Photolytic Degradation of a Homogeneous Triton X Nonionic Surfactant: Nonaethoxylated p-(1,1,3,3-Tetramethylbutyl)phenol

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Aqueous solutions of ^{14}C-labeled homogeneous nonaethoxylated tert-octylphenol (TOP-9EO) at 0.15% (w/v) concentration were irradiated with 300-nm sunlight lamps. Extraction under basic conditions with ethyl acetate isolated the tert-octylphenylpolyoxyethylene glycols, and extraction with chloroform isolated the polyethylene glycols, glycolic aldehydes, and glycolic ethers. Product purification was by thin-layer and high-performance liquid chromatography. Photoproducts were identified as their 3,5-dinitrobenzoate derivatives using direct exposure chemical ionization mass spectrometry (DCI-MS). Nine herbicides were tested as photosensitizers of TOP-9EO, and eight appeared to provide some effects. Employing sensitizers with known triplet energies, the E_t of TOP-9EO was estimated to be 53–54 kcal/mol.

INTRODUCTION

Agricultural chemicals are often combined with surface-active agents to yield commercial formulations that increase the efficacy of the active ingredients. Surfactants are commonly used with agrochemicals to improve wetting, penetration, absorption, and water solubility characteristics. On a weight to weight basis, surfactants can typically account for 5–10% of a formulated pesticide product (Layman, 1985). Surfactants are classified according to their ionic character, and the four major classes are the cationic, anionic, nonionic, and amphoteric surfactants. The anionic surfactants account for about 60% of production, but the nonionic surfactants, which account for about 30%, are the fastest growing of the four classes (Camp et al., 1985).

The effect of surfactants on the photodegradation of herbicides has not been studied very extensively. Investigation of the effects of surfactants on the photolysis rates of 2,4-D, carbaryl, and parathion on soils and in aqueous solutions was performed with sunlight and with ultraviolet lamps (Hautala, 1978). Aerosol sprays of emulsifiable concentrates of trifluralin and parathion were photolyzed in field and laboratory studies to determine their rates of degradation (Woodrow et al., 1978). Photolysis of monuron in aqueous nonionic surfactant solutions showed an increase in the photolysis rate, an elimination of the ring hydroxylation reaction, and an increase in the photoreductive dechlorination reaction (Tanaka et al., 1979). When commercial formulations of the mixed butyl esters of 2,4-D were photolyzed, photoreductive dechlorination was the primary reaction (Que Hee et al., 1979). To assist in the elucidation of the mechanism of action of acifluorfen-methyl on membrane matrices, the influence of acifluorfen-methyl on the photodegradation of β-carotene in aqueous Triton X-100 solutions was investigated (Orr and Hogan, 1985).

Four different classes of herbicides were photolyzed in aqueous nonionic surfactant solution, and protection against herbicidal photodegradation was observed with several of the surfactant-containing solutions (Tanaka et al., 1981). For a surfactant to afford protection against herbicidal photodegradation, surfactant photodecomposition was apparently occurring. Similarly, in the attempted photosensitized degradation of 2,4-D with riboflavin (Silber et al., 1976), riboflavin was being preferentially photodegradated. Thus, to obtain a better understanding of the interactions taking place between herbicides and surfactants during photolysis, surfactant photolysis studies were also needed. Therefore, the photolytic degradation of homogeneous hexaethoxylated 2,6,8-trimethyl-4-nonanol (TMN-6EO) was examined (Tanaka et al., 1986). The results with TMN-6EO should be comparable with those expected for commercially available heterogeneous Tergitol TMN-6, which has an $M_r = 451$ and an average distribution of six ethylene oxide units/molecule. A summary of current photolytic interactions of herbicides and surfactants was recently given (Tanaka, 1989). Because earlier studies were performed with an alkyl-substituted nonionic surfactant (TMN-6EO), this investigation is being carried out with homogeneous nonaethoxylated p-(1,1,3,3-tetramethylbutyl)phenol (TOP-9EO). The current results should be comparable with those expected for commercially available heterogeneous Triton X-100, which has an $M_r = 625$ and an average distribution of 9.5 ethylene oxide units/molecule. With the investigation of the photochemistry of an aryl-substituted nonionic surfactant, the differences in effects provided by alkyl- and aryl-substituted surfactants may be better understood.

EXPERIMENTAL PROCEDURES

Materials. Ethylene glycol (1EO) and diethylene glycol (2EO) were purchased from Fisher. Triethylene glycol (3EO) and tetraethylene glycol (4EO) were obtained from Aldrich. Pentaethylene glycol (5EO) and octaethylene glycol (8EO) were supplied by Columbia Organic Chemical Co. Hexaethylene glycol (6EO) was provided as a gratis sample from Atlas. tert-Octylphenol (TOPOH) was purchased from K & K, and Triton X-45 was obtained from Sigma. Homogeneous Triton X containing 9 ethylene oxide units/molecule (TOP-9EO) was purchased from Calbiochem-Behring Corp., La Jolla, CA. This material possessed a purity of about 90% by thin-layer chromatography (TLC) and exhibited a cloud point of 65–66 °C. Impurities present in the TOP-9EO were Triton X surfactants having chain lengths other than 9 ethylene oxide units. The homogeneous TOP-9EO was used as carrier material for dilution of the radiolabeled TOP-

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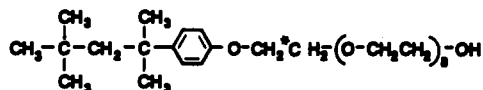*J. Agric. Food Chem.*, Vol. 39, No. 11, 1991 **2047**

Figure 1. Structure of homogeneous nonaethoxylated *p*-(1,1,3,3-tetramethylbutyl)phenol (TOP-9EO) showing the location of the ^{14}C label.

9EO. Homogeneous [14C]TOP-9EO (specific activity 8 mCi/mmol) with specific ^{14}C labeling located in the second carbon atom of the first ethylene oxide unit (Figure 1) was synthesized earlier (Tanaka and Wien, 1976). The radioactive TOP-9EO was purified before use by preparative TLC on 0.5 mm thick silica gel HF plates. First purification was accomplished with H_2O-saturated methyl ethyl ketone as developing solvent (R_f 0.12), and final purification was performed with benzene–acetone–water (50:50:1 v/v) as developing solvent (R_f 0.40). Two-dimensional TLC chromatography using a solvent of benzene–acetone (2:1 v/v) in the first dimension and benzene–acetone–water (50:50:1 v/v) in the second dimension followed by autoradiography indicated the purity of [14C]TOP-9EO to be greater than 99% with only a trace of TOP-8EO and TOP-7EO being observed as impurities. Aqueous solutions were prepared with distilled, demineralized, and carbon-filtered (Millipore Corp.) water.

Commercial grade Triton X-45 (M_r = 426) with an average ethylene oxide content of 5 EO units/molecule was chromatographed to isolate TOP-1EO through TOP-8EO. Authentic DNB standards were prepared for each isolated fraction by reaction with 3,5-dinitrobenzoyl chloride. Authentic dinitrobenzoate diester (2DNB) standards were prepared for the polyethylene glycols obtained from commercial sources. The identities of the synthetic DNB and 2DNB standards were verified by mass spectrometry.

Sensitizing agents of known triplet energy were readily purchased from commercial sources. Benzophenone, naphthalene, benzil, fluorenone, pyrene, and phenazine were recrystallized from 90% ethanol–water. Crystalline 1,2,5,6-dibenzanthracene (carcinogen) was first washed with acetone and then recrystallized from methanol. Acetophenone was used without further purification.

Equipment. Mass spectrometry was performed with a Varian CH5-DF spectrometer. Direct exposure chemical ionization mass spectrometry (DCI-MS) was accomplished using ammonia as the reagent gas. Electron impact mass spectrometry (EI-MS) was performed at 70 eV. TLC was carried out on precoated plates of Anasil GF and HF (Analabs) of 0.25- or 0.5-mm thickness. High-performance liquid chromatography was performed with a Beckman system equipped with Model 112 high-pressure pumps, Model 421 solvent program controller, Hitachi Model 100-10 detector, and Spectra-Physics Model SP4270 integrator. Separations were achieved with a Nova Pak C_{18} cartridge (8 mm × 10 cm) with 5-μm spherical particles held in a Waters Associates Model RCM-100 radial compression module. Quantitation of radioactivity was accomplished with a Packard Model 3375 liquid scintillation spectrometer using Instagel (Packard) as the counting cocktail. Autoradiography was conducted with Kodak X-Omat RP X-ray film. Photolysis experiments were carried out with the Rayonet RPR-204 photoreactor (The Southern New England Ultraviolet Co.) equipped with four RUL-3000 sunlight lamps with peak spectral energy distribution at 300 nm. Dissolution and equilibration of samples were accomplished on a New Brunswick Scientific Model G-11 gyrotory shaker.

Photolysis Experiments for Product Identification. A 0.15% (w/v) aqueous solution of [14C]TOP-9EO (2.5 mM, 100 μCi/mmol) was prepared by dissolving 0.15 g of homogeneous TOP-9EO (MW = 602) and 25 μCi of [14C]TOP-9EO in 100 mL of high-purity water. Samples of surfactant solution (10 mL) were held in standard taper Pyrex tubes with the dimensions of 15 mm o.d. × 20 cm. Each sample tube was sealed with a glass stopper held in place by a wire clamp. Photolysis of samples was performed by placing four sample tubes into the center of the photoreactor. An exposure period of 70 h was employed to afford approximately 55% loss of the [14C]TOP-9EO in the photoproduct identification experiments.

Measurement of Yields. Quantitation of photoproducts was by two-dimensional TLC followed by autoradiography and liquid

Table I. Solvent Systems Employed for Purification of 3,5-Dinitrobenzoate (DNB) Derivatives of Photolysis Products by Thin-Layer Chromatography[a]

photoproducts	solvent system	R_f
TOP-9EO-DNB	benzene–acetone (2:1)[b]	0.58
TOP-8EO-DNB	benzene–acetone (2:1)	0.67
TOP-7EO-DNB	benzene–acetone (2:1)	0.77
TOP-6EO-DNB	benzene–acetone (4:1)	0.56
TOP-5EO-DNB	benzene–acetone (4:1)	0.69
TOP-4EO-DNB	benzene–acetone (12:1)	0.50
TOP-3EO-DNB	benzene–acetone (12:1)	0.69
TOP-2EO-DNB	benzene	0.31
TOP-1EO-DNB	benzene	0.60
TOPOH-DNB	benzene	0.85
9EO-2DNB	benzene–acetone (3:1)	0.15
8EO-2DNB	benzene–acetone (3:1)	0.23
7EO-2DNB	benzene–acetone (6:1)	0.12
6EO-2DNB	benzene–acetone (6:1)	0.19
5EO-2DNB	benzene–acetone (6:1)	0.29
4EO-2DNB	benzene–acetone (6:1)	0.39
3EO-2DNB	benzene–acetone (6:1)	0.49
2EO-2DNB	benzene–acetone (6:1)	0.58
1EO-2DNB	benzene–acetone (6:1)	0.65

[a] Silica gel TLC plates of 250-μm thickness (Anasil HF). [b] Ratio v/v.

scintillation counting (LSC) according to previously described methods (Tanaka and Wien, 1986). Cochromatography with authentic standards of TOP-3EO and TOP-6EO verified location of these two photoproducts on the two-dimensional chromatogram. Standards were visualized by ultraviolet light absorption, and unknown products were located by autoradiography.

Fractionation of Photolyzed Samples. The pH of the irradiated sample was adjusted to basic conditions with 10% Na_2CO_3 (w/v), and the sample was extracted (3 × 25 mL) with ethyl acetate. The ethyl acetate fraction contained the *tert*-octylphenylpolyoxyethylene glycols. The ethyl acetate fraction was dried over anhydrous $MgSO_4$ and filtered, the solvent was removed in vacuo, and the fraction was stored in a vacuum desiccator over anhydrous $CaSO_4$. After extraction with ethyl acetate, the aqueous phase (basic condition) was extracted (3 × 25 mL) with chloroform. The chloroform layer contained the polyethylene glycols, glycolic aldehydes, and glycolic ethers. The extract was taken to dryness as described above for the ethyl acetate fraction. The basic aqueous phase was treated with 1 N HCl until the solution was acidic. The acidified aqueous fraction was then extracted (3 × 25 mL) with ethyl acetate. The combined extract was taken to dryness as described earlier.

Analysis of radioactivity in the photolyzed samples was determined by LSC, and the results were reported as a percentage of the original radioactivity present in the sample. Assay of the photolyzed solutions before sample extraction indicated that about 7.1% of the radioactivity was not accountable. The basic ethyl acetate fraction held 69.4% of the radioactivity (45% unreacted TOP-9EO and 24.4% deethoxylated byproducts). The chloroform extract contained 3% of the radioactivity. The acidic ethyl acetate layer held 0.4% of the radioactivity. Approximately 13.7% of the radioactivity remained in the residual aqueous acidic phase after three different extraction processes. The total quantity of radioactivity that was accountable from the photolyzed samples was about 93%.

Identification of Photoproducts. The 3,5-dinitrobenzoate (DNB) esters of the polyethylene glycols were prepared according to the method of Shriner et al. (1957). To the dried ethyl acetate (basic) extract were added 1 mL of chloroform, 1 mL of benzene, 115 mg (0.5 mmol) of 3,5-dinitrobenzoyl chloride, and 2 drops of pyridine. The reaction was heated at 100 °C for 16 h, and then several drops of water were added to the reaction. Sodium carbonate (10% w/v) was added to the cooled reaction until the solution was basic, and then the products were extracted (3 × 50 mL) with ethyl acetate. The extracts were combined and taken to dryness as described earlier. Initial purification of the DNB derivatives was by TLC on 0.25-mm HF plates using the appropriate solvent systems given in Table I. Final purification of the DNB esters was accomplished by HPLC under isocratic
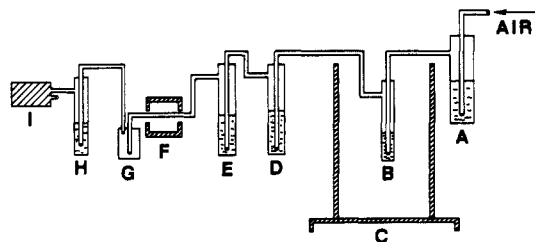
Figure 2. Apparatus for volatile product analysis: (A) 6 N NaOH, CO_2 trap; (B) surfactant solution; (C) photoreactor; (D) ethylene glycol, volatile organic material trap; (E) ethanolamine, CO_2 trap; (F) combustion furnace; (G) safety bottle trap; (H) ethanolamine, CO_2 trap for oxidized CO; (I) vacuum pump.

conditions with acetonitrile–water (88:12 v/v) at a flow rate of 1.5 mL/min.

The chloroform extract was treated as described above to prepare the DNB derivatives in this fraction. A mixture of mono- and diesters was obtained by the esterification process. Purification of the products in the chloroform extract was initially accomplished by HPLC under isocratic conditions using a solvent of acetonitrile–water (1:1 v/v) with a flow rate of 1.5 mL/min. Four fractions were collected in the HPLC purification step. Fraction 1 had a retention time of 1.5 min and contained the DNB monoesters of the polyethylene glycols. Fraction 2 consisted of three small peaks and had a retention range of 1.9–3.6 min and contained DNB monoesters of the polyethylene glycolic aldehydes and ethers. Fraction 3 had a retention time of 5.0 min and contained mainly 3,5-dinitrobenzoic acid and a small quantity of degraded surfactant. Fraction 4 had a retention time of 9.2 min and contained the DNB diesters of the polyethylene glycols. Radioactive material balance of the chloroform extract was as follows: fraction 1 (4.4%), fraction 2 (11.3%), fraction 3 (4%), fraction 4 (18.9%), and the remaining 61.4% was dispersed throughout the chromatogram without affording any specific peaks.

The photoproducts in the HPLC fractions were chromatographed by TLC to separate the DNB diesters using the appropriate elution solvent given in Table I. Final purification of the individual photoproducts for mass spectral analysis was by HPLC under isocratic conditions with acetonitrile–water (73:27 v/v) at a flow rate of 1.5 mL/min (R_t ca. 5.5 min). Photoproducts were identified by DCI-MS using ammonia as the reagent gas; therefore, the pseudomolecular ion observed was the molecular mass plus an ammonium ion (MNH_4^+).

Sensitization Experiments. For the TOP-9EO triplet energy and sensitization experiments, solutions of TOP-9EO were prepared from [^{14}C]TOP-9EO and nonradioactive TOP-9EO to obtain a 0.15% (w/v) concentration (2.5 mM) with a specific activity of 0.1 mCi/mmol. Sensitizers of known triplet energies were employed at 1.0 mM concentration, and herbicides tested as sensitizing agents were examined at 5.0 mM concentration. All solutions were prepared in 90% acetonitrile–water except for experiments with 1,2,5,6-dibenzanthracene, which were conducted in 100% acetonitrile owing to the very low solubility of dibenzanthracene. Solutions were shaken on a gyrotary shaker at 100 rpm for 16 h for sample equilibration. In these experiments, triplicate samples (2 mL) were irradiated for 10 h.

Material Balance and Volatile Products. Samples for these investigations were prepared in water and in 30% acetonitrile–water. Solutions of ^{14}C-labeled TOP-9EO and TOP-6EO were prepared at 0.015% (w/v) concentration (0.25 mM) with a specific activity of 8.0 mCi/mmol. In the material balance studies, triplicate samples (2 mL) were photolyzed for 30 h.

The apparatus shown in Figure 2 was employed in the volatile product studies. A washing tower (A) containing 200 mL of 6 N NaOH was placed before the surfactant solution (B) to be photolyzed to remove CO_2 from the incoming ambient air. An ethylene glycol trap (D; 25 mL) was placed after the surfactant solution to trap generated volatile organic material. After the glycol trap was a CO_2 trap (E) containing 25 mL of ethanol-ethanolamine (2:1 v/v) to trap CO_2 generated from the photolysis experiment. Trapping efficiencies have been demonstrated to be quantitative for CO_2 (Jeffay and Alvarez, 1961; Wang, 1967).

Table II. Mass Spectral Identification of *p-tert*-Octylphenyl (TOP) Containing Photoproducts as Their 3,5-Dinitrobenzoate Ester (DNB)

photoproduct	DCI-MS,[a] m/z (rel intensity)
TOP-8EO-DNB	770 (MNH_4^+, 100), 740 (17), 723 (10), 693 (13), 576 (84), 444 (8), 400 (9), 312 (11), 153 (15)
TOP-7EO-DNB	726 (MNH_4^+, 100), 696 (37), 679 (13), 650 (27), 532 (55), 356 (36), 312 (13), 153 (13)
TOP-6EO-DNB	682 (MNH_4^+, 100), 653, (50), 635 (5), 605 (6), 488 (27), 428 (4), 312 (6)
TOP-5EO-DNB	638 (MNH_4^+, 100), 608 (61), 561 (12), 550 (28), 444 (49), 391 (5), 356 (5), 312 (5)
TOP-4EO-DNB	594 (MNH_4^+, 100), 564 (37), 505 (2), 401 (29), 356 (1), 153 (2)
TOP-3EO-DNB	550 (MNH_4^+, 100), 521 (83), 473 (5), 408 (2), 356 (19), 312 (2), 153 (2)
TOP-2EO-DNB	506 (MNH_4^+, 100), 492 (5), 476 (72), 391 (14), 364 (5), 312 (24), 153 (1)
TOP-1EO-DNB	462 (MNH_4^+, 25), 448 (15), 432 (100), 386 (11), 373 (39), 268 (13), 239 (24), 153 (6)
TOPOH-DNB	418 (MNH_4^+, 48), 388 (100), 341 (23), 153 (21)

[a] Direct exposure chemical ionization mass spectrometry with ammonia as the reagent gas.

Then the exhaust gas from the irradiated sample was passed through a combustion furnace (F; Barber-Colman) containing CuO at 650 °C to oxidize CO to CO_2. A buffer bottle (G) was placed in line after the combustion furnace to trap water condensate. Any CO from photolysis was trapped as CO_2 in the final trap (H) of ethanol–ethanolamine (2:1 v/v; 25 mL). To the last trap was attached a low-pressure vacuum pump (I; Neptune Dyna-pump) to place the entire system under negative pressure. The system was sparged at a flow rate of 3.5 mL/min. For volatile product experiments, triplicate (5 mL) samples were photolyzed for 10 h, and after photolysis, samples were sparged for an additional 2 h prior to analysis.

Identification of Volatile Products. The ethylene glycol trap was analyzed by preparation of the dimedone derivative of the volatile aldehydes using a modified method of Shriner et al. (1957). To the ethylene glycol was added 200 mg of dimedone, 10 mL of EtOH, 5 mL of H_2O, and 1 drop of pyridine. The reaction mixture was heated at reflux for 30 min. Water (50 mL) was added to the cooled reaction, and the dimedone derivatives were extracted (3 × 25 mL) with diethyl ether. The pooled extracts were dried over anhydrous sodium sulfate. Preparative TLC in a solvent of benzene–acetone (100:4 v/v) gave a band with R_f 0.64. Assay of the band by liquid scintillation counting showed that the band contained radioactivity. EI-MS of the dimedone derivatives gave a molecular ion at m/z 292 for identification of formaldehyde and a molecular ion at m/z 306 for identification of acetaldehyde. Carbon dioxide was identified by isolating and assaying its radioactivity as its ethanolammonium carbonate salt. Carbon monoxide was identified by the fact that the radioactive gas could pass through the CO_2 trap and the organic vapor trap and upon oxidation could be trapped as $^{14}CO_2$.

RESULTS

After photolysis, the samples were extracted first under basic conditions and then under acidic conditions. The distribution of radioactivity from the fractionation process was as follows: basic ethyl acetate extract (69.4%), basic chloroform extract (2.9%), acidic ethyl acetate extract (0.4%), acidic aqueous phase (13.7%), volatile material (6.5%), and unaccountable material (7.1%). In the basic ethyl acetate extract photoproducts represented 24.4% of the radioactivity and unreacted TOP-9EO accounted for 45.0% of the activity in that fraction. The basic ethyl acetate extract held the products of Table II, and the basic chloroform extract held the products of Tables III and IV.

Table II gives the photoproducts obtained from cleavage of the polyoxyethylene glycol side chain of TOP-9EO. The photoproducts were examined as their 3,5-dinitrobenzoate

Table III. Mass Spectral Identification of the Polyethylene Glycol Photoproducts as Their 3,5-Dinitrobenzoate Diesters (2DNB)

photoproduct	DCI-MS,[a] m/z (rel intensity)
9EO-2DNB	820 (MNH_4^+, 89), 626 (100), 432 (22)
8EO-2DNB	776 (MNH_4^+, 100), 582 (63), 388 (3)
7EO-2DNB	732 (MNH_4^+, 100), 702 (4), 582 (38), 538 (96), 508 (12), 344 (8)
6EO-2DNB	688 (MNH_4^+, 100), 658 (8), 494 (44), 464 (14), 300 (5)
5EO-2DNB	644 (MNH_4^+, 100), 614 (19), 584 (7), 450 (45), 420 (34), 256 (9)
4EO-2DNB	600 (MNH_4^+, 100), 570 (9), 406 (13), 376 (2), 212 (1)
3EO-2DNB	556 (MNH_4^+, 100), 526 (31), 496 (5), 362 (91), 332 (11), 168 (8)
2EO-2DNB	512 (MNH_4^+, 100), 482 (66), 452 (27), 362 (15), 318 (9), 288 (16), 124 (39)
1EO-2DNB	468 (MNH_4^+, 13), 438 (100), 408 (76), 153 (40), 124 (76)

[a] Direct exposure chemical ionization mass spectrometry with ammonia as the reagent gas.

Table IV. Mass Spectral Identification of Polyethylene Glycolic Aldehydes and Ethers as Their 3,5-Dinitrobenzoate Ester (DNB)

photoproduct	DCI-MS,[a] m/z, MNH_4^+ (rel intensity)
DNB-$(EO)_n CH_2 CHO$	
n	
8	624 (100)
7	580 (18)
6	536 (93)
5	492 (100)
4	448 (62)
3	404 (100)
2	360 (86)
DNB-$(EO)_n CH_2 CH_3$	
n	
8	610 (7)
7	566 (100)
6	522 (72)
5	478 (100)
4	434 (92)
3	390 (100)
2	346 (18)
DNB-$(EO)_n CH_3$	
n	
7	552 (100)
6	508 (16)
5	464 (100)
4	420 (100)

[a] Direct exposure chemical ionization mass spectrometry with ammonia as the reagent gas.

esters. A pseudomolecular ion (MNH_4^+) that was equivalent to the molecular mass plus an ammonium ion was clearly observed for all identified photoproducts. Major ion fragments observed for each photoproduct were consistent with the identified compound. Photoproducts ranging from TOP-8EO down to TOPOH resulting from cleavage of ethylene oxide or multiple ethylene oxide units were identified (eq 1).

R-$(OCH_2CH_2)_8$-OCH_2CH_2OH $\xrightarrow[\text{cleavage}]{\text{O-C bond}}$ TOP-8EO through TOP-OH (1)

TOP-9EO; R = t-octylphenyl

+

9EO through 1EO

The polyethylene glycol photoproducts were identified as their 3,5-dinitrobenzoate diesters. Pseudomolecular ions (MNH_4^+) and the major ion fragments employed for the identification of the polyethylene glycols ranging from 9EO down to 1EO are given in Table III. Because all possible chain lengths of polyethylene glycols were ob-

Table V. Product Yields from Deethoxylation Reaction and Material Balance from Photolysis of TOP-9EO

photoproduct	% recovery water[a]	% recovery acetonitrile–water[b]
TOP-9EO	36.8	69.7
TOP-8EO	0.79	0.65
TOP-7EO	1.12	0.74
TOP-6EO	0.82	0.50
TOP-5EO	0.69	0.80
TOP-4EO	0.75	0.78
TOP-3EO	0.80	0.78
TOP-2EO	0.76	0.74
TOP-1EO	0.78	0.75
polar products[c]	20.7	12.5
dispersed material[d]	18.1	11.0
material loss[e]	17.9	1.1

[a] Air-equilibrated solutions of TOP-9EO (0.25 mM) in water photolyzed for 30 h. [b] Air-equilibrated solutions of TOP-9EO (0.25 mM) in 30% acetonitrile–water photolyzed for 30 h. [c] Includes polyethylene glycols, glycolic aldehydes, and glycolic ethers. [d] Radioactivity dispersed on TLC plate not observed as a spot. [e] Radioactivity not accountable either by assay of TLC plate or by assay of photolyzed solution.

served, side-chain cleavage was occurring by a random process at all of the oxygen–ethylene bonds (eq 1).

Further cleavage or oxidation of the polyoxyethylene glycol chain yielded the polyethylene glycolic ethers and polyethylene glycolic aldehydes (Table IV). The ethyl ethers were obtained by cleavage at 1 in eq 2, and the methyl ethers were obtained by cleavage at 2 in eq 3.

H-$(OCH_2CH_2)_n$-OCH_2-CH_2-OH $\xrightarrow{1}$ H-$(OCH_2CH_2)_n$-OCH_2CH_3 (2)

$\xrightarrow{2}$ H-$(OCH_2CH_2)_n$-OCH_3 (3)

$\xrightarrow{[O]}$ H-$(OCH_2CH_2)_n$-CH_2CHO (4)

n = 1-8

Therefore, cleavage was occurring at both the carbon–carbon bonds and the carbon–oxygen bonds on the polyoxyethylene chain to afford these products. Oxidation of the hydroxyl group (eq 4) afforded the polyethylene glycolic aldehydes.

Product yields from the deethoxylation process and material balance studies from photolysis both in aqueous solution and in 30% acetonitrile–water solution are given in Table V. Product yields obtained from the dealkoxylation process were all of the same order of magnitude. These results showed that side-chain cleavage was a random process with no specific chain length being favored. The rate of photodecomposition of TOP-9EO in water alone was significantly greater than in acetonitrile–water. These findings are in agreement with the results obtained with TMN-6 in water alone as compared with those in acetonitrile–water solutions (Tanaka and Wien, 1986). The increased rate of photolysis of water alone apparently occurred under micellar conditions because the concentration of surfactant (0.15%) was in excess of the cmc (0.02%). With the presence of acetonitrile in aqueous solution, the formation of micelles was apparently prevented and photolysis occurred in a homogeneous environment.

Experiments were set up to examine the yield of volatile products generated from photolysis reactions in water and in 30% acetonitrile–water solutions. The observed yields and the distribution of radioactivity obtained in these experiments are given in Table VI. The yields of CO_2, organic volatiles in the ethylene glycol trap, and CO oxidized and trapped as CO_2 were all very low. Owing to

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Table VI. Estimation of Volatile Products and Material Balance

source	% recovery water[a] TOP-9EO	% recovery acetonitrile-water[b] TOP-9EO	% recovery acetonitrile-water[b] TOP-6EO
CO_2 trap[c]	0.53	0.05	0.09
CO trap (as CO_2)[d]	0.10	0.03	0.02
glycol trap[e]	0.53	0.04	0.35
Me_2SO rinse[f]	21.9	0.16	1.56
photolyzed solution	70.8	99.2	92.8
insoluble polymer[g]	6.14	0.51	5.21

[a] Air-sparged solutions of TOP-9EO (0.25 mM) in water photolyzed for 30 h. [b] Air-sparged solutions of TOP-9EO and -6EO (0.25 mM) in 30% acetonitrile-water photolyzed for 30 h. [c] Ethanol-ethanolamine trap (2:1 v/v). [d] CO oxidized to CO_2 before trapping. [e] Ethylene glycol used to trap organic volatiles. [f] Photolyzing vessels were rinsed with Me_2SO in an ultrasonic bath. [g] Removable with strong cleaning solution.

Table VII. Compounds of Known Triplet Energies Employed as Sensitizing Agents [Air-Equilibrated Solutions of TOP-9EO (2.5 mM) and Sensitizer (1.0 mM) in 90% Acetonitrile-Water Photolyzed for 10 h]

sensitizer	E_t,[a] kcal/mol	E_{st},[b] kcal/mol	% loss of TOP-9EO	% loss from sensitizer[c]
acetophenone	74	0.99	30	+12
benzophenone	69	1.0	48	+30
naphthalene	61	0.39	25	+7
benzil	54	0.87	59	+41
fluorenone	53	0.93	12	-6
1,2,5,6-dibenzanthracene	52	0.89	29[d]	+8
pyrene	49	0.27	19	+1
phenazine	44		16	-2
control (blank)			18	

[a] Triplet energies taken from Turro (1967). [b] Singlet-triplet intersystem crossing efficiencies taken from Turro (1967) and Turro et al. (1969). [c] Loss with sensitizer minus loss observed in the control. [d] Experiment conducted in 100% acetonitrile; control showed 21% loss. Considerable photodegradation of dibenzanthracene occurred to afford a brown solution.

the location of the ^{14}C label, TOP-6EO was photolyzed in acetonitrile-water to attempt to increase the yield of radiolabeled volatile products. However, TOP-6EO afforded approximately the same results as did TOP-9EO. These data suggested that water-insoluble polymers were probably being formed. To test for polymeric material, the sample tubes were rinsed with Me_2SO using an ultrasonic bath to assist in solubilization of the polymer. From the photolyzed aqueous solutions of TOP-9EO, a significant recovery of ^{14}C label (21.9%) was obtained by rinsing the reaction vessels with dimethyl sulfoxide. Recovery of radiolabel from TOP-9EO photoreactions carried out in acetonitrile-water solutions was considerably lower (0.16%), but the formation of polymeric material in this medium was also much smaller. Strong acid or base would remove the remaining polymer adsorbed to the glass surfaces.

Volatile products identified from these experiments were carbon dioxide, carbon monoxide, formaldehyde, and acetaldehyde. As indicated by the percent of radioactivity recovered for these materials in Table VI, the yields of these products were very low.

An estimation of the triplet energy of TOP-9EO was determined using sensitizers of known triplet energy (Table VII). The losses of TOP-9EO with respect to decreasing triplet energies were observed to be random. In previous studies similar results were observed with TMN-6EO (Tanaka and Wien, 1986). With TMN-6EO, the degree of photosensitized degradation could not be correlated with E_t, E_{st}, or absorption spectrum of the sensitizing agent. In Table VII, the control solutions without addition of

Table VIII. Herbicides Employed as Sensitizing Agents [Air-Equilibrated Solutions of TOP-9EO (2.5 mM) and Sensitizer (5.0 mM) in 90% Acetonitrile-Water Photolyzed for 10 h]

sensitizer	source	% loss of TOP-9EO	% loss compared with control[a]
monuron	synthesis	44	+26
propanil	Rohm and Haas	24	+6
propham	PPG Industries	26	+8
fluometuron	Ciba-Geigy	26	+8
chlorsulfuron	Du Pont	38	+20
diphenamid	Eli Lilly	28	+10
dichlofopmethyl	Hoechst	30	+12
primisulfuron	Ciba-Geigy	64	+46
acifluorfen	Rohm and Haas	12	-6
control (blank)		18	

[a] Calculated by subtracting the control (18%) from the total percentage loss of TOP-9EO.

sensitizer showed an 18% loss of TOP-9EO. The total percentage loss of TOP-9EO provided in the third column included the losses that would be sustained without addition of sensitizer. Therefore, the estimated losses caused by the sensitizing agents (fourth column) were obtained by subtracting 18% (control) from the total photolytic loss. The positive values in the last column for benzil and all sensitizers with E_t greater than 54 kcal/mol indicated sensitized degradation. The negative values for fluorenone and phenazine indicated no sensitization, and the value for pyrene was within experimental error of being equivalent to zero. On the other hand, dibenzanthracene gave a value of +8%, but our experimental results indicated that dibenzanthracene itself was not sensitizing decomposition. Initially, dibenzanthracene was employed as received (98% purity), and a sensitization value of +26% was obtained. If dibenzanthracene were sensitizing photolysis, purification of this sensitizer would have increased rather than decreased the quantity of surfactant degraded. Therefore, an impurity in dibenzanthracene was apparently sensitizing degradation. This is further indicated by the fact that purified dibenzanthracene was decomposing during photolysis to afford a brown solution. From the data given in Table VII, the triplet energy of TOP-9EO was estimated to be about 53-54 kcal/mol.

Because surfactants are employed in combination with herbicides in agricultural chemical formulations, the sensitizing effect of herbicides on the photodegradation of TOP-9EO was examined. Table VIII shows that all herbicides tested except acifluorfen did afford sensitized degradation of TOP-9EO. These data suggest that the E_t of Triton X-100 would be expected to be higher than that of acifluorfen but lower than that of the other eight herbicides. Therefore, TOP-9EO or Triton X-100 should provide some protection for the first eight herbicides against photodegradation; on the other hand, Triton X-100 would be expected to photosensitize the degradation of acifluorfen.

DISCUSSION

In the photolysis of TOP-9EO, both carbon-oxygen and carbon-carbon bonds were cleaved to yield photodegradation products. The formation of deethoxylated products ranging from TOP-8EO to TOPOH resulted from cleavage of the carbon-oxygen bond. The identification of methyl and ethyl ethers of the polyethylene glycols demonstrated that both carbon-oxygen and carbon-carbon bonds were being cleaved. Identification of formaldehyde and acetaldehyde supported these observations. Our results could not determine if cleavage to yield ethers and oxidation to

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yield aldehydes occurred before or after cleavage of the polyoxyethylene side chain from the *tert*-octylphenyl moiety. Reactions most likely occurred under both circumstances; however, reactions after cleavage of the polyoxyethylene side chain would apparently be favored because no aldehydes or ethers were identified that contained the *tert*-octylphenyl moiety.

Initially, the total radioactivity recovered from the photolysis reactions was not equivalent to the total activity employed. In water alone, 17.9% of the radioactivity was not recovered after photolysis, and in acetonitrile–water the value was reduced to 1.1%. The loss of radioactivity in aqueous solutions was significant. Similarly in our studies with TMN-6EO (Tanaka and Wien, 1986), radioactivity loss of 23.3% was observed in aqueous solution. Therefore, it did appear that the losses of radioactivity sustained in these photolysis experiments were due to formation of volatile products. Initially it appeared that CO_2, HCHO, and HCOOH might be the main source of these losses. However, preliminary investigations with TMN-6 (Tanaka and Wien, 1986) showed that yields of these products were low. Since HCOOH on photolysis will yield CO (Calvert and Pitts, 1967), this process could account for the large losses of radioactivity observed. Upon examination of the volatile products produced from photolysis of the homogeneous Triton X surfactants (Table VI), the observed results were similar to those previously obtained from TMN-6EO photolysis. Yields of volatile organics were very low, and the yield of carbon dioxide was low. Oxidation of CO to CO_2 showed that very little CO was being produced in the photoreaction. Since radioactivity loss was not due to the escape of volatile products, our next step was to examine for insoluble byproducts. After the reaction vessels were rinsed with dimethyl sulfoxide, the short-chained polymers adsorbed to the glass surfaces dissolved into solution and the lost radioactivity became detectable. To estimate the total yield of water-insoluble polymer produced, the values given in Table VI for Me_2SO rinse and insoluble polymer must be summed. With the observation that water-insoluble polymeric material was the source of radioactivity loss, surfactant material balance in the photochemical experiments became acceptable.

Material losses given in Table V were due to undetected water-insoluble polymers that were adsorbed onto the reaction vessel walls. For TOP-9EO photolysis, the amount of insoluble polymer indicated in Table V (18, 1.1%) was different from that indicated in Table VI (28, 6.8%; obtained by summing values from Me_2SO rinse and insoluble polymer formation). In support of these observations, earlier studies on photolysis of aqueous TMN-6EO solutions showed an approximate 5% greater loss of parent material in stirred solutions as compared to that in static solutions. The greater formation of polymeric material in Table VI was apparently due to stirring action caused by sparging and the formation of film bubbles that would wet the wall of the reaction vessel to afford a greater surface area for surfactant photolysis.

Employing sensitizers of known triplet energy, the E_t of TOP-9EO was estimated to be 53–54 kcal/mol. The E_t of heterogeneous Triton X-100 would be expected to be very close to this value because Triton X-100 has an average EO content of 9.5 (Mukerjee and Mysels, 1971; Shafer and Bukovac, 1989). The triplet energy of TOP-9EO was higher than the 43–44 kcal/mol observed for the triplet energy of hexaethoxylated 2,6,8-trimethyl-4-nonanol (TMN-6EO; Tanaka et al., 1986). Triton X-100 should have a triplet energy high enough to photosensitize the

degradation of some pesticides. Those pesticides without aromatic substituents would probably be most vulnerable because their ability to dissipate excess energy would be less. On the other hand, TMN-6 has a triplet energy that would be lower than most pesticides; hence, pesticides would be expected to photosensitize degradation of this surfactant. Consequently, TMN-6 should provide protection for most pesticides against photosensitized degradation.

In a survey for surfactant effects on the photodegradation of herbicides (Tanaka and Wien, 1981), it appeared that Triton X-100 sensitized the photodegradation of monuron and propanil because loss of herbicide was greater with Triton X-100 than with Tergitol TMN-10. The results of Table VIII show, however, that monuron and propanil were not being sensitized by Triton X-100. Therefore, the enhanced degradation of monuron and propanil in the survey study was apparently effected by Triton X-100 micellar solubilization rather than photosensitized degradation. Since greater degradation was observed with Triton X-100 as compared with TMN-10 without photosensitization, micellar effects of Triton X-100 appear to be different from those of TMN-10. Solubilization of pesticides into surfactant micelles provides an environment similar to dissolution in an organic solvent. Consequently, micellar solubilization can alter the types of products produced and the rate of photodegradation. Therefore, micellar solubilization as well as surfactant triplet energy must be taken into consideration in the selection of suitable surfactants for preparation of pesticidal formulations.

In the photolysis of TMN-6EO, products containing the carboxyl moiety on the polyoxyethylene side chain were identified (Tanaka, 1989). Similarly, these types of photoproducts would be expected to be observed in the aqueous acidic fraction obtained in TOP-9EO photolysis. However, a detailed examination for photoproducts in this fraction was not performed because their total yield would be expected to be less than 1%.

Currently, there has not been much emphasis on surfactant photochemistry because surfactants are not active ingredients in pesticidal formulations. Hence, environmental fate studies are not required for registration. When registration of pesticidal formulations requires studies on adjuvants, only then will greater emphasis be placed on the photochemistry of surfactants and on the interaction of pesticides and surfactants during photolysis.

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