showing the CD profile typical of random-coil structures.

Figure 2 reports the relationship between the α-helix secondary structure content and the biological activity of the four tested samples. If the inhibitory activity of the fully oxidized native polypeptide (40% α-helix), is taken as 100%, the sample with 50% of the original α-helix content shows about 85% of residual inhibitory activity. When, following reduction of the second and third bond, the α-helix content falls to 25% of the original, an additional 20% of the biological activity is lost. Finally, the cleavage of the fourth bridge brings up a completely random-coil structure that still maintains a small residual biological activity. Our results indicate that none of the four disulfide bridges is directly involved in the active center of the inhibitor and that their concerted role is to maintain an ordered secondary structure, which is essential for the inhibitory activity of the polypeptide toward its partner protease.

The role of the modulation of the protease activity in the physiology of the plant is well documented (Ryan and Walker-Simmons, 1981b), but there is almost no information concerning the mechanisms of such modulation. Since protease inhibitors are present at every stage of the plant life, one can postulate that the modulation of the activity of the inhibitors could in turn result in the regulation of the protease activity itself. We have recently shown that such modulation in alfalfa leaves may be achieved by varying the endocellular ionic strength (Gonnelli et al., 1982), and here we bring evidence of an additional possible mechanism depending on the α-helix content of the polypeptide.

Registry No. Proteinase inhibitor, 37205-61-1.

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Photosensitized Degradation of a Homogeneous Nonionic Surfactant: Hexaethoxylated 2,6,8-Trimethyl-4-nonanol

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For a better understanding of photochemical interactions between surfactants and herbicides in formulations, a study was conducted with hexaethoxylated 2,6,8-trimethyl-4-nonanol (TMN-6) as a model nonionic surfactant. TMN-6 does not possess chromophoric groups; therefore, photodegradation must take place via the sensitization process. Twelve sensitizing agents ranging in triplet energies from 79 to 29 kcal/mol were examined to obtain an estimated triplet energy of approximately 43–44 kcal/mol for TMN-6. In addition, nine herbicides representing different herbicidal classes were tested as photosensitizers, and six of the nine herbicides sensitized TMN-6 degradation. Solutions were prepared in 30% acetonitrile–water with TMN-6 at 3.3 mM (0.15% w/v) concentration. Products identified from TMN-6 phtodegradation were TMN-5, -4, -3, -2, and -1 and TMNOH (trimethylnonanol) as well as the polyethylene glycols EO-6, EO-5, EO-4, EO-3, EO-2, and EO-1.

Agricultural chemicals of low water solubility are frequently combined with solubilizing agents to yield formulations suitable for field application. Surfactants (cationic, anionic, nonionic) are among those materials used in preparation of agricultural chemical formulations. In some instances as much surfactant, on a weight to weight basis, is applied as active ingredient.

Very few photodegradation experiments have been conducted to investigate the relationship between agricultural chemicals and surfactants. Hautala (1978) has observed an increase in light absorption as well as a small bathochromic shift in the absorption spectrum of 2,4-D and carbaryl with cationic and anionic surfactants. Que Hee et al. (1979) photolyzed the mixed butyl esters of 2,4-D in commercial formulation and found the primary reaction to be reductive dechlorination at the ortho position to yield the butyl esters of (4-chlorophenoxy)acetic acid.

The photochemistry of monuron has been studied extensively (Jordan et al., 1964; Crosby and Tang, 1969; Rosen et al., 1969; Mazzocchi and Rao, 1972; Tanaka et al., 1977); therefore, our initial investigation of surfactant–herbicide interactions was conducted with this compound. The presence of nonionic surfactant in monuron photolysis caused an increase in the photolysis rate, eliminated ring-hydroxylation reactions due to oxidation and substitution, and significantly increased the photoreductive dechlorination reaction (Tanaka et al., 1979). To deter-

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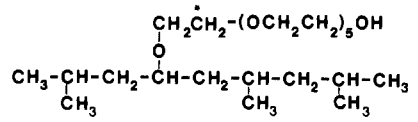

Hexaethoxylated 2,6,8-Trimethyl-4-nonanol

TMN-6

Figure 1. Structure of homogeneous TMN-6 showing the location of the ^{14}C label.

Table I. Compounds of Known Triplet Energies Employed as Sensitizing Agents (Air-Equilibrated Solutions of TMN-6 (3.3 mM) and Sensitizer (0.75 mM) in 30% Acetonitrile–Water Photolyzed for 20 h)

sensitizer	source	E_t,[a] kcal/mol	E_{st},[b] kcal/mol	% loss of TMN-6
acetone	Fisher	79	1.0	11
benzophenone	Fisher	69.1	1.0	65
biphenyl	Eastman	65.7	0.51	6
naphthalene	Eastman	60.8	0.71	24
benzil	Eastman	53.7	0.92	26
pyrene	Aldrich	48.7	0.27	13
rose bengal	Eastman	44.6		23
phenazine	Aldrich	44		16
eosin	MCB	43.0	0.76	0
anthracene	Packard	42.5[c,d]	0.70	32
crystal violet	Aldrich	39		0
naphthacene	Aldrich	29.3[d]		0

[a] Triplet energies taken from Cowan and Drisko (1976) and Calvert and Pitts (1967). [b] Singlet–triplet intersystem crossing efficiencies taken from Cowan and Drisko (1976) and Turro et al. (1969). [c] Anthracene has a second E_t at 74.4 kcal/mol. [d] Experiment conducted in cyclohexane.

mine the effect of surfactants on herbicidal photodegradation rates, a survey study was performed with a variety of herbicides in aqueous nonionic surfactant solutions (Tanaka et al., 1981). This study revealed that surfactants in some cases had the ability to provide some protection against photodegradation to selected herbicides. To provide protection to these herbicides, it would appear likely that surfactant photolysis was taking place. Therefore, the current study was undertaken to determine the effect of herbicides on surfactant photolysis and to determine the photolytic fate of nonionic surfactants in aqueous solution.

Tergitol TMN-6 (Union Carbide) was selected as a model nonionic surfactant. This surfactant was selected because it has no chromophoric groups to absorb incident radiation; therefore, photodegradation must take place via the sensitization process. Commercial TMN-6 is prepared by addition of ethylene oxide (EO) to 2,6,8-trimethyl-4-nonanol (TMNOH) to afford a product with a heterogeneous molecular distribution (M_r = 451). Thus, the average number of ethylene oxide units added to TMNOH is 6. In order to be able to identify photodegradation products, however, TMN-6 of homogeneous molecular distribution (Figure 1) was required for this investigation.

EXPERIMENTAL SECTION

Materials. Specific ^{14}C-labeled homogeneous TMN-6 was previously synthesized with a specific activity of 8 mCi/mmol (Tanaka et al., 1976), and homogeneous carrier material was prepared by the same synthetic scheme. The ^{14}C label was located in the second carbon atom of the first ethylene oxide unit attached to TMNOH (Figure 1). The radiochemical purity of [^{14}C]-TMN-6 was 99% as determined by thin-layer chromatography and autoradiography. Photosensitizers were purchased from readily available commercial sources (Table I). Benzophenone, benzil, phenazine, pyrene, biphenyl, and naphthalene were recrystallized from 90% ethanol. The purified compounds gave melting points in good agreement with those reported in the literature (Lange, 1967). Herbicides were synthesized in the laboratory or provided by the sources given in Table II. These analytical grade herbicides were of >99% purity.

Table II. Herbicides Employed as Sensitizing Agents (Air-Equilibrated Solutions of TMN-6 (3.3 mM) and Sensitizer (0.75, 7.5 mM) in 30% Acetonitrile–Water Photolyzed for 20 h)

		% loss of TMN-6	
sensitizer	source	0.75 mM	7.5 mM
monuron	synthesis	18	30
propanil	synthesis	5	11
chlorpropham	synthesis	1	9
ametryne	Ciba Geigy	6	12
chlorsulfuron	Du Pont	18	26
nitrofen	Rohm and Haas	5	a
glyphosate	Monsanto	0	0
2,4-D (Na salt)	Amchem	0	0
diquat	U.S. EPA	0	0

[a] Nitrofen was not soluble at this concentration.

Equipment. Melting points were taken on a Thomas-Hoover Unimelt apparatus. Photoreactions were conducted with a Rayonet RPR-204 photoreactor fitted with 300-nm sunlight lamps. Dissolution and equilibration of samples were accomplished on a New Brunswick Scientific G-11 gyrotory shaker. Ultraviolet–visible spectra were taken with a Varian Cary 219 spectrophotometer. Thin-layer chromatography (TLC) was conducted on 20 × 20 cm precoated plates of Anasil HF (Analabs) of 0.25-mm thickness. High-performance liquid chromatography (HPLC) was performed on a Beckman LC system (Tanaka et al., 1985). Gas chromatography was conducted on a Hewlett-Packard 5790A chromatograph equipped with flame ionization detector. Separations were accomplished on a 0.22 mm i.d. × 12 m Ultra Performance capillary column (HP 19091A) coated with a 0.33-μm film of cross-linked methyl silicone. Radioactivity was assayed in a Packard 3375 liquid scintillation spectrometer using Instagel (Packard) as the counting cocktail. Solid sample probe mass spectral analysis was performed with a Varian MAT 112S spectrometer. Spectra were taken using both electron-impact (EI, 70 eV) and chemical ionization (CI, NH_3 reagent gas) modes of sample ionization. Gas chromatography/mass spectrometry (GC/MS) was performed on a Hewlett-Packard 5992 spectrometer (EI ionization) using an Ultra Performance capillary column (HP 19091A).

Sample Preparation. Solutions were prepared in 30% acetonitrile in distilled water unless stated otherwise. The specific activity of the synthesized [^{14}C]-TMN-6 was reduced to 80 μCi/mmol with carrier TMN-6. In the photolysis experiments, the concentration of TMN-6 in solution was 3.3 mM (0.15% w/v). Sensitizers of known triplet energies were employed at 0.75 mM concentration, and herbicides that were tested as sensitizing agents were examined at both 0.75 and 7.5 mM levels. All solutions were shaken on a shaker at 100 rpm for 16 h prior to photolysis.

Sample Analysis. Two-dimensional TLC (Figure 2) was conducted, with the first dimension being developed in water-saturated methyl ethyl ketone and the second dimension being developed in benzene–acetone–water (50:50:1). Autoradiograms of the TLC plates were obtained by exposure to blue-sensitive Kodak X-ray film for 7 days. Photoproducts were removed from the TLC plates and assayed by liquid scintillation counting.

For capillary gas chromatography, the column temperature was programmed with an initial 2-min hold at 100

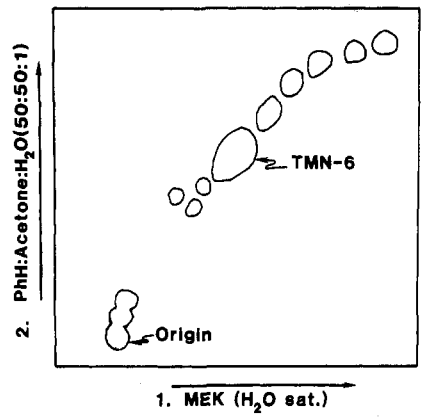

Figure 2. Autoradiogram of the two-dimensional TLC separation of photoproducts from an acetone-sensitized reaction. Solvent 1 is water-saturated methyl ethyl ketone and solvent 2 is benzene–acetone–water. The large spot at the center of the chromatogram is TMN-6, and located in orderly fashion above TMN-6 are TMN-5, -4, -3, -2, and -1. The polyethylene glycols and other polar material are located in the region of the origin.

Table III. Identification of the Deethoxylated Photoproducts of TMN-6 by GC/MS

photoproduct	R_t,[a] min	major mass spec frag, m/z (rel intens)
TMNOH	3.8	129 (23), 111 (30), 87 (25), 69 (100), 57 (26), 55 (20)
TMN-1	7.1	173 (13), 131 (72), 111 (60), 69 (100), 57 (28), 55 (22)
TMN-2	9.7	217 (12), 175 (49), 111 (44), 107 (33), 103 (60), 89 (100), 71 (28), 69 (35), 59 (50), 57 (49), 55 (29)
TMN-3	12.5	261 (5), 219 (13), 151 (12), 133 (100), 89 (58), 71 (17), 69 (17), 57 (22), 55 (11)
TMN-4	15.0	305 (6), 263 (10), 195 (14), 177 (51), 133 (32), 89 (100), 71 (20), 69 (16), 57 (27), 55 (13)
TMN-5	17.2	349 (4), 307 (4), 259 (12), 221 (10), 195 (13), 177 (17), 133 (90), 89 (100), 71 (27), 69 (17), 57 (37), 55 (15)

[a] Capillary gas–liquid chromatography.

°C followed by a temperature increase at a rate of 10 °C/min to a final temperature of 250 °C. Helium carrier gas was maintained at a flow rate of 1.5 mL/min. For GC/MS analysis, the helium flow rate was reduced to 1.0 mL/min and the final column temperature was increased to 300 °C.

Identification of Deethoxylated Photoproducts. Quadruplicate aqueous samples (5 mL) of 0.15% TMN-6 containing acetone (0.25 mL, 3.4 mmol) as sensitizing agent were photolyzed for 10 h. During this period, 75% of the TMN-6 was decomposed and a cloudy solution was obtained. The aqueous sample was passed through a C_{18} Sep Pak (Waters Associates) to separate the photoproducts from water. The Sep Pak was eluted with acetonitrile to isolate the photoproducts. Capillary GLC cochromatography and GC/MS analysis of underivatized materials verified the identity of the deethoxylated photoproducts (Table III). Their yields are given in Table IV.

Identification of Polyethylene Glycols. An aqueous solution of 0.15% [^{14}C]-TMN-6 (100 mL; sp act. 1 mCi/mmol) containing 5 mL of acetone as sensitizer was photolyzed for 25 h. This exposure period caused 75% degradation of the TMN-6. Nonglycol products were removed by treating the photolyzed sample with 50 mL of 5 N NaCl solution and extracting (3 × 25 mL) with ethyl acetate. The glycol photoproducts were removed from the aqueous phase by extraction (3 × 25 mL) with chloroform (Stolzenberg, 1982). The chloroform extract was dried over anhydrous $MgSO_4$, reduced to an oil in vacuo, and dried in a vacuum desiccator for 2 days.

Table IV. Product Yields from the Deethoxylation Reaction (Air-Equilibrated Solutions of TMN-6 (3.3 mM) and Sensitizer (0.75 mM) in 30% Acetonitrile–Water Photolyzed for 20 h)

sensitizer	% loss of TMN-6	% yield[a]			
		TMN-5	TMN-4	TMN-3	TMN-2
monuron	18.4	3.6	3.0	2.8	3.2
ametryne	6.1	6.4	3.6	3.8	3.8
chlorsulfuron	17.5	3.9	2.7	3.3	3.8
nitrofen	4.6	4.6	5.9	4.8	6.6

[a] Based on the amount of TMN-6 degraded; TMN-1 and TMNOH partially volatile.

Using the method of Shriner et al. (1957), the 3,5-dinitrobenzoate (3,5-DNB) esters of the polyethylene glycols were prepared. In a 2-mL vial containing the glycol mixture was added 115 mg (0.5 mmol) of 3,5-dinitrobenzoyl chloride, 2 drops of pyridine, and 1 mL of $CHCl_3$–PhH (1:1). The mixture was heated at 95 °C for 16 h. Then, a few drops of water were added and hydrolysis of excess 3,5-DNB chloride was accomplished at 95 °C for 15 min. The cooled reaction was made basic with about 10 mL of 2.5 N NaOH and the mixture of 3,5-DNB mono- and diesters were extracted (3 × 50 mL) with ethyl acetate. The extract was dried as described above.

Separation of the 3,5-DNB mono- and diesters was accomplished by HPLC using a Waters Radial Pak C_{18} column (5 mm i.d.) of 10-μm particle size. This separation was developed with a mixture of known standard esters at moderate concentration and equivalent distribution. With isocratic conditions using 55% acetonitrile–water with a flow rate of 1.5 mL/min, the monoester mixture eluted as a group at 1.0 min and diester mixture eluted as a second group at 5.5 min.

TLC cochromatography with known standard esters was conducted on the mixture of 3,5-DNB mono- and diesters. Chromatograms of the monoesters were developed in benzene–acetone (3:1, v/v), and the products were located by ultraviolet light absorption and by autoradiography (2-week exposure). All monoesters ranging from EO-1 through EO-6 were detected. Chromatograms of the diesters were developed in benzene–acetone (6:1, v/v), and the TLC plates were exposed to X-ray film for 2 weeks. Diesters ranging from EO-2 through EO-6 were detected by autoradiography. EO-1 was only observed by ultraviolet light absorption.

The CI/MS was performed on the intact HPLC fraction of the diesters because their yields were much lower than those of the monoesters. Individual pseudomolecular ions (M + 18) were monitored in the mass spectrum of the diester mixture (Table V). The monoester fraction could be separated into three bands by preparative TLC. The three bands were further purified by HPLC, and each fraction was examined by CI/MS (Table V).

Sensitization Experiments. All samples were dissolved in acetonitrile–water except for the anthracene and naphthacene solutions. Owing to insolubility problems, anthracene and naphthacene samples were prepared in cyclohexane. To examine sensitizing agents, triplicate samples (2 mL) were photolyzed for 20 h, in 20-mL Pyrex tubes for each sensitizing agent. The quantity of TMN-6 degraded was estimated by means of TLC and liquid scintillation counting.

Ultraviolet–Visible Light Spectrometry. Spectral examination of sensitizing agents was performed at 30 μM concentration. All spectra were scanned in quartz cells from 500 to 230 nm to cover the spectral distribution of

Table V. Identification of Polyethylene Glycols by TLC Cochromatography and CI/MS

glycols	TLC: R_f 3,5-DNB[a] diester	TLC: R_f 3,5-DNB[b] monoester	CI/MS, M + 18: m/z (rel intens) 3,5-DNB[c] diester	CI/MS, M + 18: m/z (rel intens) 3,5-DNB[d] monoester	major ion frag from 3,5-DNB monoester, m/z (rel intens)
EO-6	0.23	0.13	688[e]	494 (100)	300 (38), EO-6 + 18
EO-5	0.34	0.21	644[f]	450 (100)	256 (70), EO-5 + 18; 239 (16)
EO-4	0.43	0.31	600	406 (5)[f]	
				406 (11)[g]	
EO-3	0.54	0.42	556	362 (100)	168 (55), EO-3 + 18; 127 (73)
EO-2	0.61	0.52	512	318 (3)[g]	
EO-1	0.68	0.63			

[a] DNB = dinitrobenzoate; developed in benzene–acetone (6:1, v/v). [b] Developed in benzene–acetone (3:1, v/v). [c] Analyzed as total diester HPLC fraction. [d] Analyzed as three fractions. [e] Observed in EO-6 monoester fraction. [f] Observed in EO-5 monoester fraction. [g] Observed in EO-3 monoester fraction.

the sunlight lamps. The primary light band for the photoreactor ranged from 270 to 350 nm (peak at 300 nm), with additional small bands appearing in the blue region at 375, 405, and 435 nm. When Pyrex vessels are employed in the photolysis experiments, light of less than approximately 280 nm is filtered out. Only above 290 nm is a significant quantity of light transmitted through Pyrex glass (Calvert and Pitts, 1967). Therefore, in the current study, the absorption spectrum of each sensitizing agent was compared between 275 and 400 nm to determine whether the quantity of light adsorbed could be correlated with the quantity of TMN-6 degraded.

RESULTS AND DISCUSSION

TMN-6 was found to be photodegraded much faster in aqueous solution than in 30% acetonitrile–water. In aqueous solution with herbicides of Table II, increases in photodegradation of surfactant ranged from as low as 1% for chlorsulfuron to as high as 42% for chlorpropham. It appears that, in aqueous media, the critical micelle concentration (CMC) is exceeded and photolysis of surfactant then takes place under micellar conditions. In 30% acetonitrile–water, however, the acetonitrile is apparently present in high enough concentrations to prevent micelle formation even though the concentration of TMN-6 (0.15% w/v) is in excess of its CMC (0.084% w/w; Mukerjee and Mysels, 1971). To obtain uniform conditions for direct comparison of results, 30% acetonitrile–water was employed as solvent because almost all sensitizers were completely solubilized in this solvent.

Surfactant samples photolyzed with acetone as sensitizer were monitored for product yields after 5- and 20-h exposure periods. The yields of deethoxylated products (TMN-2 through TMN-5) were approximately the same at both exposure levels. Since a greater number of photoproducts was obtained after 20 h of photolysis, this exposure period was selected for this study.

In Table I are given the photosensitizers of known triplet energies (E_t) that were used for estimation of the triplet energy of TMN-6. The sensitizers with E_t values above that of phenazine (44 kcal/mol) all caused degradation of TMN-6. Those with E_t values less than 44 kcal/mol did not sensitize surfactant degradation. Anthracene, with an E_t of 42.5 kcal/mol, appears to be an exception, causing 32% loss of surfactant; however, this sensitized degradation is apparently afforded by a second triplet state of 74.4 kcal/mol (Cowan and Drisko, 1976). Thus, the data in Table I suggest that the triplet energy of TMN-6 is in the region of 43–44 kcal/mol.

The loss of TMN-6 with respect to decreasing triplet energies in Table I is quite random for the different sensitizing agents. In these data no correlation can be observed between triplet energy of the sensitizer and the quantity of TMN-6 degraded. If a high triplet energy is not the primary cause for surfactant degradation, perhaps singlet–triplet intersystem crossing efficiencies (E_{st}) might play a role in effecting the observed random results. Upon comparison of E_t and E_{st} values in Table I with percent loss of TMN-6, it was clear that the E_{st} values were not directly associated with the random losses. Therefore, if high E_t and E_{st} values are not responsible for these data, perhaps the quantity and quality of light being absorbed by the sensitizing agent might be responsible. To follow this contention, the ultraviolet–visible light absorption spectra were taken of each sensitizing agent. Again, no correlation was observed with respect to absorption spectrum, triplet energy, and loss of TMN-6. Therefore, it does appear that TMN-6 degradation does not take place by triplet energy transfer alone. Where greater than expected degradation of TMN-6 is occurring, sensitizing agents are apparently reacting directly with the surfactant. To examine this further, rose bengal bound to polymeric beads (Sensitox II; Chemical Dynamics Corp.) was tested for comparison with rose bengal in solution. Sensitox II afforded only a 5% loss of TMN-6 whereas rose bengal in solution initiated a 23% loss. Thus, direct reaction of rose bengal with surfactant was significantly inhibited in polymer-bound materials, causing considerable reduction in sensitized degradation.

Since herbicides are mixed with surfactants in formulations, these agricultural chemicals were also tested as sensitizing agents to determine whether they might effect surfactant photodecomposition. Nine different classes of herbicides given in Table II were tested, and these herbicides were examined at 0.75 and 7.5 mM concentrations. At 0.75 mM level, the first six herbicides sensitized the degradation of TMN-6 to varying degree. Increasing the concentration of herbicide to 7.5 mM level demonstrated greater sensitization effects. Monuron and chlorosulfuron showed the greatest effect at the 7.5 mM level with 30 and 26% losses of surfactant, respectively. On the other hand, glyphosate, 2,4-D, and diquat showed no sensitizing effect at either concentration. Therefore, some herbicides are capable of sensitizing photodecomposition of surfactant; however, not all herbicides are capable of sensitizing degradation.

In Table III are given the capillary GLC retention times and the major ion fragments observed in mass spectral identification of the deethoxylated photoproducts. Analyses were accomplished by GC/MS using the EI mode of ionization. Molecular ions were not observed for the different TMN compounds owing to the instability of the alkyl chain during EI mass spectrometry. Cleavage of the alkyl chain on either side of the C-4 carbon (cf. Figure 1) of the alkyl chain resulted in losses of masses 57 and 99, which were characteristic mass losses for all the deethoxylated photoproducts. Further fragmentation of the M − 57 and M − 99 ions at the first ether linkage connecting the oxygenated side chain with the alkyl moiety gave major ion fragments at m/z 69 and 111 due to losses of H_2O,

EO-1, or EO-2 for TMNOH, -1, and -2, respectively. Base peak for TMNOH and TMN-1 was at m/z 69; however, the base peak for TMN-2 was at m/z 89, which was due to a diethylene glycol ion fragment. Similarly, the base peak for TMN-3 was at m/z 133, resulting from a triethylene glycol ion fragment. As the polyethylene glycol chain became longer in TMN-4 and -5, base peak intensities for tetraethylene glycol (m/z 177) and pentaethylene glycol (m/z 221) ion fragments were not observed. Either fragmentation was no longer favored at the first ether linkage, or there was further fragmentation of the EO-4 and EO-5 ion fragments to afford base peak response at m/z 89 (EO-2 ion fragment) for TMN-4 and -5.

Yields of the deethoxylated products obtained after 20-h exposure period are given in Table IV. While concentrating samples for quantitation, TMN-1 and TMNOH were not recovered completely, owing to the volatility of these photoproducts. Therefore, their estimated yields were not presented in this table. The yields reported in Table IV were calculated as a percentage of TMN-6 that was actually degraded. The deethyloxylated product yields appear to be of approximately the same order of magnitude; hence, the data indicate that steady-state concentrations are apparently being measured. In this regard, additional evidence is provided by the fact that approximate equivalent yields of deethoxylated products were obtained at both 5- and 20-h exposure periods.

The polyethylene glycol photoproducts were identified by TLC cochromatography and CI/MS of their mono- and diesters prepared with 3,5-dinitrobenzoyl chloride (Table V). Pseudomolecular ions (M + 18) were observed for EO-2 through EO-6 diesters; however, an M + 18 ion was not observed for the EO-1 diester. The advantage of the diester derivative is that ion fragments from a diester pseudomolecular ion cannot be mistaken for a pseudomolecular ion of a shorter chain glycol diester because both ends of the glycol are capped with ester functions.

When the three preparative TLC fractions of the monoesters were examined by CI/MS, base peak response was observed for the pseudomolecular ions of EO-6, EO-5, and EO-3. The M + 18 ion for EO-4 was observed in both the EO-5 and EO-3 mass spectra while that of EO-2 was observed in the EO-3 spectra. No evidence for an M + 18 ion was noted for the EO-1 monoester by CI/MS.

Authentic standards of the 3,5-DNB mono- and diesters ranging from EO-1 through EO-6 were examined by CI/MS. All standards except for the mono- and diester of EO-1 gave base peak response for the M + 18 ion. The diester of EO-1 gave a pseudomolecular ion with a relative intensity of about 8%, and the monoester gave a M + 18 ion of only 2%. Owing to the low response of the EO-1 ester standards for a pseudomolecular ion by CI/MS, it is understandable that their respective M + 18 ions were not observed in the diester mixture or in the monoester fractions even though their presence was detected by TLC.

Having identified the different deethoxylated products, it is clear that the polyethylene glycol chain is being cleaved at all ether linkages to yield TMN-5 through TMNOH as photoproducts. The question of whether this is a stepwise clipping of the ethylene oxide chain to yield a successively shorter chain or whether ether cleavage is a random process arises. The approximate equivalent yields of deethoxylated products given in Table IV could indicate a stepwise process. However, with the identification of the glycol photoproducts ranging from hexaethylene glycol down to ethylene glycol, it is clear that cleavage of the polyoxyethylene side chain is indeed a random process.

Further studies are being conducted to identify additional photoproducts resulting from cleavage of the polyoxyethylene side chain. With the identification of some key intermediates involved in the oxidation of the glycol side chain, perhaps the pathway and mechanism of deethoxylation can be elucidated.

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Registry No. EO-1, 107-21-1; EO-2, 111-46-6; EO-3, 112-27-6; EO-4, 112-60-7; EO-5, 4792-15-8; EO-6, 2615-15-8; TMN-1, 10137-98-1; TMN-2, 101566-88-5; TMN-3, 86832-10-2; TMN-4, 101566-89-6; TMN-5, 101566-90-9; TMN-6, 14149-99-6; TMNOH, 123-17-1; PEG, 25322-68-3; Me_2CO, 67-64-1; benzophenone, 119-61-9; biphenyl, 92-52-4; naphthalene, 91-20-3; benzil, 134-81-6; pyrene, 129-00-0; rose bengal, 11121-48-5; phenazine, 92-82-0; anthracene, 120-12-7; monuron, 150-68-5; propanil, 709-98-8; chlorpropham, 101-21-3; ametryne, 834-12-8; chlorsulfuron, 64902-72-3; nitrofen, 1836-75-5.

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