Survey for Surfactant Effects on the Photodegradation of Herbicides in Aqueous Media

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The effects of 0.2% heterogeneous Tergitol TMN-10 and Triton X-100 on the photodegradation of herbicides were studied in aqueous solution. The phenylureas, carbamates, amides, and triazines were the four classes of herbicides examined. Compounds were selected to give a range of water solubilities for each class. A straightforward relationship between water solubility and surfactant effects was not observed. In the presence of surfactant under qualifying conditions, however, an increase in herbicidal photodegradation was observed as water solubilities decreased. Generally, herbicides having low water solubilities and a chloro substituent(s) on the aromatic ring other than 3,4-dichloro substitution showed this effect consistently.

Since pesticides are generally applied as formulations which include surface-active agents, the influence of surfactants on the photodegradation of pesticides should be investigated. Currently, little is known about the effects of surfactants on the photochemistry of pesticides. Hautala (1978) has observed that surfactants can shift the ultraviolet light absorption spectrum of aqueous 2,4-D methyl ester solutions toward longer wavelengths. This bathochromic shift would therefore allow for an increase in ultraviolet sunlight absorption by the herbicide.

Recently, we reported on the photolysis of monuron in aqueous solution in the presence of both alkyl- and aryl-substituted nonionic surfactants (Tanaka et al., 1979). With constant dosage of light irradiation, addition of surfactant caused an increase in the rate of monuron degradation. Two factors appear to be primarily responsible for altering the rate of pesticide photodegradation in aqueous surfactant solutions. First, solubilization of the solute from the aqueous media into an organic environment within the surfactant micelles enhances photoreductive dehalogenation. This apparently occurs because the bond dissociation energies (Calvert and Pitts, 1967) of carbon–hydrogen bonds are lower than those of oxygen–hydrogen bonds. Second, aryl-substituted surfactants may have the ability to photosensitize pesticide decomposition.

If solubilization by micelles is an important factor, herbicidal water solubility should play an important role in determining surfactant influences on photodegradation rates. If surfactant photosensitization reactions are involved, significant increases in the rate of herbicidal degradation should be observed with aryl-containing surfactants. Finally, the question remains whether or not the addition of nonionic surfactants to aqueous solutions of herbicides always increases the rate of photodegradation. Therefore, the effects of heterogeneous Tergitol TMN-10 and Triton X-100 on the photodegradation of four classes of herbicides in aqueous solution were examined.

EXPERIMENTAL SECTION

Materials. Tergitol TMN-10 is a heterogeneous nonionic surfactant with a hydrophobic moiety of 2,6,8-trimethyl-4-nonanol and a hydrophilic side chain of poly(oxyethylene glycol) with an average of 10 ethylene oxide units. Triton X-100 contains a hydrophobic moiety of p-(1,1,3,3-tetramethylbutyl)phenol and a hydrophilic group

of poly(oxyethylene glycol) with an average of 9.5 ethylene oxide units in the side chain. TMN-10 and X-100 were purchased from Sigma Chemical Co. X-100 was received as neat material and TMN-10 as a 90% aqueous solution. Monuron, linuron, and diuron were supplied by E. I. du Pont de Nemours. Fluometuron, metobromuron, ametryne, atrazine, and prometone were provided by CIBA-Geigy. Propham, chlorpropham, and PPG-124 were obtained from PPG Industries. Alachlor and propachlor were donated by Monsanto. Individual compounds were provided by the following: propanil from Rohm and Haas; diphenamid from Eli Lilly; barban from Spencer; dichlormate from Union Carbide. Chemical structures for the above compounds are given in Table I. The mono- and dichloropropionanilides were prepared by reaction of propionyl chloride with appropriately substituted chloroanilines, and these compounds were kindly provided by Dr. R. E. Kadunce. Impurities present in samples were removed by high-pressure liquid chromatography (LC). Therefore, all materials used in this study were homogeneous by LC examination.

Sample Preparation. Aqueous solutions of herbicide or herbicide analogue were prepared for photolysis by stirring weighed amounts of material at defined concentrations (Tables I and II) in distilled water at 60 °C for 2 h. The herbicide-containing solutions were allowed to stand overnight and then were filtered to remove any particulate matter.

All herbicide solutions with 0.2% (w/w) surface-active agent were prepared by the addition of 0.2 g of active surfactant (TMN-10 or X-100) and 100 mL of aqueous herbicide solution into 250-mL Erlenmeyer flasks. The Erlenmeyer flasks were stoppered, magnetically stirred for 1 h, and then placed on a G-10 gyrotary shaker (New Brunswick Scientific, Edison, NJ) at 120 rpm for 16 h to allow equilibration of the herbicide between the aqueous phase and the organic micellar phase.
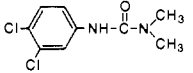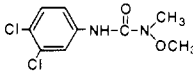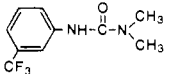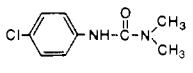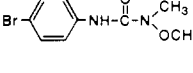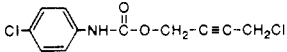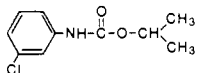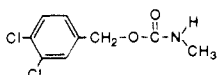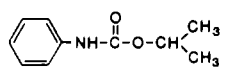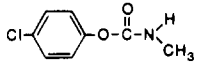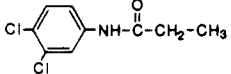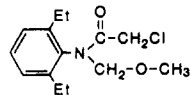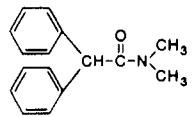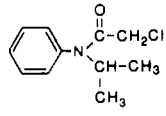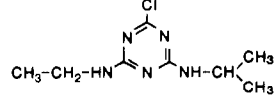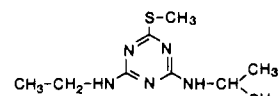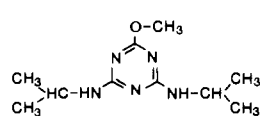
For the photodegradation experiments of Tables I and II, samples were prepared in triplicate and the experiments were duplicated at a minimum. Where unusual results were obtained, experiments were replicated additional times to ensure that the effects were authentic.

Sample Irradiation. A Rayonet photoreactor fitted with 300-nm sunlight lamps was used as the light source, and 10-mL samples were photolyzed in 20-mL Pyrex tubes (Tanaka et al., 1977). Samples were preheated at 50 °C for 15 min to allow temperature equilibration with the photoreactor, and all samples were irradiated for 135 min. After photolysis, the samples were transferred into 20-mL screw-cap vials and held for LC analysis.

Sample Analysis. Measurement of unreacted parent material after photolysis was carried out with a Waters

Table I.   Effect of Surfactants on the Photolability of Four Classes of Herbicides

common name	structure	H_2O sol, ppm	irradn concn, ppm	% loss		
				H_2O	TMN-10[a]	X-100[a]
		Phenylureas				
diuron	Cl,Cl-C$_6$H$_3$-NH-C(=O)-N(CH$_3$)(CH$_3$)	42[b,f]	40	84	56	80
linuron	Cl,Cl-C$_6$H$_3$-NH-C(=O)-N(CH$_3$)(OCH$_3$)	75[b,f]	75	67	40	75
fluometuron	CF$_3$-C$_6$H$_4$-NH-C(=O)-N(CH$_3$)(CH$_3$)	90[b,f]	90	31	38	35
monuron	Cl-C$_6$H$_4$-NH-C(=O)-N(CH$_3$)(CH$_3$)	230[c,f]	100	40	64	75
metobromuron	Br-C$_6$H$_4$-NH-C(=O)-N(CH$_3$)(OCH$_3$)	330[b,f]	100	59	53	60
		Carbamates				
barban	Cl-C$_6$H$_4$-NH-C(=O)-O-CH$_2$-C≡C-CH$_2$Cl	11[b,g]	10	22	76	99
chlorpropham	Cl-C$_6$H$_4$-NH-C(=O)-O-CH(CH$_3$)(CH$_3$)	88[e,g]	80	21	51	76
dichlormate	Cl,Cl-C$_6$H$_3$-CH$_2$-O-C(=O)-N(H)(CH$_3$)	170[e,g]	100	4	6	23
propham	C$_6$H$_5$-NH-C(=O)-O-CH(CH$_3$)(CH$_3$)	250[e,g]	100	1	1	1
PPG-124	Cl-C$_6$H$_4$-O-C(=O)-N(H)(CH$_3$)	570[e,g]	100	88	77	84
		Amides				
propanil	Cl,Cl-C$_6$H$_3$-NH-C(=O)-CH$_2$-CH$_3$	120[h]	100	37	32	51
alachlor	(Et,Et)-C$_6$H$_3$-N(C(=O)-CH$_2$Cl)(CH$_2$-O-CH$_3$)	242[b,g]	100	1	1	85
diphenamid	(C$_6$H$_5$)$_2$CH-C(=O)-N(CH$_3$)(CH$_3$)	260[d,g]	100	0	0	0
propachlor	C$_6$H$_5$-N(C(=O)-CH$_2$Cl)(CH(CH$_3$)CH$_3$)	580[c,g]	100	1	1	37
		Triazines				
atrazine	2-Cl-4-(NH-CH(CH$_3$)$_2$)-6-(NH-CH$_2$-CH$_3$)-triazine	33[d,g]	30	8	6	17
ametryne	2-S-CH$_3$-4-(NH-CH(CH$_3$)$_2$)-6-(NH-CH$_2$-CH$_3$)-triazine	185[c,g]	100	17	15	27
prometrone	2-O-CH$_3$-4-(NH-CH(CH$_3$)$_2$)-6-(NH-CH(CH$_3$)$_2$)-triazine	750[c,g]	100	1	1	5

[a] 0.2% surfactant in water.   [b] Solubility at 25 °C.   [c] Solubility at 20 °C.   [d] Solubility at 27 °C.   [e] Solubility temperature not given.   [f] Kearney and Kaufman (1975).   [g] WSSA (1974).   [h] Experimental measurement at 20 °C; WSSA (1974) reported 500 ppm at an unreported temperature.

Table II. Effect of Surfactants on the Photodegradation of a Series of Mono- and Dichloropropionanilides

name	H$_2$O sol, ppm[a]	irradn concn, ppm	% loss		
			H$_2$O	TMN-10[b]	X-100[b]
4-Cl-PA[c]	200	100	5	13	50
3-Cl-PA	500	100	15	7	55
2-Cl-PA	1200	100	3	3	63
3,5-Cl$_2$-PA	58	50	16	53	79
2,5-Cl$_2$-PA	60	50	12	23	87
2,4-Cl$_2$-PA	100	100	18	18	60
3,4-Cl$_2$-PA (propanil)	120[d]	100	31	29	45
2,3-Cl$_2$-PA	130	100	0	0	46
2,6-Cl$_2$-PA	545	100	0	2	23

[a] Water solubility was determined experimentally at 20 ± 2 °C. [b] 0.2% surfactant in water. [c] PA = propionanilide. [d] WSSA (1974) reported 500 ppm at an unreported temperature.

Table III. Acetophenone Photosensitized Reactions in 0.2% Aqueous TMN-10

compd	irradn concn, ppm	% loss	
		control	acetophenone[a]
linuron	75	39	100
alachlor	100	1	18[b]
dichlormate	100	6	100
atrazine	33	8	92
2-Cl-PA[c]	100	1	100
2,3-Cl$_2$-PA	100	0	100

[a] Triplet energy 74 kcal/mol (Turro, 1967). [b] Became cloudy after photolysis. [c] PA = propionanilide.

Associates LC equipped with two 6000-psi high-pressure pumps, Model 660 solvent programmer, μBondapak C$_{18}$ column, Varian Varichrom detector (using 254 nm), and Shimadzu data processor. Gradient elutions were conducted with acetonitrile and water (Tanaka et al., 1979). By use of pure authentic reference materials, standard curves were prepared for each compound analyzed by the LC system. Direct analysis of photolyzed samples without prior extraction and cleanup could be performed without surfactant interference.

Solubility Determination of Mono- and Dichloropropionanilides. Material in excess of the water solubility of each compound was added to approximately 100 mL of distilled water in 250-mL Fleaker flasks. Samples were stirred magnetically for 2 h at 60 °C, capped, and allowed to stand at room temperature (20 ± 2 °C) for 2 days. Excess material was removed by filtration, and water solubility was determined by LC analysis.

Sensitization Study. Selected herbicides and propanil analogues from Tables I and II that appeared to be photosensitized by X-100 were tested for photolability by sensitization reaction with acetophenone. Triplicate samples were prepared in 0.2% TMN-10 aqueous solutions for each compound tested (concentration given in Table III) as described earlier. Photosensitized samples with 3.8 mg (0.032 mmol/10 mL) of acetophenone were equivalent in molar concentration to X-100 (average M_r of 628) samples used at 0.2% concentration. Control samples did not contain acetophenone. Samples were photolyzed and analyzed as previously described.

RESULTS AND DISCUSSION

In Table I are given the four classes of herbicides investigated. Compounds within each class are listed in order of increasing water solubility. Because water solubilities vary over a wide range, concentration of material

photolyzed was limited for the relatively insoluble compounds. Where possible, however, 100 ppm of herbicide was photolyzed. Determination of photolability at constant light dosage is not possible by direct comparison of values in Table I because all photolyzed solutions were at different molar concentrations. Therefore, only a qualitative measure of photolability can be estimated between the different herbicides. Surfactant effects provided by TMN-10 are primarily due to micellar solubilization of herbicide because TMN-10 is an alkyl-substituted surfactant that does not absorb ultraviolet light. Hence, the effect of micellar solubilization is determined by comparing the losses observed in the H$_2$O column with those observed in the TMN-10 column of Table I. Solubilization effects are also observed with X-100; however, the chromophoric aryl group of X-100 absorbs ultraviolet light and may provide photosensitization effects. Therefore, if degradation losses are considerably greater than those observed in H$_2$O or TMN-10, photosensitized herbicidal decomposition by X-100 is indicated.

If herbicidal photodecomposition in Table I was less than 20% in H$_2$O alone, the effects of micellar solubilization were either negligible or nonexistent. Above 20% degradation, however, the effects of micellar solubilization ranged from small to very significant. These results are exemplified by fluometuron, monuron, barban, and chlorpropham. The lack of substituents on the phenyl ring affords photostability to diphenamid, propachlor, and propham in H$_2$O alone or with TMN-10. The attachment of two unsubstituted phenyl rings makes diphenamid extremely resistant to photodegradation even in the presence of X-100. Herbicides with a 3,4-dichloro substitution on the phenyl ring (diuron, linuron, and propanil) appear to be partially protected from degradation in the presence of TMN-10. The percent degradation of these herbicides in the presence of TMN-10 is less than in H$_2$O alone. This protective effect, however, is not demonstrated with dichlormate, a herbicide that contains a 3,4-dichlorobenzyl moiety. Therefore, to determine if chlorine substitution patterns can affect photolability, a series of mono- and dichloropropionanilides were photolyzed.

Water solubilities for the substituted propionanilides were measured experimentally (Table II). The measured solubility of propanil (120 ppm) was much lower than the 500 ppm reported in the literature (WSSA, 1974). In our studies with 500 ppm of propanil, crystals appeared in the flask after the solution was allowed to cool and stand at room temperature. If water solubilities of the propionanilides exceeded 100 ppm, surfactant effects provided by micellar solubilization during photolysis were either small or nonexistent.

In water alone, the 2-chloro-, 2,3-dichloro-, and 2,6-dichloropropionanilides were photostable whereas 3,4-dichloropropionanilide (propanil) was the most photolabile propionanilide tested. With surfactant, TMN-10 affords a small protective effect with the 3-chloro and 3,4-dichloro isomers. On the other hand, the 3,5- and 2,5-dichloro isomers show a high degree of photolability in the presence of TMN-10. Owing to their low water solubility, the 3,5- and 2,5-dichloro isomers are apparently partitioned efficiently into the micelles where reductive dechlorination occurs at a higher rate than in the aqueous phase.

The data in Table II show that chloro substitution at specific positions on the aromatic ring does not consistently demonstrate a protective effect. The results suggest that 3,4-dichlorophenyl-containing herbicides might have the ability to transfer absorbed energy to the surfactant. Consequently, these herbicides would then cause surfac-

tant decomposition during photolysis, and thus a protective effect would be provided by TMN-10. In this regard, we have observed that monuron enhances the photodegradation of TMN-6 in aqueous solution (Tanaka and Wien, 1979).

The small increases in degradation observed with X-100 in comparison with TMN-10 may be due to the greater ability of X-100 to solubilize the herbicide or to shift the herbicidal absorption spectrum toward longer wavelengths. The significant increases in photodegradation with X-100 (Tables I and II), however, suggest surfactant-sensitized reactions. For study of the sensitization effect (Table III), compounds that appear to be sensitized by X-100 were selected to represent each class of materials examined in Tables I and II. Acetophenone was used as a sensitizer because of its high triplet energy (E_T = 74 kcal/mol) and its high efficiency of intersystem crossing (E_{ST} = 0.99) (Turro, 1967). The results in Table III show that nearly all selected compounds were totally decomposed in the acetophenone-sensitized reactions. Surprisingly, however, alachlor in the presence of acetophenone was only 18% decomposed whereas in the presence of X-100 the material was 85% decomposed. X-100 appears to strongly photosensitize the decomposition of alachlor (Table II), but acetophenone in the presence of TMN-10 effects only limited sensitized decomposition of alachlor. Therefore, acetophenone appears to either photosensitize TMN-10 decomposition or react with TMN-10 to reduce the concentration of surfactant micelles in solution. To support this contention, we observed the separation of acetophenone from solution after photolysis for only the alachlor samples. This is the first evidence we have observed that clearly demonstrates that surfactants can provide good protection against pesticidal photodegradation.

The large losses observed in Tables I and II afforded by the apparent sensitized reaction with X-100 generally do not approach 100% as was experienced with acetophenone (Table III). The lower degradation losses observed with X-100 in comparison with acetophenone could be caused by a lower efficiency of light absorption and by a lower efficiency of intersystem crossing by X-100.

The absorption spectra of X-100 and acetophenone containing TMN-10 were taken in aqueous solution and in acetonitrile; the results verify that acetophenone more efficiently absorbs the incident radiation. Acetophenone has an intersystem crossing efficiency that is essentially quantitative; hence, it is very unlikely that X-100 would be as efficient. Consequently, even though X-100 appears to photosensitize the degradation of some herbicides, the percentage losses would not be expected to be as high as those experienced with acetophenone as sensitizer.

CONCLUSIONS

Surfactants cause an increase in the photodegradation rate of herbicides that have low water solubilities, chloro

substituent(s) on the aromatic ring, and triplet energies lower than that of the added surfactant. If the above requirements are not fulfilled, the addition of surfactant has a variable effect on the photodegradation rate of herbicides in aqueous solution.

Surfactant solubilization effects are best demonstrated with the carbamates, barban and chlorpropham. These compounds have low water solubilities and show a marked increase in photodegradation rate in the presence of TMN-10. On the other hand, the photolability of the selected amides and triazines is essentially unaffected by solubilization into the TMN-10 micelles. In the reaction involving X-100, however, it appears that photosensitized degradation of the amides and triazines is occurring.

This study has demonstrated that nonionic surfactants can either enhance or suppress herbicidal photodegradation. By careful selection of surfactants in formulation, herbicidal lifetimes with respect to photodecomposition in aqueous media can apparently be either encouraged or discouraged. Since pesticides are photolyzed as vapors and aerosols after aerial application (Woodrow et al., 1978), an extremely photolabile pesticide might be protected against photodecomposition with appropriate additives. For more careful selection of surfactants, an important factor is knowledge of the triplet energies of the surfactants and pesticides in question. Thus, for enhanced degradation the surfactant E_T must exceed that of the pesticide, and for protection the surfactant E_T must be lower than that of the pesticide.

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