy)propionic acid] and inactive ones [(2,4,6-trichlorophenoxy)acetic acid and (\pm)-2-(3,5-dichlorophenoxy)propionic acid] has been carried out. Although there are structural differences occurring in members of this series, there appears to be no direct stereochemical relationship with herbicidal activity.

Since the discovery of the auxin and herbicidal property of (2,4-dichlorophenoxy)acetic acid (2,4-D) in 1942 (Zimmerman and Hitchcock), a number of plant growth regulators of the phenoxyalkanoic acid type have been synthesized. Their chemistry and postulated mode of action have been reviewed (Garraway and Wain, 1976).

The members of the series that have been available for commercial use are 2,4-D, (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T), (4-chloro-2-methylphenoxy)acetic acid (MCPA), and their propionic acid analogues; 2-(2,4-di-



chlorophenoxy)propionic acid (2,4-DP or dichloroprop), 2-(2,4,5-trichlorophenoxy)propionic acid (2,4,5-TP or fenoprop), 2-(4-chloro-2-methylphenoxy)propionic acid (MCPP or mecoprop).

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