Rate Constants for Metam-Sodium Cleavage and Photodecomposition in Water

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Metam-sodium is a soil fumigant with many important uses in agriculture. In soil the compound is rapidly and efficiently converted to methyl isothiocyanate (MITC), a volatile biologically active product. In this laboratory study the kinetics of conversion of metam-sodium to MITC, methylthiourea (MTU), and 1,3-dimethylthiourea (DMTU) in water were investigated. In the dark metam-sodium decomposed with a rate constant of 3.3×10^{-4} min^{-1} ($t_{1/2}$ = 35 h, 25 °C, pH 7) and was converted to MITC with a yield of 15 mol %. In spite of weak absorption of near-UV light, metam-sodium photodegraded rapidly in the photoreactor with a near-UV quantum yield of 0.36 ± 0.093 (n = 7). Photoproducts included MITC and DMTU, and the MITC yield was 19 mol %. These findings demonstrate that metam-sodium is considerably more stable in water than in soil. When exposed to midday, midsummer sunlight in shallow water, however, the compound is predicted by modeling to photodecompose with a half-life of less than 1 h.

INTRODUCTION

Metam-sodium (sodium *N*-methylcarbamodithioate) is an important commercial pesticide used to control soil fungi, nematodes, insects, and weeds. Metam-sodium also is a wood preservative used on utility poles, marine pilings, and structural timbers (Miller and Morrell, 1990). Metam-sodium is formulated as a 32.7% solution which is diluted with water and applied directly to soil, where it decomposes to methyl isothiocyanate (MITC), a volatile, biologically active product believed to account for metam-sodium's fumigant action.

The environmental fate of metam-sodium and its breakdown products in soil have been studied extensively in an effort to improve its efficacy and to avoid persistent phytotoxicity associated with residual MITC. The conversion of metam-sodium to MITC in soil is usually complete within a few hours to a day (Lloyd, 1962; Smelt and Leistra, 1974; Smelt et al., 1989), and the conversion efficiency is very high, i.e., 90–98% depending on soil type (Smelt et al., 1989). Metam-sodium behaves similarly in soil slurries, with 71–94% conversion to MITC in 1 h.

Comparatively little information is available on the fate of metam-sodium in water. The major decomposition reactions of metam-sodium in strongly acidic and basic media are summarized in Figure 1. Acid-catalyzed cleavage to carbon disulfide and an alkylamine is a general reaction of dithiocarbamates and is the basis for the carbon disulfide evolution method for determination of dithiocarbamate pesticides (AOAC, 1990). The reaction is faster for dialkyldithiocarbamates than it is for monoalkyldithiocarbamates such as metam-sodium (Joris et al., 1970). The first dissociation constant of metam-sodium is 1.3×10^{-3} (Miller and Latimer, 1962), and thus the reaction is not important above pH 5.0. At pH >11 metam-sodium loses a second proton and decomposes to MITC and sulfur.

At near-neutral pH, two chemical reactions may be important: (i) oxidation to dimethylthiuram disulfide (DMTD), an intermediate which is further oxidized to MITC (Turner and Corden, 1963), and (ii) a monomolecular cleavage reaction again yielding MITC and hydrogen sulfide (Joris et al., 1970), also shown in Figure 1. According to Joris and co-workers the oxidative coupling reaction is thermodynamically unfavorable below pH 9.5. Therefore, only the horizontal cleavage reaction is expected to be important in natural water.

In addition to decomposition by cleavage, metam-sodium is photochemically unstable. The reported photochemical half-lives for metam-sodium exposed to sunlight are very short, between 30 min (Spurgeon, 1990) and 1.6 h (Worthing, 1991).

In this investigation the kinetics of metam-sodium's horizontal cleavage reaction and photochemical decomposition were studied in the laboratory. Reaction rate constants and the near-UV quantum yield (Φ) were measured. The yields of several decomposition products including MITC, methylthiourea (MTU), and 1,3-dimethylthiourea (DMTU) also were obtained. MITC is more toxic than metam-sodium, being both a potent irritant and lachrymator, and thus it must be considered in evaluating metam-sodium's occupational (Collina and Maini, 1979) and environmental health effects. Carefully measured rate constants such as those sought in this study are essential to the successful application of environmental fate models now widely used as predictive tools.

EXPERIMENTAL PROCEDURES

Chemicals. Hexadecyltrimethylammonium bromide (CTAB), MITC, MTU, and DMTU were obtained from Aldrich Chemical Co. (Milwaukee, WI). Metam-sodium (dihydrate) (98% pure based on CS_2) was obtained from Cresent Chemical (Hauppauge, NY). Trifluralin was an analytical reference standard provided by the U.S. Environmental Protection Agency (Research Triangle Park, NC). Reagent grade disodium EDTA (dihydrate) was obtained from Spectrum Chemical (Gardena, CA).

Determination of Metam-Sodium. As a low molecular weight, ionic compound, metam-sodium is not retained on reversed-phase columns without mobile phase additives such as quaternary amine detergents (Mullins and Kirkbright, 1987). Metam-sodium was determined here using an aminopropylsilyl bonded normal-phase column (Supelcosil LC-NH_2, 250 × 4.6 mm, 5 μm; Supelco, Inc., Bellefonte, PA) eluted with 0.75 mL/min water–methanol (3:1 v/v) containing 0.2–0.4 mM disodium

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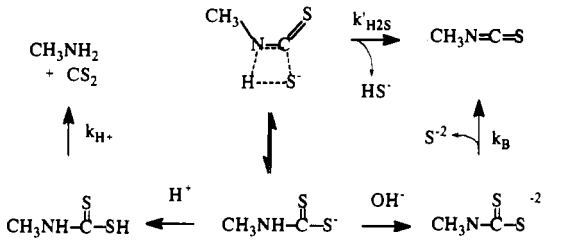

Figure 1. Decomposition pathways for metam-sodium in water under acidic, basic, and near-neutral conditions.

EDTA, 10 mM (pH 7.0) phosphate buffer, and 10 mM CTAB. Alternatively, a cyanopropyl column (Spheri-5 Cyano column, 220 × 4.6 mm, 5 μm; Applied Biosystems, Inc.; Foster City, CA) eluted with 1.0 mL/min water–methanol (3:2 v/v) containing the same concentrations of EDTA, phosphate buffer, and CTAB was used (Spurgeon, 1990). Mobile phases containing detergent were degassed by sonication under reduced pressure before use.

Metam-sodium was detected by absorption at 290 nm with a sensitivity of 0.02 absorbance unit full scale (AUFS). The detector was calibrated between 1 and 250 mg/L (parts per million) using freshly prepared methanol solutions. Even though methanolic solutions were refrigerated, metam-sodium decomposition was evident after several days and therefore both calibration and stock solutions were prepared daily.

Determination of Thioureas and MITC. A reversed-phase column (Supelco LC-18, 250 × 4.6 mm, 5 μm) eluted with 1.5 mL/min of water–methanol (4:1 v/v) was used to determine MTU, DMTU, and MITC. The compounds were detected by UV absorbance at 240 nm, where as little as 0.05 mg/L of the thioureas and 0.5 mg/L of MITC are detected with a sensitivity of 0.02 AUFS. The retention times for MTU, DMTU, and MITC were 2.5, 3.0, and 9.4 min, respectively. A breakdown product formed by MITC in methanol eluted at 7.3 min.

Stability of Metam-Sodium and Its Decomposition Products in Buffer. Metam-sodium decomposition in 50 mM (pH 7.0) phosphate buffer was studied at various concentrations (3.0, 0.30, and 0.030 mM; 390, 39, and 3.9 mg/L) at 25 °C. Metam-sodium was first dissolved in acetonitrile (or methanol) and a small volume transferred to the buffer to obtain the desired metam-sodium concentration. The organic cosolvent amounted to 2.5, 0.5, or 0.05 vol % of the buffer solutions. Serum bottles with Teflon-lined septum caps were used with no headspace to minimize loss of volatile products. The bottles were wrapped with foil and placed in a thermostated shaker bath which agitated the samples and maintained temperature. Periodically for up to 1 month samples were analyzed for metam-sodium, MITC, MTU, and DMTU by direct injection of the buffer onto the appropriate HPLC system.

Several additional variables were considered which may effect metam-sodium decomposition in natural water including naturally occurring oxidants and suspended sediment. The 0.30 and 0.030 mM solutions were amended by addition of 2.0 g/100 mL of a very fine river sediment, National Bureau of Standards (NBS) Standard Reference Material (SRM) No. 1645. The sediment formed a suspension which gradually settled over the period of the experiment. Sediment-containing samples were filtered (Gelman Sciences Acrodisc cartridge filters, 0.45 μm) prior to HPLC analysis. Buffered metam-sodium solutions were treated with 10^{-4} M hydrogen peroxide prepared by transferring an aliquot of 10^{-2} M hydrogen peroxide stock solution.

Photochemical Reactivity: Quantum Yield Determination. Photodecomposition rates for metam-sodium, DMTU, MITC, and MTU were investigated by irradiating the compounds in a laboratory photoreactor which provides near-UV quantum yields (Draper, 1985, 1987). Φ values obtained are necessary for modeling direct photolysis reactions in natural water using procedures developed by the U.S. Environmental Protection Agency (Zepp and Cline, 1977; Zepp, 1978).

Stock solutions (10 mg/mL) in acetonitrile or methanol were diluted to 100 mg/L in 50 mM (pH 7.0) phosphate buffer. Because of the greater sensitivity in analysis, MTU, DMTU, and MITC were irradiated at lower concentrations in the same phosphate buffer solution, e.g., 10, 10, and 50 mg/L, respectively. Samples were held in sealed borosilicate test tubes (UV cutoff ~280 nm) in a merry-go-round apparatus and were irradiated with Rayonet

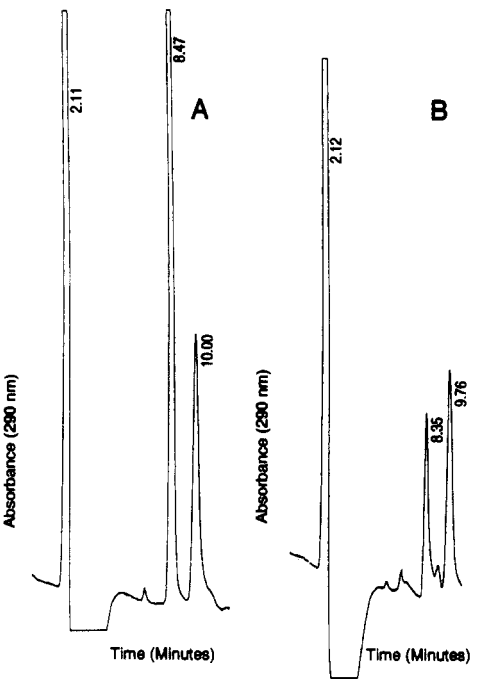

Figure 2. HPLC separation of 50 mg/L metam-sodium (A) and an aged 50 mg/L metam-sodium solution (B). An aminopropyl silyl column and micellar mobile phase were used giving a metam-sodium t_R of 8.4 min. The scales and signal attenuation are the same in (A) and (B).

RPR-3500 fluorescent blacklight lamps in a Rayonet RPR-100 photoreactor (Southern New England Ultraviolet Co., Hamden, CT). The lamps emit between 310 and 410 nm and have maximal output at about 350 nm.

Light intensity was determined by simultaneous irradiation of a chemical actinometer, a 25 μg/L solution of trifluralin in isooctane (Draper, 1987). In this solvent the trifluralin Φ is 0.018, giving a convenient half-life for the laboratory photoreactor. Trifluralin was determined by gas chromatography by direct injection of the isooctane solution on an instrument equipped with an electron capture detector and megabore column.

Both the loss of the parent compound (to obtain disappearance Φ) and the formation of products were determined by direct analysis of the irradiated solutions by HPLC. Absorption spectra of metam-sodium and its decomposition products were determined in dilute methanol solution, and molar extinction coefficients (ε) were calculated for wavelengths above 297.5 nm as needed for determination of Φ.

Metam-sodium is a polydentate ligand which would be expected to coordinate trace metal ions in natural water. The influence of trace metal ion content on metam-sodium photodecomposition was investigated by irradiating the pesticide with ferric sulfate and/or disodium EDTA. One equivalent (relative to metam-sodium) of disodium EDTA or $Fe_2(SO_4)_3$, each in 1 mL of distilled water, was added to the buffered metam-sodium solution immediately prior to irradiation.

RESULTS AND DISCUSSION

Determination of Metam-Sodium and Its Decomposition Products. The commercial metam-sodium standard available to this laboratory contained a nonpolar contaminant which eluted after metam-sodium on either the aminopropylsilyl or cyanopropyl bonded-phase column. The contaminant was resolved to baseline on either of the columns (Figure 2) with typical retention times of the contaminant (relative to metam-sodium) of 1.14 and 1.39 min for the aminopropyl and cyanopropyl columns, respectively. Using a C_{18} reversed-phase column and a micellar mobile phase with or without added EDTA, metam-sodium was retained but gave broad peaks.

Metam-sodium, even in dilute methanolic solutions under refrigeration, breaks down over a period of days.

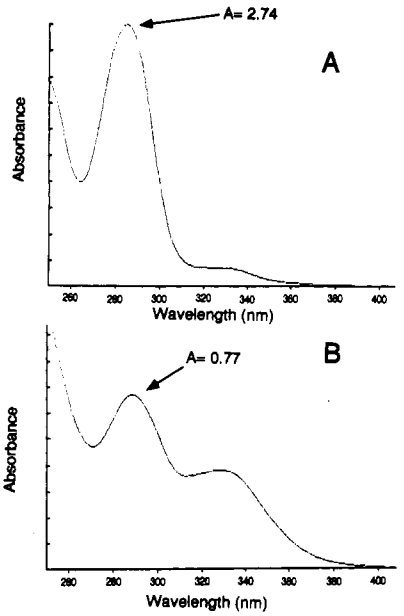

Figure 3. Absorption spectra for metam-sodium (A) and aged metam-sodium (B) in methanol. The nominal concentration was 3.0×10^{-4} molar.

The absorption spectrum of a freshly prepared metam-sodium solution is shown in Figure 3. Metam-sodium absorbs with a maximum at 285 nm [($\epsilon = 9 \times 10^{-3}$ L (mol cm)$^{-1}$]. This absorption band diminishes with time, and a shoulder absorbing at 330 nm becomes prominent (Figure 3). The loss of metam-sodium (t_R = 8.4 and 8.5 min) and preservation of the contaminant observed on analysis of these same solutions by HPLC (Figure 2) are consistent with the observed spectral changes. In 3 weeks the metam-sodium concentration dropped by ~75%. Further evidence that the spectrum of "aged" metam-sodium is due to the contaminant was obtained by use of a diode array detector (unpublished results).

Metam-sodium's instability in water and organic solvents as noted here, as well as contamination of the commercially available standard, may lead to errors in metam-sodium determination. The contaminant is easily confused with metam-sodium. MITC also is unstable in methanol solutions and yields a more polar breakdown product. The compound has a retention time of 0.78 relative to MITC on a C_{18} reversed-phase column and may be the cyclic dithione 2,4-dimethyl-1,2,4-thiazolidine-3,5-dithione, reportedly a common impurity in MITC (Miller, 1989).

Stability of Metam-Sodium and MITC in Buffer. At high metam-sodium concentrations, a rapid initial breakdown of the pesticide was observed. Within 1 h the concentration dropped from 640 to 530 mg/L, and after 24 h, the metam-sodium concentration reached 430 mg/L. The half-life was ~50 h, although this was difficult to estimate in this experiment due to error in measuring the initial metam-sodium concentration—the first data point was obtained at 10 min when significant breakdown had already occurred. Moreover, the HPLC method for determination of metam-sodium was most accurate between 1 and 250 mg/L.

At lower concentrations, the rapid initial breakdown was not observed (Figure 4), and metam-sodium determination is more accurate. The metam-sodium concentration dropped from 39 to 15 mg/L in 73 h and then to 1.4 mg/L in 170 h, approximating first-order kinetics. The calculated rate constant is 3.3×10^{-4} min^{-1} at 25 °C, corresponding to a 35-h half-life. Dilute hydrogen peroxide (10^{-4} M) did not have a measurable effect on the decomposition of metam-sodium, as after 170 h, the metam-sodium concentration was about the same, 1.6 mg/L. River sediment appeared to accelerate the decomposition rate, as no metam-sodium was detected after 170 h.

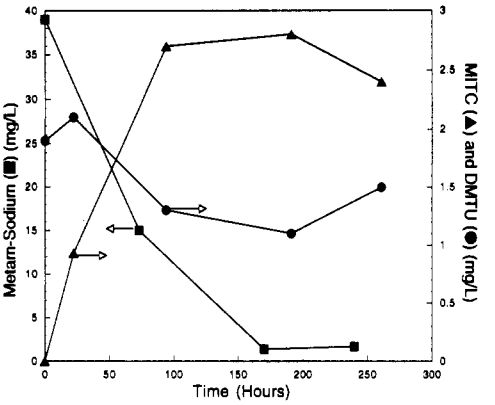

Figure 4. Decomposition of metam-sodium in pH 7 phosphate buffer at 25 °C.

Table I. Relationship between Metam-Sodium Concentration and MITC, DMTU, and MTU Yields in Water

	initial metam-sodium concn		
compound	390 mg/L[a]	39 mg/L[b]	3.9 mg/L[b]
initial [MTU]	3.6	ND[c]	ND
initial [DMTU]	10	1.9	0.066
initial [MITC]	3.8	ND	ND
[MTU]	ND	ND	ND
[DMTU]	6.3	2.1	0.13
[MITC]	37	2.8	1.6

[a] Products determined only at t_0 and 456 h (19 days). [b] Products determined at various times between t_0 and 310 h (13 days). [c] ND, not detected.

When metam-sodium was first dissolved in buffer, MTU, DMTU, and MITC were each detected (Table I). A 390 mg/L metam-sodium solution contained 3.6 (1% relative to metam-sodium), 10 (3%), and 3.8 (1%) mg/L of MTU, DMTU, and MITC, respectively. After 20 days, MTU could not be detected, the DMTU concentration was lower (6.3 mg/L), and MITC increased ~10-fold to 37 mg/L. During the same 20-day period metam-sodium concentration decreased by 395 mg/L. Thus, the overall efficiency of metam-sodium conversion to MITC is approximately 15% of the theoretical stoichiometric yield. MITC (in the absence of metam-sodium) is relatively stable by comparison, with 73% remaining after 19 days at 25 °C.

At a lower metam-sodium concentration, 39 mg/L, MTU was below the detection limit, DMTU levels were high initially and dropped throughout the experiment, and MITC increased to a maximum concentration of 2.8 mg/L after 191 h (Figure 4). In this case the yield of MITC was 13 mol %, and as before, the yield was not affected by either hydrogen peroxide or sediment.

At the lowest metam-sodium concentration, 0.033 mM, MITC concentrations reached 1.6 mg/L, 60% of the highest levels reached in 0.3 mM solutions, corresponding approximately to a quantitative yield. Hydrogen peroxide or suspended sediment again had no effect on MITC production.

Photochemical Reactivity of Metam-Sodium and Its Products. Metam-sodium's absorption band at 285 nm drops off abruptly above 300 nm with an extinction coefficient of about 10^3 L (mol cm)$^{-1}$ at 310 nm. The chromophore overlaps the emission spectrum of the fluorescent blacklight lamp used in the laboratory photoreactor (Table II) as well as sunlight. The extinction coefficients in Table II were based on a freshly prepared

Table II. Typical Spectral Irradiance Values for the Laboratory Photoreactor and Metam-Sodium Molar Extinction Coefficients

wavelength, nm	photon irradiance, photon (cm s)$^{-1}$	metam-sodium extinction coeff, L (mol cm)$^{-1}$
297.5		4960
300		3670
302.5		2580
305		1790
307.5		1290
310	3.9 E + 13	975
312.5	7.5 E + 13	803
315	1.2 E + 14	718
317.5	1.9 E + 14	683
320	2.6 E + 14	670
323.1	6.3 E + 14	665
330	1.6 E + 15	650
340	3.1 E + 15	479
350	4.0 E + 15	231
360	3.6 E + 15	115
370	2.4 E + 15	58
380	1.4 E + 15	29
390	6.3 E + 14	11
400	2.8 E + 14	4
410	9.6 E + 13	

[a] The absorption spectrum was obtained from a freshly prepared 50 mg/L methanolic solution.

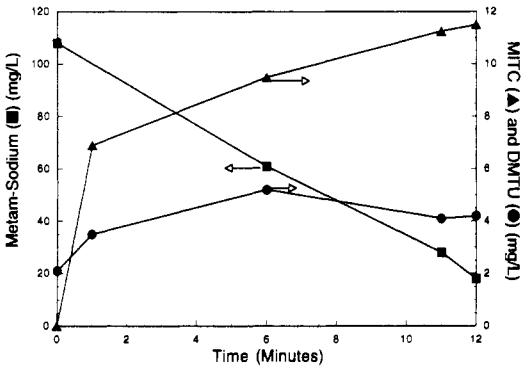

Figure 5. Photodecomposition of metam-sodium in the laboratory photoreactor and appearance of MITC and DMTU photoproducts.

solution of metam-sodium, but a portion of the absorbance, particularly above 310 nm, is attributable to the contaminant.

In spite of the weak chromophore, metam-sodium photodegraded very rapidly in the laboratory photoreactor (Figure 5). Half-lives ranged from 2.9 to 8.4 min and varied with the light intensity which ranged from 3500 to 6400 μW/cm^2. At high concentrations, i.e., between 30 and 100 mg/L, the photodecomposition of metam-sodium deviated from first order with the slope of the semilog plot increasing with time (Figure 6). Below 30 mg/L the kinetics approximated first order.

Metam-sodium's disappearance quantum yield was very high, ranging from 0.20 to 0.46. While data from two typical experiments (Table III) appear to show an effect of the organic cosolvent (1% of the photolysis solution), the differences were not statistically significant. The error in determination of Φ was attributed to the deviation from first-order kinetics as well as analytical error. The relative standard deviation in half-life estimates averaged 35% (n = 6), which accounted for most of the error in estimating the quantum yield.

The mean value of Φ was 0.36 ± 0.093 (n = 7). Φ indicates the efficiency of a given photochemical process and is the ratio of the photochemical reaction rate to the rate of light absorption. Most photolabile compounds have quantum yields of 0.01 or less, as most radiant energy absorbed is

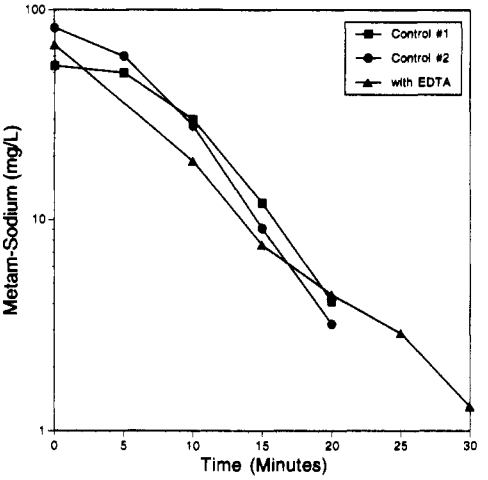

Figure 6. Photodecomposition of metam-sodium in phosphate buffer (A) and in phosphate buffer with added disodium EDTA (B). The light intensity was 3600 μW/cm^2 for the two controls and 5000 μW/cm^2 in the experiment with EDTA.

Table III. Photodecomposition Kinetics, Photoreactor Light Intensities, and Disappearance Quantum Yields for Metam-Sodium

condition	metam-sodium half-life, min	trifluralin half-life, min	light intensity, μW/cm^2	quantum yield
1% methanol	4.4 ± 2.9	15 ● 2.4	3400	0.42
1% acetonitrile	8.4 ● 0.3	14 ● 1.0	3700	0.20

Table IV. Effect of Ferric Iron and EDTA on the Photodecomposition of Metam-Sodium

treatment	metam-sodium k, min^{-1}	metam-sodium $t_{1/2}$, min	trifluralin $t_{1/2}$,[b] min	exptl quantum yield
control	0.23	3.0 (0.55)[a]	11 (0.071)	0.46
EDTA	0.12	5.6 (1.8)	10 (1.4)	0.22
Fe^{3+}	0.22	3.2 (0.98)	12 (1.4)	0.48
EDTA/Fe^{3+}	0.12	5.6 (2.0)	8.5 (1.8)	0.19

[a] Numbers in parentheses are standard deviations. [b] Light intensities varied between 4200 and 5900 μW/cm^2.

dissipated in nonproductive photophysical processes. Thus, metam-sodium photodegrades efficiently, near the theoretical Φ maximum of 1.

The identified photoproducts of metam-sodium included MITC, which was recovered in moderate yield, 19 mol % at 12 min. The net conversion to DMTU was about 6%. Each of the potential photoproducts determined, DMTU, MTU, and MITC, was stable under similar conditions with no detectable photodecomposition occurring after 5 h of irradiation in the laboratory photoreactor.

The direct photolysis rate for metam-sodium in shallow water was estimated using the approach of Zepp and Cline (1977). In midday, midsummer sunlight (latitude 40° N) and 10 cm deep water, metam-sodium is predicted to photodecompose with a half-life of ~44 min. As the water depth increases, metam-sodium photodegrades less rapidly—with a depth of 0.5 m the expected half-life is 220 min. Seasonal changes in the intensity and wavelength distribution of solar UV light decrease the spectral overlap at other times of the year. For the shallow water case, metam-sodium's direct photolysis half-lives are 51, 44, 81, and 127 min for spring, summer, fall, and winter, respectively.

EDTA modified the photodecomposition of metam-sodium in two ways: (i) the photodecomposition kinetics became first order (Figure 6) and (ii) metam-sodium's photoreactivity (and apparent Φ) was lower (Table IV).

Introduction of ferric iron as $Fe_2(SO_4)_3$ had no observable effect on the photodegradation rate, and supplementation with both EDTA and Fe^{3+} was equivalent to addition of EDTA alone. Even though EDTA appears to strongly influence metam-sodium's half-life, the sample sizes are small and the dispersion in the data is too great to be conclusive. The mean metam-sodium half-lives with and without added EDTA were not significantly different at the 90% confidence level.

While the available data are inconclusive, the trend suggests that dissolved metal ions (but apparently not Fe^{3+}) may accelerate metam-sodium's photodecomposition. Deviations from first-order kinetics may also be explained by coordination of dissolved metal ions. As metam-sodium photodegrades, both the proportion of metam-sodium (or *N*-methyldithiocarbamic acid) coordinated to metal ions and the ligand's photodecomposition rate increase.

CONCLUSION

Metam-sodium's instability in water and organic solvents and contamination of the commercially available standards can lead to errors in metam-sodium determination by HPLC. Reliable determination of metam-sodium requires a micellar mobile phase, preparation of standards daily, and some form of confirmation either by spectroscopy or by an independent method of analysis. Confirmation can be achieved by exposing the sample to near-UV light to look for disappearance of the analyte, as has been done in the confirmation of polybrominated biphenyl, for example.

In the dark the major decomposition pathway for metam-sodium in water is a cleavage reaction yielding MITC and hydrogen sulfide. The rate of metam-sodium decomposition measured in this study, 3.3×10^{-4} min^{-1} (25 °C), is in good agreement with the horizontal cleavage rate constant reported by Joris and co-workers (Joris et al., 1970). The yield of MITC is dependent on metam-sodium concentration with yields of 13–15 mol % for metam-sodium solutions between 10 and 10^3 mg/L. At very low concentrations the conversion efficiency to MITC appears to be higher. Suspended sediments accelerate metam-sodium decomposition.

In spite of a weak chromophore metam-sodium is highly photoreactive in near-UV light. Its wavelength-averaged, near-UV Φ is 0.36 ± 0.093. Most photolabile pesticides by comparison have quantum yields of less than 0.01, and thus metam-sodium photodegrades with exceptional efficiency. MITC (19 mol %) and DMTU (6%) are major photoproducts of metam-sodium in water, and these products resist further photodegradation. Photochemical breakdown of metam-sodium appeared to be slower in the presence of the chelating agent EDTA, but the large differences between control and treated samples were not statistically significant.

These findings point to major differences in the fate of metam-sodium in natural water and soil. In particular, metam-sodium decomposes much more rapidly and in higher yield to MITC in soil. Sunlight plays an important role in determining metam-sodium's persistence in natural water.

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