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AQUATIC ENVIRONMENTAL CHEMISTRY
2-(THIOCYANOMETHYLTHIO) BENZOTHAZOLE AND
RELATED BENZOTHAZOLES

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NWRI Contribution # 91-62

MANAGEMENT PERSPECTIVE

Benzothiazoles are an important class of industrial chemicals that can enter the aquatic environment via several pathways. As a result of their use as vulcanization accelerators, they can reach surface waters in wastewater from industries such as tire plants and also due to leaching from waste rubber such as rubber dust along roads. Other routes include the discharge of automobile radiator fluids and other cooling waters in which benzothiazole-based compounds are used as corrosion inhibitors, the disposal of waste photographic solutions, and the use and manufacture of benzothiazole-based pesticides. The greatest use is in the rubber industry and we have previously studied the aquatic pathways of benzothiazoles originating in a chemical plant in Elmira, Ontario, that manufactured compounds for tire manufacturing. However, the most significant source of benzothiazoles to Canadian waters at this time is likely the use of the pesticide Busan 30WB as an alternative to chlorophenols in anti-sapstain agents for the lumber industry. This use is heaviest in British Columbia, particularly in the Fraser River estuary.

The active ingredient in Busan is 2-(thiocyanomethylthio)benzothiazole, or TCMTB. In response to a request from EP-P&Y for estimates of the halflife and fate of TCMTB in surface waters, we reviewed the available information. We could find very little information in the open literature about the properties of TCMTB that would allow us to predict the fate of this compound in surface waters. To correct this gap, and with the support of PESTFUND, we conducted a series of studies to measure basic chemical properties of TCMTB and related compounds. We also determined the rates and products of various degradation routes. The study drew on our previous experience since some of the TCMTB degradation products were compounds we had encountered in Canagagigue Creek, downstream from Elmira, Ontario.

Based on our results, we conclude that TCMTB and its hydrolysis product mercaptobenzothiazole (MBT) are unlikely to persist or bioaccumulate. Chemically stable end products appear to be benzothiazole (BT) itself, 2-(methylthio)-benzothiazole (MTBT) and 2-hydroxybenzothiazole. Little information regarding the toxicity of these end products is available. In view of their apparent environmental stability, toxicity testing appears to be appropriate.

In our studies, we also identified the products of reaction between MTBT and chlorine. Such reactions could occur in sewage plants discharging MTBT-containing wastewater that has been disinfected with chlorine and also in drinking water plants during disinfection if the water source was contaminated with MTBT. We are unable to assess the environmental significance of these reaction products because, to our knowledge, with the exception of our initial identification of them in Canagagigue Creek, they have not been reported or studied. Now that we have identified a route of their formation, we are in a better position to assess whether their occurrence is likely to be widespread and whether they warrant toxicity testing.

Our results should be useful in predicting the persistence and fate of TCMTB in waters after spills and accidental discharges and also in designing monitoring programs such as that being designed for the Water Quality component of the Fraser River Estuary Management Program (FREMP).

PERSPECTIVES DE LA DIRECTION

Les benzothiazoles sont une importante classe de produits chimiques industriels qui peuvent pénétrer de plusieurs façons dans le milieu aquatique. Utilisés comme accélérateurs de la vulcanisation, ils peuvent atteindre les eaux superficielles par les eaux usées des usines de fabrication de pneus et par lessivage des déchets de caoutchouc, comme la poussière de caoutchouc le long des routes. Les rejets du liquide des radiateurs d'automobile et d'autres eaux de refroidissement dans lesquelles des composés à base de benzothiazole sont utilisés comme inhibiteurs de corrosion, l'élimination des déchets de solutions utilisées en photographie, l'utilisation et la fabrication de pesticides à base de benzothiazoles sont d'autres voies d'acheminement. L'industrie du caoutchouc est la plus grande consommatrice de ces produits et nous avons déjà étudié les voies aquatiques de pénétration des benzothiazoles générés par une usine chimique d'Elmira (Ontario) qui produisait des composés destinés à la fabrication de pneus. Toutefois, à l'heure actuelle, la source la plus importante de benzothiazoles dans les eaux canadiennes, est sans doute le Busan 30WD (pesticide) utilisé comme produit de remplacement des chlorophénols dans les agents anti-coloration employés dans l'industrie du sciage. Son usage est beaucoup plus répandu en Colombie-Britannique, notamment dans l'estuaire du Fraser.

L'ingrédient actif du Busan est le 2-(thiocyanométhylthio) benzothiazole, ou TCMTB. En réponse à une demande de la Protection de l'environnement, région du Pacifique et du Yukon, relativement à une estimation de la demi-vie et du devenir du TCMTB dans les eaux de surface, nous avons étudié les données accessibles. Nous avons trouvé très peu d'information dans les documents généraux sur les propriétés du TCMTB qui nous permettraient de prévoir le devenir de ce composé dans ces eaux. Afin de combler cette lacune, nous avons effectué une série d'études permettant d'évaluer les caractéristiques physiques de base du TCMTB et des produits connexes, et ce, grâce à l'aide de PESTFUND. Nous avons également calculé le taux de dégradation et déterminé les produits obtenus par les différentes voies de dégradation. Les auteurs de l'étude se sont inspirés de notre expérience antérieure étant donné que certains produits de dégradation du TCMTB étaient des produits dont nous avons déjà signalé la présence dans le ruisseau Canagagigue, en aval d'Elmira (Ontario).

D'après les résultats que nous avons obtenue, il est peu probable qu'il y ait persistance ou bioaccumulation de TCMTB et de son produit d'hydrolyse, le mercaptobenzothiazole (MBT). Les produits chimiques finals stables semblent être le benzothiazole (BT) lui-même, le 2-(méthylthio)-benzothiazole (MTBT) et le 2-hydroxybenzothiazole. Nous disposons de peu de données sur la toxicité de ces produits. Vu leur apparente stabilité dans l'environnement, il semble tout à fait approprié d'effectuer des études de toxicité.

Dans le cadre de nos études, nous avons également identifié les produits de réaction entre le MTBT et le chlore. De telles réactions peuvent se produire dans des usines d'épuration des eaux d'égout rejetant des eaux usées contenant du MTBT traitées au chlore et aussi dans les usines d'épuration de l'eau (eau potable) au cours du processus de désinfection si la source d'eau était contaminée par du MTBT. Nous ne sommes pas en mesure d'évaluer l'importance environnementale de ces produits de réaction parce que, à notre connaissance, à l'exception de notre première identification de ces produits dans le ruisseau Cangagigue, ils n'ont pas été signalés ou étudiés. Maintenant que nous connaissons une voie de formation, nous sommes mieux placés pour déterminer si leur présence s'étendra ou s'ils justifient des études de toxicité.

Les résultats obtenus devraient permettre de prévoir la persistance et le devenir du TCMTB dans l'eau après des déversements et des rejets accidentels, et d'élaborer des programmes de surveillance comme ceux qui sont mis en oeuvre dans le cadre du volet de la qualité de l'eau du Programme d'aménagement de l'estuaire du fleuve Fraser.

Abstract -- BUSAN 30WB (R) is an alternative to pentachlorophenol as an anti-sapstain agent in the lumber industry. The active ingredient is 2-(thiocyanomethylthio)benzothiazole (TCMTB). Very little information is available in the open literature on the fate of TCMTB in aquatic environments, and we wish to report our studies on TCMTB and related benzothiazoles, some of which are potential transformation products of TCMTB. We measured the water solubility and octanol-water partition coefficients of TCMTB, benzothiazole (BT), 2-mercaptobenzothiazole (MBT) and 2-(methylthio)benzothiazole (MTBT). The water solubility of TCMTB at 24 °C is 40 mg/L and the log K_{ow} is 3.12. At pH 8 and 24 °C in dilute borax-phosphate buffer, the half-life of TCMTB was 750 hours and in seawater (pH 7.8 to 8.0, 24 °C) it was about 740 hours. Attempts to measure sediment-water partitioning of TCMTB resulted in production of traces of MTBT, presumed to result from biological methylation of MBT released by hydrolysis of TCMTB. MTBT was produced directly from MBT in the presence of sediment. In phosphate buffer, TCMTB readily underwent direct photolysis in sunlight to produce MBT in about 50% yield, and traces of BT. The photochemistry of MBT, the major photolysis product of TCMTB, was studied in some detail. Sunlight quantum yields of TCMTB and MBT are estimated to be 0.01 and 0.002, respectively. Sunlight photolysis of MBT in phosphate buffer with and without dissolved organic matter, and in a natural water, led to three products: benzothiazole (28 to 47%), 2-hydroxybenzothiazole (4 to 5%), and an unidentified product. On the basis of our laboratory and field results, and literature reports on the occurrence of benzothiazoles, we propose a partial pathway for this family of benzothiazoles in aquatic environments. TCMTB and MBT are unlikely to persist or bioaccumulate. Stable end products appear to be BT, MTBT and 2-hydroxybenzothiazole.

RÉSUMÉ

Le BUSAN 30WD(R) est un produit de remplacement du pentachlorophénol comme agent anti-coloration employé dans l'industrie du sciage. L'ingrédient actif est le 2-(thiocyanométhylthio) benzothiazole (TCMTB). Les documents généraux contiennent très peu d'informations sur le devenir du TCMTB dans le milieu aquatique, et nous désirons présenter un rapport sur nos études sur le TCMTB et les benzothiazoles connexes, dont certains sont des produits de transformation potentiels du TCMTB. Nous avons mesuré sa solubilité dans l'eau et le coefficient de partage octanol-eau du benzothiazole (BT), du 2-mercaptobenzothiazole (MBT) et du 2-(méthylthio) benzothiazole (MTBT). La solubilité du TCMTB dans l'eau à 24 °C est de 40 mg/L et la log K_{OE} est de 3,12. À pH 8 et à 24 °C dans un tampon borax-phosphate dilué, la demi-vie du TCMTB était de 750 heures et dans l'eau de mer (pH 7, 8 à 8,0, 24°C), elle était d'environ 740 heures. Les essais visant à mesurer le coefficient de partage sédiment-eau du TCMTB ont produit des traces de MTBT, résultant sans doute de la méthylation biologique du MBT libéré par hydrolyse du TCMTB. Le MTBT était produit directement à partir du MBT en présence de sédiments. Dans un tampon phosphate, le TCMTB est photolysé rapidement et directement à la lumière solaire en MBT dans une proportion de 50 % environ, et en BT à l'état de trace. Les propriétés photochimiques du MBT, le principal produit de photolyse du TCMTB, a été étudié en détail. Les rendements quantiques de la lumière solaire pour le TCMTB et la MBT sont évalués respectivement à 0,01 et à 0,002. La photolyse solaire du MBT dans un tampon phosphate, avec et sans matière organique dissoute, et dans une eau naturelle, a donné trois produits: le benzothiazole (28 à 47 %), le 2-hydroxybenzothiazole (4 à 5 %) et un produit non identifié. D'après les résultats de nos études en laboratoire et sur le terrain, et des rapports dans la littérature sur la présence des benzothiazoles, nous proposons une voie d'acheminement partielle pour cette famille de benzothiazoles dans le milieu aquatique. La persistance ou la bioaccumulation du TCMTB et du MBT sont peu probables. Les produits finals stables semblent être le BT, le MTBT et le 2-hydroxybenzothiazole.

Running head: Aquatic environmental chemistry of benzothiazoles.

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AQUATIC ENVIRONMENTAL CHEMISTRY OF
2-(THIOCYANOMETHYLTHIO)BENZOTHAZOLE
AND RELATED BENZOTHAZOLES

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Abstract -- BUSAN 30WB (R) is an alternative to pentachlorophenol as an anti-sapstain agent in the lumber industry. The active ingredient is 2-(thiocyanomethylthio)benzothiazole (TCMTB). Very little information is available in the open literature on the fate of TCMTB in aquatic environments, and we wish to report our studies on TCMTB and related benzothiazoles, some of which are potential transformation products of TCMTB. We measured the water solubility and octanol-water partition coefficients of TCMTB, benzothiazole (BT), 2-mercaptobenzothiazole (MBT) and 2-(methylthio)benzothiazole (MTBT). The water solubility of TCMTB at

24°C is 40 mg/L and the log K_{ow} is 3.12. At pH 8 and 24°C in dilute borax-phosphate buffer, the half-life of TCMTB was 750 hours and in seawater (pH 7.8 to 8.0, 24°C) it was about 740 hours. Attempts to measure sediment-water partitioning of TCMTB resulted in production of traces of MTBT, presumed to result from biological methylation of MBT released by hydrolysis of TCMTB. MTBT was produced directly from MBT in the presence of sediment. In phosphate buffer, TCMTB readily underwent direct photolysis in sunlight to produce MBT in about 50% yield, and traces of BT. The photochemistry of MBT, the major photolysis product of TCMTB, was studied in some detail. Sunlight quantum yields of TCMTB and MBT are estimated to be 0.01 and 0.002, respectively. Sunlight photolysis of MBT in phosphate buffer with and without dissolved organic matter, and in a natural water, led to three products: benzothiazole (28 to 47%), 2-hydroxybenzothiazole (4 to 5%), and an unidentified product. On the basis of our laboratory and field results, and literature reports on the occurrence of benzothiazoles, we propose a partial pathway for this family of benzothiazoles in aquatic environments. TCMTB and MBT are unlikely to persist or bioaccumulate. Stable end products appear to be BT, MTBT and 2-hydroxybenzothiazole.

Keywords -- TCMTB Mercaptobenzothiazole MBT Hydrolysis Photolysis

INTRODUCTION

Benzothiazoles are an important class of industrial chemicals. They are used as vulcanization accelerators in the manufacture of rubber, as pesticides, as corrosion inhibitors in anti-freeze, and as photosensitizers in photography. Possible routes of entry into the environment are water

and air emissions from their manufacture, rubber dust from tires, pesticide application, and cooling water to which they have been added as corrosion inhibitors. Production of benzothiazoles in the United States was greater than 150 million kg in 1981 [1]. 2-Mercaptobenzothiazole (MBT)¹ and its metal salts are the most common industrial benzothiazoles. Various sulfenamides of MBT are used as vulcanization accelerators.

2-(Thiocyanomethylthio)benzothiazole (TCMTB) is an active fungicidal ingredient in several formulations of BUSAN^(R) pesticides. BUSAN 30WB^(R), for example, is an alternative to chlorophenols as an anti-sapstain agent in the lumber industry. Structural formulas, chemical names and abbreviations are given in Figure 1.

While there is an extensive literature on the production and use of benzothiazoles, there are considerably fewer reports on their environmental occurrence, and fewer still on their environmental fate. Several benzothiazoles have been reported in aquatic environments: benzothiazole (BT) in river water [2-6], drinking water [7,8], street runoff [9], tire plant wastewater [7], sediment [9], and liver of starry flounder [9]; 2-mercaptobenzothiazole (MBT) in tire plant wastewater [10]; 2-(methylthio)benzothiazole (MTBT) in river water [2,5], drinking water [7], and liver of starry flounder [9]; 2-hydroxybenzothiazole (HOBT)² in

^{1,2} Both MBT and HOBT can exist in two tautomeric forms, as shown in Figure 1. We have elected to use the more common nomenclature (mercapto- and hydroxy-) while recognizing that these are the less predominant forms.

drinking water [7,8]; and 2-(methylsulfinyl)benzothiazole (MSiBT) and 2-(methylsulfonyl)benzothiazole (MSoBT) in river water [5]. HOBT, MBT and MTBT have also been identified in water extracts of rubber seals in disposable syringes [11].

We had previously reviewed the properties and health aspects of benzothiazoles and their occurrence in aquatic environments [12], and identified a family of benzothiazoles in a small southern Ontario creek [5]. These benzothiazoles were of industrial origin and entered the creek in municipal sewage effluent. The current study of TCMTB was initiated because of a need for information on the aquatic environmental chemistry of TCMTB in support of new regulations for wood protection agents.

In this report, we describe our research on the physical properties of TCMTB, BT, MBT and MTBT; the hydrolysis and photolysis of TCMTB; the biomethylation and photolysis of MBT; and the hypochlorite oxidation of MTBT.

EXPERIMENTAL

Materials

Pure TCMTB was kindly provided by Dr. Grace Bonner of Buckman Laboratories, Memphis, TN. BT was supplied by Aldrich Chemical Company, Milwaukee, WI. MBT was supplied by Matheson, Coleman and Bell, Norwood, OH. MTBT and bis-(2-benzothiazolyl)disulfide (MBTS) were from Pfalz and Bauer, Stamford, CT. MBTS was recrystallized from toluene and had T_m 174 to 176°C, lit. T_m 180°C [13]. 2-Hydroxybenzothiazole (HOBT) was synthesized by hypochlorite oxidation of benzothiazole [14] and had T_m 136 to 138°C, lit. T_m 138 to 139°C [15]. MSiBT and MSoBT were synthesized by

oxidation of MTBT with one or two equivalents of *m*-chloroperbenzoic acid in DCM according to the method of Vernin et al. [16]. MSiBT had T_m 66 to 67°C, lit. T_m 66 to 68°C [16]. MSoBT had T_m 89 to 90°C, lit. T_m 80 to 82°C [16], 90 to 92°C [17].

Dichloromethane (DCM), acetonitrile UV (MeCN), chloroform and isooctane were from American Burdick & Jackson, Muskegon, MI, and methanol (MeOH) was obtained from Caledon Chemicals, Georgetown, ON. 1-Octanol was obtained from Fisher Scientific, Fair Lawn, NJ. Purified water was provided by a Millipore Milli-Q^(R) system. Supelclean LC-18 tubes were purchased from Supelco Canada, Oakville, ON.

Dissolved organic matter (DOM) was isolated from a water sample taken from Canagagigue Creek at Floradale, Ontario. The water was filtered, acidified, and passed through an XAD-4 column. DOM was eluted with ammonium hydroxide-methanol and the eluate evaporated to dryness. The DOM was predominantly fulvic acid. Suspended sediment was collected from Canagagigue Creek by continuous-flow centrifugation and stored frozen. Canagagigue Creek water was filtered through glass fiber and membrane filters and had 8.2 mg/L of dissolved organic carbon (DOC).

High Performance Liquid Chromatography (HPLC)

Gas chromatography (GC) cannot be used to analyze TCMTB due to instability at high temperatures [18]. Thus, HPLC has been used to analyze TCMTB [18-20]. HPLC was carried out using a 25 cm by 4.6 mm Whatman Partisil 10 ODS-2 C₁₈ reverse phase column with a 7 cm by 2.1 mm guard column packed with CO:Pe11 ODS. An Altex 110A pump and a Beckman 210 injector with 20 or 100 µl loop, Waters 441 detector operating at 280 nm or

Waters 440 detector operating at 254 nm, and a Hewlett-Packard 3380 integrator were used. MBT, BT, TCMTB and MTBT were separated in less than 10 minutes with MeCN:water (50:50, v/v) as the mobile phase at a flowrate of 2.0 ml/min. For analysis of MBTS, a mobile phase of MeOH:water (90:10, v/v) at a flowrate of 2.0 ml/min was used. Detector response was determined with standards made up in either pure MeCN or MeCN:water (50:50, v/v). The retention time and response of MBT is pH-dependent, presumably due to ionization above pH 7 [21]. For quantitative determination of MBT, the pH of the injection solution was kept at 7 or less.

Gas Chromatography (GC)

GC analysis was carried out on three systems. The first was a Hewlett-Packard 5720 chromatograph using a flame ionization detector and a 30 m by 0.252 mm i.d. capillary column coated with DB-17 (J&W Scientific, Rancho Cordova, CA). Flow rate of helium carrier was about 0.8 ml/min. The column was programmed from 80 to 260° or 100 to 260°C at 4°C/min. A Hewlett-Packard 3380 integrator was used. The second system was a Hewlett-Packard model 5710 with flame ionization detector and a 30 m by 0.32 mm i.d. capillary column coated with SPB-5 (Supelco, Bellefonte, PA). Helium carrier flow rate was about 1.4 ml/min. The column was programmed from 100 to 260°C at 4°C/min. A Hewlett-Packard 3396 integrator was used. Field samples were analyzed on this instrument operating in nitrogen-selective mode using a 30 m by 0.252 mm i.d. capillary column coated with DB-1 (J&W) and programmed from 90 to 260°C at 4°C/min with a helium flow rate of 0.8 ml/min. The third system was a Hewlett-Packard model 5890

chromatograph with 30 m by 0.32 mm i.d. SPB-5 column programmed from 80 to 280°C at 4°C/min, and Hewlett-Packard Chemstation data system.

Gas Chromatography-Mass Spectrometry (GC-MS)

GC-MS analyses were carried out on a Hewlett-Packard model 5890 chromatograph equipped with a 12 m by 0.2 mm i.d. capillary column coated with Ultra 1, and programmed from 60 to 240°C at 6°C/min. Mass spectra were obtained with a Hewlett-Packard 5971A Mass Selective Detector connected to a Hewlett-Packard MS Chemstation data system.

Spectral and Light Measurements

Ultraviolet (UV) and visible spectra were measured with a Varian model DMS 100 spectrophotometer using 1 cm quartz cells. Incident solar radiation was measured with a LI-1000 recording light meter equipped with LI-190SA quantum sensor (LI-COR, Lincoln, NE). This sensor measures light in the 400-700 nm range.

Water Solubility

Saturated solutions were prepared at room temperature ($24 \pm 1^\circ\text{C}$) by gently stirring an excess of pure material with pure water for several days. Liquids were suspended in a small glass cup just below the liquid surface to prevent formation of suspensions. The mixtures were then filtered through glass wool or glass fiber filters to remove undissolved material. BT solutions were diluted and analyzed by HPLC. MBT, MTBT, and TCMTB solutions were analyzed directly by HPLC.

Octanol-Water Partition Coefficients

Water-saturated 1-octanol was prepared by vigorously stirring 1-octanol (200 ml) with water (10 ml), letting the layers separate and then centrifuging at 1300 rpm for 45 min. 1-Octanol-saturated water was prepared in the same way from 1-octanol (2 ml) and water (200 ml). This procedure is described by Ribo [22].

Stock solutions of 1 mg/ml of test compound in water-saturated 1-octanol were prepared. Stock solution (10 ml) and 1-octanol-saturated water (40 ml) were shaken gently in a 125 ml separatory funnel for 15 min and the layers were let separate for 1 h. A small portion of the lower (water) layer was drawn off and discarded. Two portions were then drawn off dropwise into centrifuge tubes, centrifuged at 1300 rpm for 45 min, and analyzed directly by HPLC. The remainder of the lower layer was removed, the upper layer was drawn off by pipet into centrifuge tubes, centrifuged at 1300 rpm for 45 min, diluted 100-fold with MeCN:water (50:50, v/v), and analyzed by HPLC. $\log_{10} K_{ow}$ was calculated from the ratio of the concentration in each phase.

TCMTB Hydrolysis

The first series of hydrolysis experiments was carried out in 0.05 M tris-(hydroxymethyl)methylamine (Tris) buffer solutions. The buffer (9 ml) at the target pH, and a saturated water solution of TCMTB (1 ml) were placed in a 16 by 150 mm screw cap tube. The pH was checked and adjusted if needed. The tubes were let stand in the dark at the test temperature (5, 15 or 24°C). For sub-ambient temperatures, a shaking water bath was used. At appropriate times, aliquots were analyzed directly by HPLC.

After these preliminary experiments, the procedure was modified to minimize or eliminate rate enhancement by Tris buffer, and analytical precision was improved by diluting samples 50:50 (v/v) with MeCN for injection and rinsing the injector with pure MeCN between injections to minimize adsorption of analytes in the injector.

For determining the yield of MBT, a saturated solution of TCMTB in water was mixed with an equal volume of 0.01 M Tris at the test pH (8.00), and the pH checked and adjusted if needed. This solution was placed in dark flasks at room temperature. At appropriate times, duplicate aliquots (4.00 ml) were removed, 1.0 ml of 0.1 M potassium phosphate buffer (pH 6.0) was added and the volume made up to 10.0 ml with MeCN. Previous tests had shown that the pH of the resultant aqueous solutions was 6.4 to 6.7. These solutions were then analyzed by HPLC. The standard was 0.010 mg/ml of MBT and TCMTB in the same buffer-solvent combination.

Buffer-dependence was investigated by carrying out hydrolyses in various buffers at pH 8.00. Buffer solution (100 ml) and saturated aqueous TCMTB solution (100 ml) were mixed together and the pH adjusted to 8.00. The solution was placed in a red (dark) volumetric flask and let stand at room temperature ($24 \pm 2^\circ\text{C}$). At appropriate times, duplicate 5.00 ml aliquots were pipetted into 10 ml volumetric flasks and the sample made to volume with MeCN and analyzed by HPLC. A separate 10 ml sample was used to check the pH. The pH in the test solutions was 8.00 ± 0.05 throughout the experiment. Two different buffers were tested; Tris at 0.05 and 0.005 M, and Kolthoff's borax-phosphate buffer [23] at 1/2 and 1/20 strength. The borax-phosphate buffer (pH 8.0, 1/20 strength) was approximately 0.0025 M in borax and 0.005 M in potassium dihydrogen phosphate. Further

experiments were carried out in 1/20 borax-phosphate buffer at pH 7.0 and 9.0 at room temperature, and at pH 8.0 at 15 and 5°C using the same procedure. Below pH 8 the proportion of borax to phosphate in the buffer was lower, and above pH 8 it was higher.

An analogous set of hydrolysis experiments was carried out in wellwater, Fraser River water and seawater from British Columbia at $24 \pm 2^\circ\text{C}$ in the dark. Again, pH was determined at every analysis point.

TCMTB Sediment-Water Partitioning

The suspended sediment from Canagagigue Creek contained about 6% organic carbon and had a high clay content. Before use, a portion of the frozen sediment was mixed with sufficient water to give a thick paste which was 55% water by weight.

Wet sediment, equivalent to about 1 g dry weight, was added to 500 ml of water in each of two 1-L screw cap Erlenmeyer flasks and shaken for 1 h to disperse the sediment. A further 500 ml of water containing approx. 100 μg of TCMTB was added to the test flask, and 500 ml of water was added to the blank flask. A third flask containing approx. 100 μg of TCMTB in 1000 ml of water was used as a control. The flasks were shaken at 180 strokes/min on a reciprocal shaker for 12 h at room temperature, then let stand for another 12 h.

Sediment was resuspended and collected by pressure filtration through a 142 mm, 5.0 μm Teflon filter (Millipore LSWP) on top of a glass fiber filter (Gelman A/E). Both the filtrate and filters were analyzed for TCMTB. The pH of the filtrates was 8.0 (blank) and 8.3 (TCMTB).

The recovered filtrate (960-980 ml) was extracted with DCM (3 x 50 ml). The extracts were dried (Na_2SO_4), and reduced to small volume. After solvent exchange into MeCN the extracts were analyzed by HPLC. The measured TCMTB concentration in the control was 85 $\mu\text{g/L}$ and zero in the blank. The test sample (TCMTB plus sediment) extract contained no detectable TCMTB, but did contain a peak corresponding to a few per cent of MTBT. This was confirmed by GC analysis from retention time comparison and peak enhancement with authentic material on a DB-17 column and by GC-MS [$m/z(\%)$ for sample, 181(100), 166(12), 148(70), 136(18), 122(12), 108(34), 82(15), 69(29)] and [$m/z(\%)$ for authentic MTBT, 181(100), 166(8), 148(71), 136(16), 122(10), 108(34), 82(10), 69(16)].

The filters were rolled up and cut into 1 cm sections into a 25 by 150 mm screw cap tube. Then 30 ml of a mixture of MeCN:0.01 M potassium phosphate buffer, pH 6.0 (3:1, v/v) was added to each tube and the filter macerated with a glass rod. The tubes were shaken horizontally on a reciprocal shaker for 6 h at 180 strokes/min. A further 10 ml of MeCN-buffer was added and the tubes were let stand overnight.

The tubes were centrifuged for 15 min at 1000 rpm. Supernatant (30 ml) was drawn off and passed through a Whatman GF/F filter. A further 10 ml of MeCN-buffer was added to each tube, the tube shaken for 0.5 h, centrifuged, and a further 12 to 14 ml of supernatant drawn off (nominal recovery of extract at this point was 85-90%). The MeCN was removed on a rotary evaporator and the residue (in buffer) was applied to a 1 g Supelclean LC-18 column which had been activated with 2 ml MeCN and rinsed with 2 ml of buffer. The column was washed with 10 ml of buffer, 10 ml of MeCN:buffer (1:3, v/v), and then 10 ml of MeCN:buffer (1:1, v/v). Previous

experiments had shown that the TCMTB elutes in the last fraction, which was worked up by removing most of the MeCN under a stream of argon and extracting the aqueous residue with DCM (3 x 5 ml). The DCM extracts were dried (Na_2SO_4) and reduced to a small volume. After solvent exchange into MeCN, the extracts were analyzed by HPLC. The blank and TCMTB test samples contained no detectable TCMTB. The control (TCMTB without sediment) contained a small peak for TCMTB due to retention of TCMTB solution by the filters.

The MeCN-buffer (1:3) fractions, which would contain any MBT, were reduced to approx. 1 ml and analyzed by HPLC. No MBT was found in these fractions.

MBT Methylation (Biotic)

MBT was incubated with Canagagigue Creek suspended sediment (see above). Suspended sediment (2.95 g wet weight, 1.33 g dry weight) was suspended in 500 ml of water by shaking for 1 h on a reciprocal shaker. Water (300 ml) and an aqueous solution of MBT (200 ml of 29 mg/L) were added. Water (800 ml) and MBT solution (200 ml) were used as a control. Both flasks were shaken in reduced light at room temperature for 12 h on a reciprocal shaker at 180 strokes/min, then let stand overnight in the dark.

The control (1000 ml) was filtered through pre-washed diatomaceous earth and the filtrate was extracted with DCM (3 x 50 ml). The combined extracts were dried (Na_2SO_4), reduced to small volume and solvent exchange into MeCN carried out.

One-half (500 ml) of the sediment-MBT mixture was filtered using pre-washed diatomaceous earth and glass fiber filters. The pH of the filtrate was 8. The filtrate was extracted with DCM as above and the solvent exchanged with MeCN, final volume 1.0 ml. The aqueous layer was acidified to pH 2 with DCM-extracted 6 N hydrochloric acid. It was then extracted with DCM. The DCM extracts were dried (Na_2SO_4) followed by solvent exchange into MeCN.

Qualitative analysis by HPLC showed only MBT in the control sample and the sediment-MBT pH 2 extracts. The sediment-MBT pH 8 extract contained both MBT and MTBT. The MTBT was confirmed by GC retention time match and peak enhancement on an SPB-5 column and by GC-MS [m/z (%) for sample, 181(100), 166(12), 148(77), 136(20), 122(13), 108(34), 82(10), 69(26)].

The remainder of the sediment-MBT sample (500 ml) was let stand at room temperature in the dark for one week. A portion (400 ml) was decanted and centrifuged. It was then extracted with 3 x 50 ml of DCM as above with solvent exchange into MeCN. This was analyzed quantitatively by HPLC. The concentration in the aqueous phase was 0.1 mg/L, corresponding to about a 2% yield of MTBT from MBT.

Sunlight Photolysis

Sunlight photolyses were carried out in solutions buffered with 0.01 M potassium phosphate at pH 6.0 (TCMTB) or 7.0 (MBT, carbazole and MTBT). A solution of potassium dihydrogen phosphate, pure or natural water, and the test compound (added as a water solution) was adjusted to the target pH with 0.1 N potassium hydroxide. In some experiments, 10 or 20 mg/L of DOM

was added. When used, filter sterilization was done by filtration through a 0.2 μm membrane filter using glassware that had been heated at 110°C for several hours. The photolysis solution was divided between a light sample placed in a clear volumetric flask made of borosilicate glass, and a dark sample placed in a red borosilicate volumetric flask or in a screw cap tube (50 ml) wrapped in aluminum foil. Initial concentrations were determined directly for those samples with higher concentration (3 to 15 mg/L) after dilution of a 5 ml aliquot 50:50 (v/v) with MeCN and analysis by HPLC. For more dilute samples (2 mg/L or less), an aliquot of 5 or 10 ml was extracted with DCM (3 x 5 ml). After drying of the DCM extracts (Na_2SO_4) and solvent exchange into MeCN, initial concentrations were determined by HPLC analysis. For carbazole, which was analyzed by GC, the DCM extracts were reduced to small volume, an internal standard added in isooctane, the volume reduced to effect solvent exchange into isooctane, and the extract analyzed by GC using an SPB-5 column.

Sunlight irradiations were carried out by placing the light and dark samples outside during the daytime and recording the incident solar radiation and air temperature. The samples were brought indoors overnight and the light samples placed in the dark. The course of the reaction was followed by analysis directly by HPLC, or by analysis by HPLC or GC after DCM extraction, or by following UV absorbance. Rates are expressed in terms of total incident solar radiation in E/m^2 measured by the quantum sensor. At the end of the experiment, the concentration of the test compound in the dark sample was determined. In all cases, it was within experimental error of the initial concentration measured for the light sample. In some experiments, product studies were done on the light sample

which remained at the end of exposure. The experimental conditions are summarized in Table 1.

Photolysis Studies - TCMTB

The light sample (240 ml) from irradiation of a solution of TCMTB (initial concentration 8.3 mg/L) for two days (67 E/m^2) was extracted with DCM (4 x 10 ml). The combined extracts were dried (Na_2SO_4), concentrated, and analyzed by GC on a DB-17 column. The presence of BT was confirmed by retention time match and peak enhancement with authentic material. Direct analysis by HPLC also showed traces of BT. The dark sample contained unchanged TCMTB.

TCMTB photolysis kinetics were determined by short term irradiation of a solution with initial concentration 8.3 mg/L (Table 1). The disappearance of TCMTB and appearance of MBT and BT was followed by HPLC.

Photolysis Product Studies - MBT

The light sample (approx. 400 ml) from irradiation of a solution of MBT (initial concentration 11.1 mg/L) in phosphate buffer (pH 7.0) for four days (63 E/m^2) was extracted with DCM (3 x 50 ml). The reaction flask was rinsed with this DCM to extract any DCM-soluble material which might have precipitated onto the container walls. The combined extracts were dried (Na_2SO_4), concentrated, and solvent exchange into MeCN (2.0 ml) carried out. This extract should contain neutral and weakly basic products. The odor of benzothiazole was evident. The aqueous portion from the above was acidified with 6 N hydrochloric acid to a pH of 1.5 and extracted with DCM (3 x 50 ml). The combined extracts were dried (Na_2SO_4), concentrated, and

solvent exchange into MeCN (2.0 ml) carried out. This extract should contain acidic products. However, the odor of benzothiazole was also evident in this fraction. These fractions were analyzed by HPLC using the MeCN-water and MeOH-water mobile phases. With the MeCN-water system, the base/neutral fraction had a major peak with the same retention time as BT, a minor peak with the same retention time as HOBT, and traces of starting material. The acid fraction had a major peak with the same retention time as BT, a trace peak with the same retention time as HOBT, and traces of starting material. The presence of BT in both of these fractions was confirmed by GC retention time match and peak enhancement on an SPB-5 column and by GC-MS [m/z (%) for BT in base/neutral fraction, 135(100), 108(33), 91(7), 82(11), 69(20)], [m/z (%) for BT in acid fraction, 135(100), 108(33), 91(6), 82(12), 69(21)] and [m/z (%) for authentic BT, 135(100), 108(29), 91(6), 82(10), 69(20)]. HOBT was confirmed in the base/neutral fraction by GC-MS [m/z (%) for HOBT in base/neutral fraction, 151(100), 123(76), 96(79), 69(19)] and [m/z (%) for authentic HOBT, 151(100), 123(61), 96(65), 69(15)]. HPLC analysis of the base/neutral fraction with the MeOH-water system showed a minor peak eluting just prior to MBTS. There was not a separate peak for MBTS, but the presence of trace quantities was indicated by a trailing shoulder on the prior peak. The acid fraction contained a trace of the unidentified product and no detectable MBTS.

The MBT photolytes (approx. 400 ml, initial MBT concentration of 1.9 mg/L) irradiated for four days (36 E/m^2) in Canagagigue Creek water (8.2 mg/L of DOM) and in phosphate buffer containing 10 mg/L of Canagagigue Creek DOM were extracted in an analogous fashion. HPLC analysis in both solvent systems showed similar product distributions to the photolysis

carried out in phosphate buffer. Low yields (1-2%) of a peak corresponding to MBTS were observed in these samples, but the identity was not confirmed.

Hypochlorite Oxidation of MTBT

A solution of 5 mM sodium bicarbonate (100 ml, pH 8.3), MTBT (2 ml, 12 mg/L in water) and commercial bleach (0.25 ml, 6% w/v of sodium hypochlorite) was let stand in the dark for 1.25 h. Sodium thiosulfate solution (2 ml of 0.2 M) was added to react with excess hypochlorite. The reaction mixture was extracted with chloroform (3 x 5 ml). The extracts were dried (Na_2SO_4), concentrated, and analyzed by GC on an SPB-5 column. No starting material remained and two peaks corresponding to MSiBT and MSoBT were present in approx. a 10:1 ratio. The yield was quantitative. A control sample with bicarbonate buffer and MTBT, but no hypochlorite, showed only starting material, and a reagent blank with bicarbonate buffer and hypochlorite showed no peaks on GC analysis.

Field Studies

Field studies were carried out in the summer of 1984 on an eight km reach of Canagagigue Creek downstream of Elmira, Ontario. The creek receives an input of variable quantities of BT, MTBT, MSiBT and MSoBT from the effluent of the Elmira Water Pollution Control Plant [5]. The treatment plant receives effluent from a chemical plant which manufactures several benzothiazole compounds. Typical creek flows in the summer are 0.3 to $1.0 \text{ m}^3/\text{s}$. We had previously established the relationship between flow and time-of-travel making sampling of a discrete water mass feasible.

Monthly sampling was conducted from May to October at seven or eight sites for water, and at six sites for sediment caught in 3.8 cm x 38 cm stainless steel tubes placed in the creek bed. Water samples were all collected on the same day in a downstream direction according to time-of-travel, while the sediment samples were the material accumulated during the preceding one-month period. The sediment samples were stored frozen until analysis.

Filtered water samples (2 L) were extracted with DCM (2 x 150 ml). The combined extracts were dried (Na_2SO_4), concentrated, and an internal standard added in toluene. The extracts were then analyzed by GC for BT, MTBT, MSiBT and MSoBT on the DB-1 column.

Thawed sediment samples (2 to 4 g dry weight) were Soxhlet extracted with hexane:acetone (60:40, v/v). The extracts were back-extracted with one L of water, dried (Na_2SO_4), concentrated, and cleaned up by gel permeation chromatography on Biobeads S-X3 with hexane:DCM (55:45, v/v). The eluate was concentrated, an internal standard added, and GC analysis for BT, MTBT, MSiBT and MSoBT carried out on the DB-1 column.

RESULTS AND DISCUSSION

Water Solubility and Octanol-Water Partition Coefficient

Water solubilities and octanol-water partition coefficients for the four test compounds are given in Table 2. BT is a liquid and the other three are solids at room temperature. The high solubility for BT (3000 mg/L) is probably due to its high polarity and the fact that it is a liquid at room temperature. The measured solubilities for MTBT and MBT compare well with literature values (125 vs. 110 mg/L [24] for MTBT and 120 vs. 100-120 mg/L [25] for MBT). TCMTB was moderately soluble at 24°C (40 mg/L). The solubilities of MBT and TCMTB at 5°C were about 40% of that at 24°C. Solubilities were also determined in a natural water (from Canagagigue Creek) at different nominal pH values (accurate pH adjustment was difficult due to low ionic strength). The solubility of TCMTB was not enhanced in creek water, but that of MBT was, and showed a pH-dependence indicating that the ionized form is more soluble (Table 3).

Octanol-water partition coefficients (K_{ow}) are given in Table 2. BT is the least hydrophobic and has the lowest K_{ow} . MBT is intermediate, and MTBT and TCMTB are the most hydrophobic. This is consistent with their structures. Agreement with literature values is good for BT and MTBT [26,24]. The difference for MBT is probably due to pH-dependence (Table 4). The partition coefficient for TCMTB did not change significantly in creek water and was not pH-dependent.

TCMTB Hydrolysis

In 0.005 M Tris at 24°C and pH 8.0 MBT was produced in quantitative yield. The other products are presumed to be formaldehyde (CH_2O) and thiocyanate (SCN^-) (Scheme 1).

Preliminary experiments at pH 8.0 had shown a dependence of the pseudo-first-order hydrolysis rate constant (k_h) on buffer concentration when using Tris buffer. This was examined further by using Tris at two concentrations and a borax-phosphate buffer at two concentrations (Table 5). There is approximately a seven-fold increase in hydrolysis rate in 0.05 M Tris as compared to 0.005 M Tris. With borax-phosphate buffer, rates are slower still, and there is less dependence on buffer concentration. From these results, 1/20 strength borax-phosphate was selected for subsequent experiments. Rate enhancements due to the buffer appear to be minimal, and this single buffer can cover a pH range from 6-9. In this buffer, an approximately linear dependence of hydrolysis rate constant on hydroxide ion concentration was observed over the pH range of 7-9 (Table 5). From the rate constants shown in Table 5, it can be concluded that neutral and acid-catalyzed hydrolysis of TCMTB are unimportant in the pH range of most natural waters.

Hydrolysis rate constants and half-lives for TCMTB in three natural waters from British Columbia are given in Table 5. Since pH could not be controlled in this experiment, the ranges of measured pH are given instead to compare the different results. After allowances are made for differing pH, it appears that there are some differences in hydrolysis rates between these natural waters. Hydrolysis is slowest in Fraser River water and

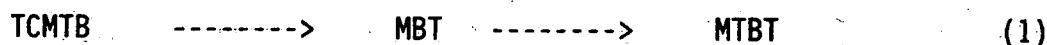
fastest in seawater. In fact, the rate in seawater (pH 7.83-7.96) is very close to that in 1/20 borax-phosphate (pH 8.0).

These results indicate that both specific and general base catalysis could be important reactions affecting the fate of TCMTB in surface waters.

TCMTB Sediment-Water Partitioning

Using the empirical relationship of Karickhoff [27] the predicted organic carbon based partition coefficient ($\log_{10} K_{oc}$) is 2.74 for a compound with a $\log_{10} K_{ow}$ of 3.12. For a sediment containing 5% organic carbon, this corresponds to a sediment-water partition coefficient (K_p) of 27. At 1 $\mu\text{g/L}$ TCMTB, this would give a sediment concentration of approx. 0.03 $\mu\text{g/g}$ of sediment (dry wt.). This is well below the detection limit of about 1 $\mu\text{g/g}$ for the method worked out in this study. For this reason, the partitioning experiment was carried out with a TCMTB concentration of approx. 100 $\mu\text{g/L}$. As well, a very high sediment concentration of 1 g/L was used in order to have sufficient material for analysis.

This experiment gave an unanticipated result. All of the TCMTB disappeared and the only detectable product was a few per cent of MTBT. The probable sequence is hydrolysis followed by (biological) methylation (1).



This latter process would explain the presence of MTBT in Canagagigue Creek [5] where there is no known industrial source of MTBT, but there is a source of MBT.

MBT Methylation (Biotic)

MBT incubated in the presence of suspended sediment isolated from Canagagigue Creek was converted in low yield to MTBT, probably by biologically-mediated methylation of the mercapto group. The biological methylation of thiols has been reported in the literature [28,29]. Drotar et al. [29] observed methylation of MBT by cell-free extracts of bacteria (*Corynebacterium* sp. and *Pseudomonas* sp.) isolated from soil and water. The quantitative significance of this reaction in aquatic environments is difficult to assess, but it offers a plausible means by which MBT (and any derivatives which degrade to it) can be converted into the relatively stable MTBT.

TCMTB Photolysis

In dilute potassium phosphate buffer solutions at pH 6, TCMTB breaks down rapidly by direct photolysis in sunlight (Figure 2) giving MBT as the major product (about 50% yield) and traces of BT. A partial reaction pathway is shown in equation (2).



This is supported by the observation that MBT also breaks down by direct photolysis in sunlight to give BT in moderate yield. Because MBT is the primary product of TCMTB photolysis, the photolysis of MBT was studied further.

MBT Photolysis

Two laboratory studies have been reported on the photolysis of MBT in organic solvents using ultraviolet lamps and pyrex vessels [30,31]. Bis-(2-benzothiazolyl)disulfide (MBTS) was postulated as the first intermediate in the irradiation of MBT in 96% ethanol in the presence of oxygen [30]. This was proposed to undergo oxidation to bis-(2-benzothiazolyl)disulfone which, upon cleavage and hydrolysis, produced benzothiazole sulfate isolated in 95% yield. Irradiation of MBT in MeCN in the presence of oxygen gave MBTS, BT, HOBT and unchanged MBT [31]. A different mechanism was proposed based on unsymmetrical cleavage of the disulfide followed by hydrogen abstraction by the benzothiazolyl radical to give BT. HOBT was proposed to result from oxidation of the benzothiazolyl radical and by oxidation of MBT (thione form) by singlet oxygen. We carried out the sunlight photolysis of MBT in dilute phosphate buffer without and with DOM, and in a natural water, in order to identify the products to test if one (or both) of the above mechanisms might be operative under natural conditions.

After irradiation of MBT in phosphate buffer (pH 7), and DCM extraction, HOBT (4%), BT (11%) and traces of an unidentified product were produced. Acidification of the aqueous phase yielded a further 18% yield of BT. Similar results were obtained for irradiations of MBT in the presence of 10 mg/L of DOM (pH 7) with a 5% yield of HOBT and an 18% yield of BT in the neutral fraction and a further 27% yield of BT after acidification. For irradiations in a natural water (pH 7.1) the HOBT and BT yields were 5 and 21% with a further 26% of BT after acidification.

Traces (1-2%) of MBTS were indicated by HPLC, but not confirmed, in the last two cases.

The production of HOBT and BT (without acidification) is consistent with the mechanism of Abdou et al. [31]. The release of further BT after acidification is not explained by either mechanism. Clearly some other process is involved in the aquatic photochemistry of MBT. Further experimentation is required to distinguish between the many possibilities presented by the chemistry of the various oxidation states of sulfur [32]. Benzothiazolesulfinate is one possible intermediate. Acidification would liberate the free sulfinic acid which could then desulfinate, in a manner analogous to decarboxylation, to produce benzothiazole and sulfur dioxide. This reaction has been proposed for production of *m*-dinitrobenzene in the hydrolysis of 2,4-dinitrobenzenesulfonyl chloride [33]. We are carrying out further work to elucidate this mechanism.

The environmentally important conclusion to be drawn from our results is that BT and HOBT are the anticipated stable products of MBT photolysis in aquatic environments.

Photolysis Rates and Sunlight Quantum Yield

In addition to information about photodegradation products, some estimation of the rates of photodegradation in natural systems is needed to predict the photochemical fate of contaminants. Rate plots for TCMTB, MBT and a reference compound, carbazole, are presented in Figure 2 as per cent of initial concentration versus incident solar radiation in E/m^2 . The rate plot for MBT (initial concentration 11.1 mg/L, $A_{313}=1.25$) is linear indicating a zero-order reaction at these high concentrations and

absorbance because all of the incident radiation which results in a photoreaction is absorbed. At lower concentrations or in the presence of other absorbing species, the rate plots are nonlinear indicating first-order or mixed-order reaction, because not all of the effective radiation is being absorbed by the target molecules.

Environmental photolysis rates and half-lives can be calculated if the sunlight quantum yields are known [34]. Sunlight quantum yields for TCMTB, MBT and carbazole were calculated from the measured incident solar radiation values and reaction rates using an adaptation of the method of Leifer [35]. The basic equation is:

$$I_{a\lambda} = I_{o\lambda}(A/V)F_{s\lambda}F_{c\lambda}$$

Where

$I_{a\lambda}$ = light absorbed by the chemical, E/cm^3

$I_{o\lambda}$ = incident radiation for wavelength interval centered on λ , E/cm^2

(A/V) = area to volume ratio for the reaction cell, cm^2/cm^3

$F_{s\lambda}$ = fraction of light absorbed by the system

$F_{c\lambda}$ = fraction of light absorbed by the chemical

And

$$F_{s\lambda} = \{1 - 10^{-(\alpha_{\lambda} + \epsilon_{\lambda}[C])\ell}\}$$

$$F_{c\lambda} = \epsilon_{\lambda}[C]/(\alpha_{\lambda} + \epsilon_{\lambda}[C])$$

$I_{o\lambda}$ was calculated from measured light values (400 to 700 nm) using the table of solar irradiance values in Leifer [35]. A/V was calculated assuming hemispherical geometry for the reaction flask; ℓ was assumed to be

equal to the computed radius for the hemisphere. Attenuation values for the solvent (α_λ) and molar absorptivities for the chemical (ϵ_λ , L/mol/cm) are given in Table 6. The attenuation coefficient for 0.01 M potassium phosphate, pH 7, was zero from 297.5 to 360 nm. $[C]$ is the concentration of chemical (mol/L); the initial concentration was used in these calculations. $I_{a\lambda}$ was summed over the wavelength (centered) range of 297.5 to 360 nm for a measured incident radiation of one E/m^2 .

From the concentration versus E/m^2 relations (Figure 2) the $\Delta[C]$ (mol/cm³) per E/m^2 of incident radiation was calculated for the test compounds (Table 7) using the most appropriate rate expression (first-order for TCMTB and carbazole, zero-order for MBT). The sunlight quantum yields (Φ) were calculated from the ratio $\Delta[C]/\Sigma I_{a\lambda}$ (mol/cm³)/(E/cm^3) and are summarized in Table 7. The calculated quantum yield for the reference compound, carbazole, agreed with the literature value [36] by better than a factor of two (Table 7). The literature value was determined under similar photolysis conditions, but solar radiation was determined by actinometry rather than by direct measurement with a light meter. The estimated quantum yield for MBT in dilute phosphate buffer was slightly higher than in a natural water or buffer containing DOM, consistent with direct photolysis (rather than sensitized photolysis).

Using these quantum yields, the disappearance rates and half-lives were calculated for dilute solutions of TCMTB and MBT in pure water for spring, summer, fall and winter at 40°N and 50°N latitude (Table 8) using the method of Zepp and Cline [34] as elaborated in Leifer [35].

The relationship between the light screening factor, S_λ , and absorbance has been computed [37]. S_λ is the ratio of the first-order rate

constant in pure water containing light-absorbing substances (humic acids) to the first-order rate constant in pure water. For example, S_{λ} is 0.74 at 300 nm for a 0.1 m pathlength of our 10 mg/L DOM solution. Table 8 contains the wavelength-averaged first-order rate constants for TCMTB and MBT in pure water containing 10 mg/L DOM and a pathlength of 1.0 m.

The estimated half-lives for both TCMTB and MBT are in the order of one day or less for dilute solutions in surface waters and full sunlight for conditions that would be found in southern Canada or the northern United States, even in the presence of moderate concentrations of DOM. Direct photolysis offers a plausible route for rapid degradation of these compounds in well-mixed receiving waters in the absence of high turbidity or ice cover.

MTBT Photolysis

Unlike TCMTB and MBT, MTBT proved to be stable toward direct photolysis by sunlight. At an initial concentration of 14 mg/L in dilute phosphate buffer at pH 7, MTBT concentrations remained unchanged after the equivalent of about five cloudless summer days of solar radiation (165 E/m^2 , Table 1).

Our previous field observations of two oxidation products of MTBT, the sulfoxide (MSiBT) and sulfone (MSoBT), in Canagagigue Creek [5] led us to investigate the sensitized photolysis of MTBT, since photo-oxidation of the sulfide moiety was a plausible route to MSiBT and MSoBT [38]. Exposure of natural waters containing humic matter to sunlight results in generation of hydrogen peroxide [39,40]. Superoxide has been proposed as the precursor of hydrogen peroxide in this process [41]. We exposed dilute

potassium phosphate solutions (pH 7) containing 12 mg/L of MTBT and 20 mg/L of DOM to direct sunlight for the equivalent of 10 to 12 cloudless summer days (375 E/m^2) (Table 1). After this time, the MTBT concentration had declined by less than 20%, and no photolysis products were detected by HPLC analysis. We concluded that MTBT is resistant to both direct and sensitized photolysis by sunlight, and that photolysis of MTBT is not the route to MSiBT and MSoBT in natural aquatic environments.

Hypochlorite Oxidation of MTBT

Since we were able to rule out photo-oxidation of MTBT as a plausible source of MSiBT and MSoBT in aquatic environments, another possibility was examined. Reaction of MTBT with hypochlorite under conditions simulating those for chlorination of sewage effluent resulted in a quantitative yield of MSiBT (the sulfoxide) and MSoBT (the sulfone) in about a 10:1 ratio. The most likely source of MSiBT and MSoBT in Canagagigue Creek was through oxidation of MTBT in the Elmira Water Pollution Control Plant during the effluent chlorination stage. Since MTBT has been found by other investigators in river water [2], drinking water [7], and biota [9], its wide distribution in aquatic systems seems likely. If so, then smaller quantities of MSiBT and MSoBT might be expected to result from chlorination of drinking water and sewage effluent.

Field Observations

Disappearance kinetics for BT, MTBT, MSiBT and MSoBT in Canagagigue Creek at low flow ($0.28 \text{ m}^3/\text{s}$) and high flow ($0.91 \text{ m}^3/\text{s}$) on two successive days in August, 1984 are shown in Figure 3. BT shows good first-order

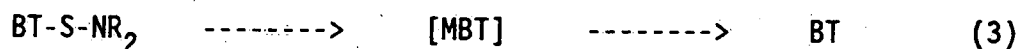
disappearance kinetics under both low and high flow conditions ($k=0.26$ and 0.24 h^{-1} , respectively). Disappearance kinetics for the other three benzothiazoles fell within the range of 0.03 to 0.06 h^{-1} at low flow and 0.06 to 0.08 h^{-1} at high flow, three to eight times slower than BT. These rates correspond to half-lives of about three hours for BT and 10 to 20 hours for the others. The rates for BT are similar to those observed for 2,4- and 3,4-dichlorophenol in the same system [42]. The field results indicate that benzothiazoles, especially BT, can be removed quite rapidly from systems such as Canagagigue Creek, probably by a combination of biodegradation and volatilization. Biodegradation in the biofilm was proposed as the major route of chlorophenol degradation in this creek [42]. Of the four benzothiazoles, only BT partitioned onto suspended particles to any degree. The lack of partitioning for MTBT was somewhat surprising since its partition coefficient is an order of magnitude greater than that of BT. While the octanol-water partition coefficients for MSiBT and MSoBT were not measured, they would be expected to be less than that of MTBT from their HPLC retention times, and their absence on particulate material is less surprising.

Fate Pathway

On the basis of the present study, and others in the literature, a partial pathway can be formulated for TCMTB and MBT in aquatic systems (Scheme 2). Hydrolysis and/or photolysis of TCMTB leads to MBT which can either photolyze to BT and HOBT, or undergo biomethylation to MTBT. Our results would predict that stable products from TCMTB and MBT degradation would be BT, HOBT and MTBT, and these have been reported in aquatic

systems. Under conditions such as drinking water or sewage disinfection with chlorine, it is possible that BT and MTBT can undergo oxidation by hypochlorite to HOBT [14] and MSiBT/MSoBT, respectively. We found two reports of HOBT in drinking water [7,8]. To our knowledge, the only report of MSiBT and MSoBT is that of Carey et al. [5]. There is apparently very little information on the toxicity of BT, HOBT, MTBT, MSiBT and MSoBT to aquatic organisms.

A further possibility is the transformation of sulfenamides of MBT into MBT as proposed by Spies et al. [9] (Equation 3). The MBT can then undergo conversion to BT by photolysis.



BT and MTBT were found in biota and sediment [9], but our solubility data and field results indicate that these are likely minor environmental compartments for these compounds. Bioconcentration factors for BT and MTBT in leeches from Canagagigue Creek were 100-400 and 250-350, respectively [43]. These comparatively low values were attributed to rapid clearance from the animals.

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References

1. United States International Trade Commission. 1982. Synthetic Organic Chemicals. United States Production and Sales 1981. USITC Publication 1292 (US Government Printing Office, Washington DC); cited in Spies et al. 1987.
2. Burnham, A.K., G.V. Calder, J.S. Fritz, G.A. Junk, H.J. Svec and R. Vick. 1973. Trace organics in water: their isolation and identification. J. Amer. Water Works Assoc. 65:722-725.
3. Meijers, A.P. and R. Chr. van der Leer. 1976. The occurrence of organic micropollutants in the river Rhine and the river Maas in 1974. Water Res. 10:597-604.
4. Jungclaus, G.A., V. Lopez-Avila and R.A. Hites. 1978. Organic compounds in an industrial wastewater; a case study of their environmental impact. Environ. Sci. Technol. 12:88-96.
5. Carey, J.H., M.E. Fox, B.G. Brownlee, J.L. Metcalfe, P.D. Mason and W.H. Yerex. 1983. The fate and effects of contaminants in Canagagigue Creek. 1. Stream ecology and identification of major contaminants. Inland Waters Directorate, Ottawa, ON, Scientific Series no. 135, ix, 37 pp.

6. Moore, R.A. and F.W. Karesek. 1984. GC/MS identification of organic pollutants in the Caroni River, Trinidad. Intern. J. Environ. Anal. Chem. 17:203-221.
7. Coleman, W.E., R.G. Melton, F.C. Kopfler, K.A. Barone, T.A. Aurand and M.G. Jellison. 1980. Identification of organic compounds in a mutagenic extract of a surface drinking water by a computerized gas chromatography/mass spectrometry system (GC/MS/COM). Environ. Sci. Technol. 14:576-588.
8. Crathorne, B., M. Fielding, C.P. Steel and C.D. Watts. 1984. Organic compounds in water: Analysis using coupled-column high-performance liquid chromatography and soft-ionization mass spectrometry. Environ. Sci. Technol. 18:797-802.
9. Spies, R.B., B.D. Andresen and D.W. Rice, Jr. 1987. Benzothiazoles in estuarine sediments as indicators of street runoff. Nature 327:697-699.
10. Jungclaus, G.A., L.M. Games and R.A. Hites. 1976. Identification of trace organic compounds in tire manufacturing plant wastewater. Anal. Chem. 48:1894-1896.
11. Salmons, G., A. Assaf, A. Gayte-Sorbier, and Ch.B. Airaud. 1984. Mass spectral identification of benzothiazole derivatives leached

- into injections by disposable syringes. Biomed. Mass Spectrom. 11:450-454.
12. Brownlee, B.G., J.H. Carey and M.E. Fox. 1981. A review of benzothiazoles in the aquatic environment. Inland Waters Directorate, Ottawa, ON, Scientific Series no. 126, v, 5 pp.
 13. Merck and Co. 1989. The Merck Index, 11th ed. Merck and Co., Inc., Rahway, NJ, p. 532.
 14. Lin, S. and R.M. Carlson. 1984. Susceptibility of environmentally important heterocycles to chemical disinfection: Reactions with aqueous chlorine, chlorine dioxide, and chloramine. Environ. Sci. Technol. 18:743-748.
 15. Konishi, K.-i., I. Nishiguchi and T. Hirashima. 1984. A facile one-pot synthesis of benzothiazolones from 2-halonitrobenzenes. Synthesis 254-255.
 16. Vernin, G., C. Siv et J. Metzger. 1978. Synthèse et étude physico-chimique de sulfures, sulfoxydes et sulfones en série thiazolique. J. Heterocyclic Chem. 15:1361-1366.
 17. Sutoris, V., P. Foltínová and A. Gáplovsky. 1980. Benzothiazole compounds. XVII. 2-Alkyl- and 2-aralkylsulfonylbenzothiazoles and their antimicrobial activity. Chem. zvesti 34:404-412.

18. Daniels, C.R. and E.P. Swan. 1987. HPLC assay of the anti-stain chemical TCMTB applied to lumber surfaces. J. Chromatog. Sci. 25:43-45.
19. Warner, J.S., T.M. Engel and P.J. Mondron. 1985. Determination of MBTS and TCMTB in industrial and municipal wastewaters. United States Environmental Protection Agency Report EPA/600/4-85/028, vi, 38 pp.
20. Parbery, C. and C.D. Taylor. 1989. Determination of methylene bis(thiocyanate) and 2-(thiocyanomethylthio)benzo[d]thiazole in leather process liquors by high-performance liquid chromatography. Analyst 114:361-363.
21. Danehy, J.P. and K.N. Parameswaran. 1968. Acidic dissociation constants of thiols. J. Chem. Eng. Data 13:386-389.
22. Ribo, J.M. 1988. The octanol/water partition coefficient of the herbicide chlorsulfuron as a function of pH. Chemosphere 17:709-715.
23. Chemical Rubber Co. 1970. Handbook of Biochemistry. Selected Data for Molecular Biology. H. A. Sober, ed., Chemical Rubber Co., Cleveland, OH, pp. J234-237.

24. Platford, R.F. 1983. The octanol-water partitioning of some hydrophobic and hydrophilic compounds. Chemosphere 12:1107-1111.
25. Lomakina, L.N. and E.K. Yakovskaya. 1969. Determination of solubility and the acid dissociation constant of 2-mercaptobenzothiazole. Vestn. Mosk. Univ. Khim. 24:73-76; Chem. Abstr. 72:36378e (1970).
26. Hansch, C. and A.J. Leo. 1979. Substituent Constants for Correlation Analysis in Chemistry and Biology. Wiley, New York, NY.
27. Karickhoff, S.W. 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere 10:833-846.
28. Drotar, A.-M. and R. Fall. 1985. Microbial methylation of benzenethiols and release of methylthiobenzenes. Experientia 41:762-764.
29. Drotar, A.-M., G.A. Burton, Jr., J.E. Tavernier and R. Fall. 1987. Widespread occurrence of bacterial thiol methyltransferases and the biogenic emission of methylated sulfur gases. Applied. Environ. Microbiol. 53:1626-1631.

30. Párkányi, C. and A.O. Abdelhamid. 1985. Photodegradation of pesticides: Photolysis of 2-mercaptobenzothiazole and 2-mercaptobenzimidazole. Heterocycles 23:2917-2926.
31. Abdou, W.M., M.M. Sidky and H. Wamhoff. 1987. Photochemistry of pesticides, 12. On the photoconversion of 1,3-dihydro-2H-benzimidazole-2-thione, 2(3H)-benzothiazolethione, and 2-chlorobenzothiazole. Z. Naturforsch. 42b:1153-1158.
32. Kice, J.L. 1980. Mechanisms and reactivity in reactions of organic oxyacids of sulfur and their anhydrides. In V. Gold and D. Bethell, eds., Advances in Physical Organic Chemistry, vol. 17, Academic Press, New York, NY, pp 65-181.
33. Kharasch, N., Wm. King and T.C. Bruice. 1955. Derivatives of sulfenic acids. XVII. Hydrolysis of 2,4-dinitrobenzenesulfonyl chloride. J. Amer. Chem. Soc. 77:931-934.
34. Zepp, R.G. and D.M. Cline. 1977. Rates of direct photolysis in aquatic environment. Environ. Sci. Technol. 11:359-366.
35. Leifer, A. 1988. The Kinetics of Environmental Aquatic Photochemistry. American Chemical Society, Washington, DC.
36. Picel, K.C., M.S. Simmons and V.C. Stamoudis. 1987. Sunlight photolysis of selected indoles and carbazole in aqueous coal-oil

- systems. In R.G. Zika and Wm.J. Cooper, eds., Photochemistry of Environmental Aquatic Systems, ACS Symposium Series 327, American Chemical Society, Washington, DC, pp. 44-60.
37. Mill, T., W.R. Mabey, D.C. Bomberger, T.-W. Chou, D.G. Hendry and J.H. Smith. 1982. Laboratory protocols for evaluation of the fate of organic chemicals in air and water. U.S. Environmental Protection Agency, U.S. Government Printing Office, Washington, DC. EPA 600/3-82-022.
38. Patel, J.R., E.B. Overton and J.L. Laseter. 1979. Environmental photooxidation of dibenzothiophenes following the Amoco Cadiz oil spill. Chemosphere 8:557-561.
39. Draper, W.M. and D.G. Crosby. 1983. The photochemical generation of hydrogen peroxide in natural waters. Arch. Environ. Contam. Toxicol. 12:121-126.
40. Cooper, W.J. and R.G. Zika. 1983. Photochemical formation of hydrogen peroxide in surface and ground waters exposed to sunlight. Science 220:711-712.
41. Baxter, R.M. and J.H. Carey. 1983. Evidence for photochemical generation of superoxide ion in humic waters. Nature 306:575-576.

42. Carey, J.H., M.E. Fox, B.G. Brownlee, J.L. Metcalfe and R.F. Platford. 1984. Disappearance kinetics of 2,4- and 3,4-dichlorophenol in a fluvial system. Can. J. Physiol. Pharmacol. 62:971-975.
43. Metcalfe, J.L., M.E. Fox and J.H. Carey. 1988. Freshwater leeches (Hirudinea) as a screening tool for detecting organic contaminants in the environment. Environ. Monit. Assessment 11:147-169.

Table 1. Experimental conditions for sunlight photolysis experiments.

Test Compound and Initial Concentration (mg/L)	Medium ^a	pH	Outdoor Air Temp. (°C)	Total Solar Radiation (E/m ²) ^b	Per Cent Reaction
TCMTB (8.3)	K-P, fs	6.0	15-25	66.9	98
TCMTB (8.3)	K-P, fs	6.0	10-20	15.8	83
MBT (3.2)	K-P, fs	7.0	15-25	20.9	>95
MBT (11.1)	K-P	7.0	5-20	62.8	>99
MBT (1.9)	CCW, fs	7.1	1-10	36.3	>99
MBT (1.9)	DOM(10), fs	7.0	1-10	36.3	97
MTBT (14.0)	K-P	7.0	20-30	165.3	< 5
MTBT (11.9)	DOM(20), fs	7.0	15-25	375.4	<20
Carbazole (0.8)	K-P	7.0	5-20	45.3	>95

^a K-P is 0.01 M potassium phosphate, CCW is Canagagigue Creek water, DOM(\bar{x}) is 0.01 M potassium phosphate buffer with \bar{x} mg/L of DOM, fs is filter sterilized.

^b As measured by a quantum sensor responding to photosynthetically active radiation (400-700 nm).

Table 2. Water solubility (S) and octanol-water partition coefficients (K_{ow}) for the test compounds.

Compound	S, mg/L	S, mg/L	$\log_{10} K_{ow}$	$\log_{10} K_{ow}$
	(Temp. °C)	(Temp. °C)	at 24°C	Literature
	This study	Literature	This study	
BT	3000 (24)		1.99	2.04 ^a
MTBT	125 (24)	110 (22) ^b	3.10	3.0 ^b
MBT	120 (24)	100-120 (20) ^c	2.41	1.61 ^a
	54 (5)			
TCMTB	40 (24)		3.12	
	16 (5)			

^a Hansch and Leo [26].

^b Platford [24].

^c Lomakina and Yakovskaya [25].

Table 3. Solubility (S) of MBT and TCMTB in creek water at various temperatures and pH.

Compound	Temp. (°C)	Nominal pH	S, mg/L
MBT	24	6.5	190
	24	7.5	230
	24	8.5	260
TCMTB	24	6.5	40
TCMTB	5	6.5	16
	5	8.5	15

Table 4. Octanol-water partition coefficients (K_{ow}) for MBT and TCMTB in creek water at various temperatures and pH.

Compound	Temp. (°C)	Nominal pH	$\log_{10} K_{ow}$
MBT	23	6.5	1.43
	23	7.5	1.38
	24	8.5	0.95
TCMTB	24	6.5	3.15
	24	8.5	3.15

Table 5. Pseudo-first-order hydrolysis rate constants (k_h) and half-lives ($t_{1/2}$) for TCMTB in buffers and three natural waters from British Columbia.

Buffer/Source	pH	Temp. ($^{\circ}\text{C}$)	k_h (h^{-1})	$t_{1/2}$ (h)
0.05 M Tris	8.0	24	0.0175	40
0.005 M Tris	8.0	24	0.00252	275
1/2 borax-phosphate	8.0	24	0.00120	578
1/20 borax-phosphate	7.0	24	0.0000832	8330
1/20 borax-phosphate	8.0	24	0.000918	755
1/20 borax-phosphate	9.0	24	0.00834	83
1/20 borax-phosphate	8.0	15	0.000159	4360
1/20 borax-phosphate	8.0	5	0.0000375	18500
Wellwater	7.62-7.74	24	0.000555	1250
Fraser River Water	7.66-7.92	24	0.000256	2710
Seawater	7.83-7.96	24	0.000937	740

Table 6. Molar absorptivities (ϵ) for TCMTB, MBT and carbazole at pH 7, and attenuation coefficients (α) for a natural water, and a DOM solution at discrete wavelengths from 297.5 to 360 nm.

Wavelength nm	ϵ , TCMTB L/mol/cm	ϵ , MBT L/mol/cm	ϵ , Carbazole L/mol/cm	α , CCR ^a 1/cm	α , DOM ^b 1/cm
297.5	9430	11200	5580	0.031	0.029
300.0	9360	12490	3470	0.029	0.028
302.5	8690	14020	2630	0.026	0.025
305.0	7360	15480	2440	0.024	0.024
310.0	4750	16950	2580	0.022	0.022
312.5	3810	19230	2810	0.019	0.019
315.0	2840	19000	2810	0.016	0.018
317.5	1940	18180	3050	0.015	0.016
320.0	1470	16650	3380	0.013	0.014
323.1	1070	15250	3570	0.012	0.012
330.0	540	9500	2770	0.007	0.009
340.0	470	1700	1740	0.003	0.005
350.0	330	470	190	0.000	0.002
360.0	0	180	90	0.000	0.000

^a Canagagigue Creek water.

^b DOM (10 mg/L) in 0.01 M potassium phosphate, pH 7.0.

Table 7. Initial concentrations, reaction rates and sunlight quantum yields for the test compounds.

Compound (Solvent) ^a	Initial [C] mol/L	Reaction Rate (mol/l)/(E/m ²)	Sunlight Quantum Yield (Φ), mol/E
Carbazole (K-P, pH 7)	4.7×10^{-6}	3.6×10^{-7}	0.0023 ^b
TCMTB (K-P, pH 6)	3.5×10^{-5}	3.9×10^{-6}	0.0099
MBT (K-P, pH 7)	6.7×10^{-5}	1.1×10^{-6}	0.0019
MBT (CCR, pH 7.1)	1.1×10^{-5}	4.5×10^{-7}	0.0015
MBT (DOM, pH 7)	1.1×10^{-5}	3.7×10^{-7}	0.0013

^a K-P is 0.01 M potassium phosphate; CCR is Canagagigue Creek water; DOM is 10 mg/L of DOM in 0.01 M potassium phosphate.

^b The literature value measured by Picel et al. [36] is 0.0036.

Table 8. First-order direct photolysis rate constants (k_d) and half-lives ($t_{1/2}$) in full sunlight at 40°N and 50°N for the four seasons.

Compound	40°N		50°N	
	k_d (d ⁻¹)	$t_{1/2}$ (d)	k_d (d ⁻¹)	$t_{1/2}$ (d)
TCMTB in pure water				
spring	7.4	0.09	5.9	0.12
summer	9.7	0.07	8.7	0.08
fall	4.1	0.17	4.4	0.16
winter	2.1	0.32	0.9	0.79
TCMTB in water + 10 mg/L DOM				
spring	3.1	0.22	2.6	0.27
summer	3.9	0.18	3.6	0.19
fall	1.8	0.40	1.8	0.39
winter	1.0	0.71	0.4	1.6
MBT in pure water				
spring	11.1	0.06	9.0	0.08
summer	14.0	0.05	12.8	0.05
fall	6.2	0.11	9.2	0.08
winter	3.3	0.21	1.4	0.51
MBT in water + 10 mg/L DOM				
spring	4.2	0.17	3.5	0.20
summer	5.2	0.13	4.8	0.14
fall	2.4	0.30	3.3	0.21
winter	1.3	0.53	0.6	1.2

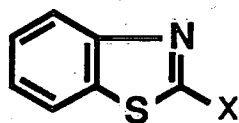
Figure Legends

Figure 1. Structural formulas, chemical names and abbreviations for the benzothiazoles.

Figure 2. Photolysis rates (as per cent of initial concentration versus measured solar radiation) for TCMTB (initial concentration 8.3 mg/L in phosphate buffer, pH 6), carbazole (initial concentration 0.8 mg/L in phosphate buffer, pH 7), MBT (initial concentration 11.1 mg/L in phosphate buffer, pH 7), MBT(CCW) (initial concentration 1.9 mg/L in Canagagigue Creek water, pH 7.1), and MBT(DOM) (initial concentration 1.9 mg/L in phosphate buffer with 10 mg/L DOM, pH 7).

Figure 3. Disappearance kinetics for BT, MTBT, MSiBT and MSoBT in Canagagigue Creek under low flow (A) ($0.28 \text{ m}^3/\text{s}$) on 84-08-14, and under high flow (B) ($0.91 \text{ m}^3/\text{s}$) on 84-08-15.

Figure 1.



$x = \text{H}$ Benzothiazole (BT)

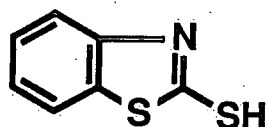
$x = \text{SCH}_3$ 2-(Methylthio)benzothiazole (MTBT)

$x = \text{SCH}_2\text{SCN}$ 2-(Thiocyanomethylthio)benzothiazole (TCMTB)

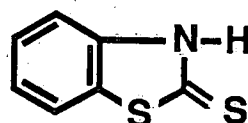
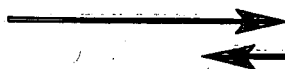
$x = \text{S(O)CH}_3$ 2-(Methylsulfinyl)benzothiazole (MSiBT)

$x = \text{S(O)}_2\text{CH}_3$ 2-(Methylsulfonyl)benzothiazole (MSoBT)

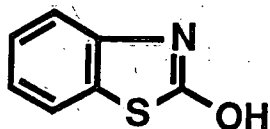
$x = \text{S-S-Benzothiazolyl}$ Bis-(2-Benzothiazolyl)disulfide (MBTS)



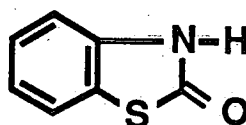
**2-Mercaptobenzothiazole
(MBT)**



2(3H)-Benzothiazolethione



**2-Hydroxybenzothiazole
(HOBT)**



2(3H)-Benzothiazolone

Figure 2.

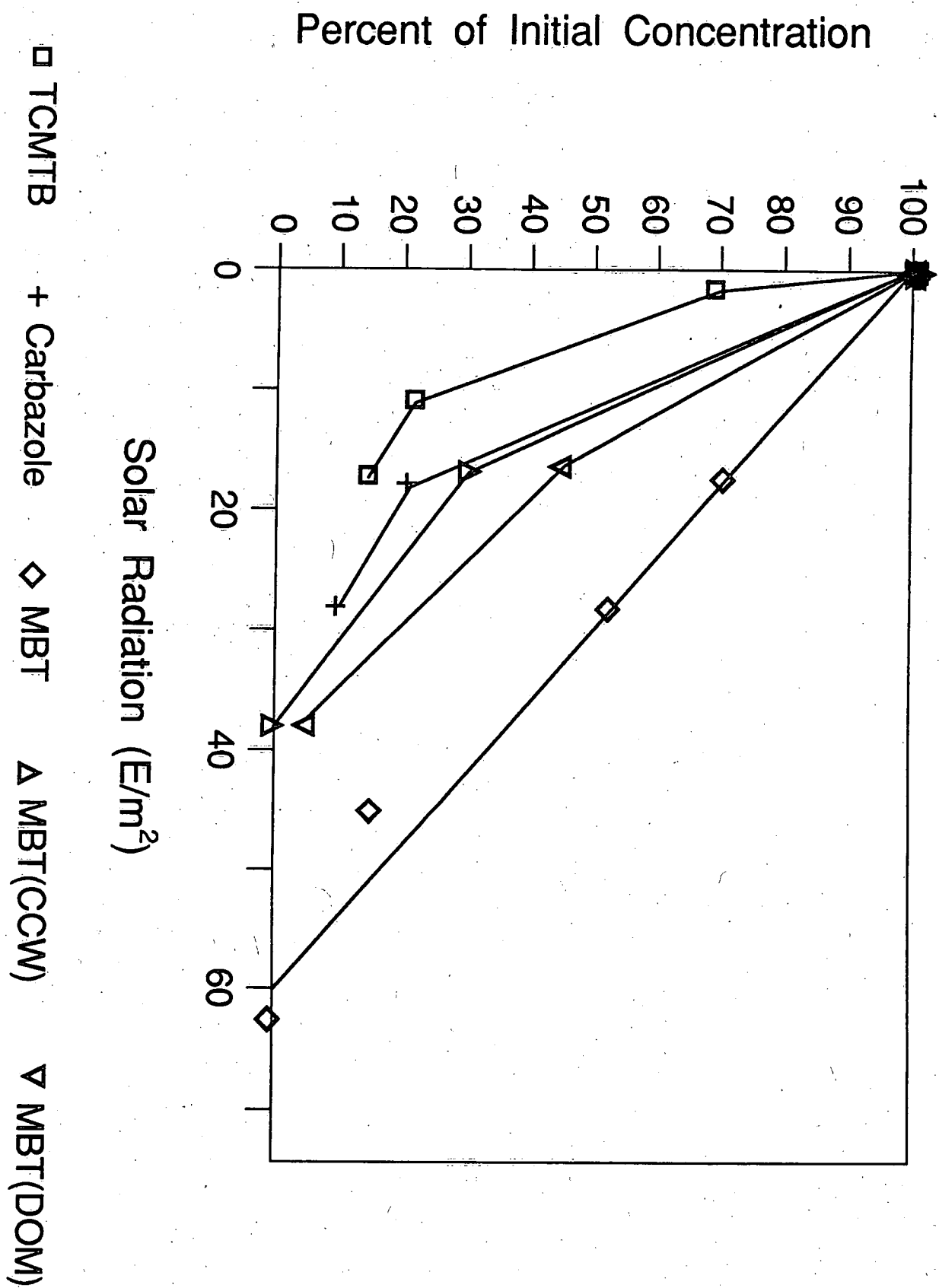
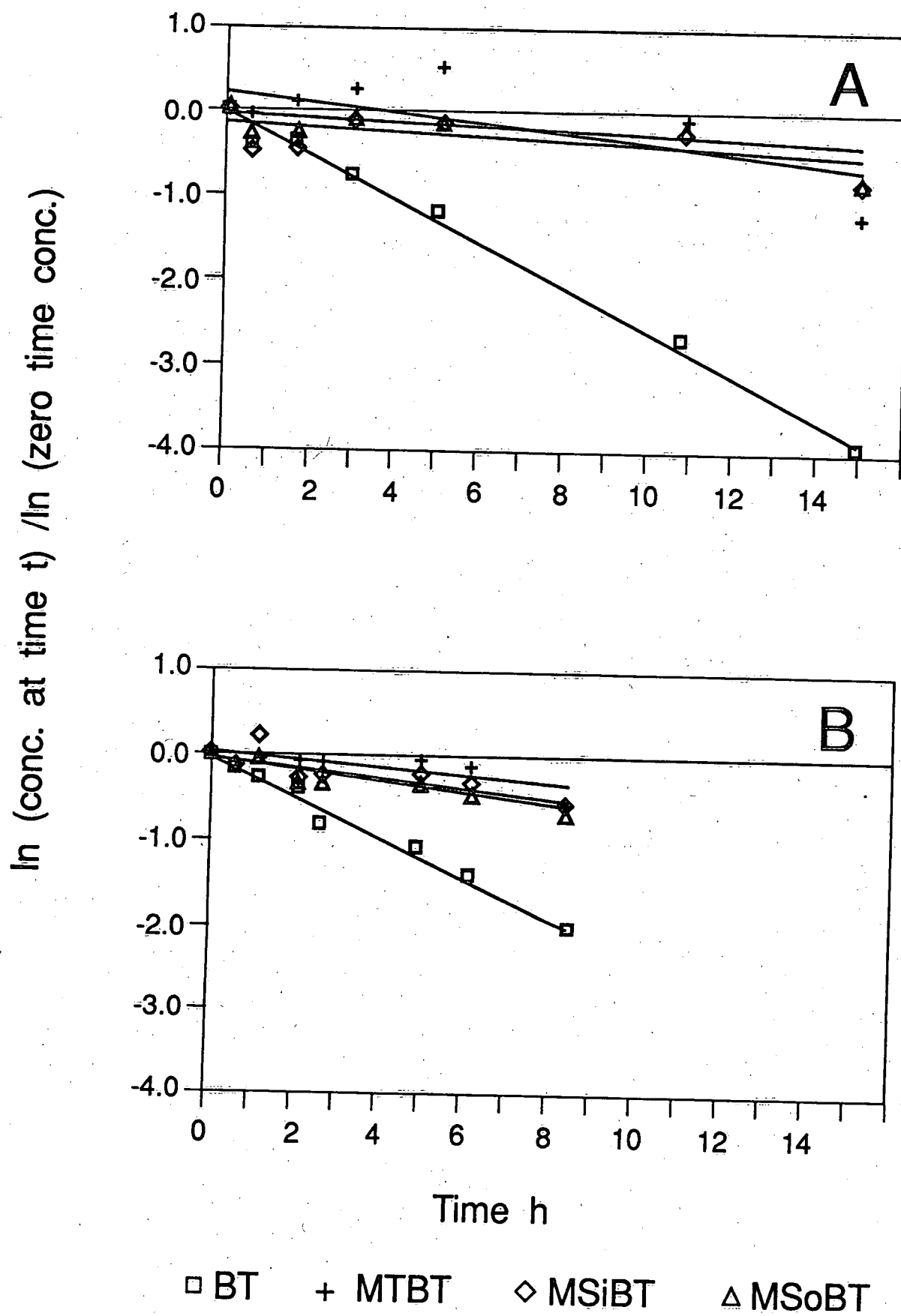
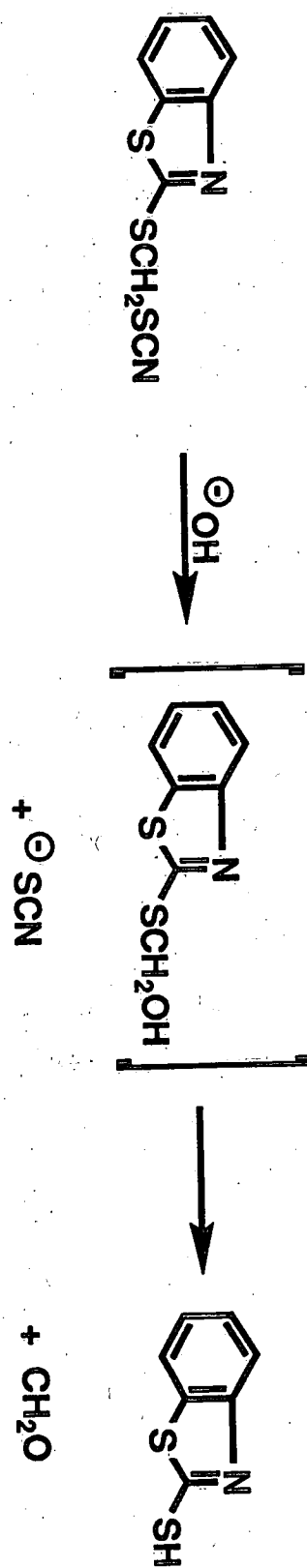
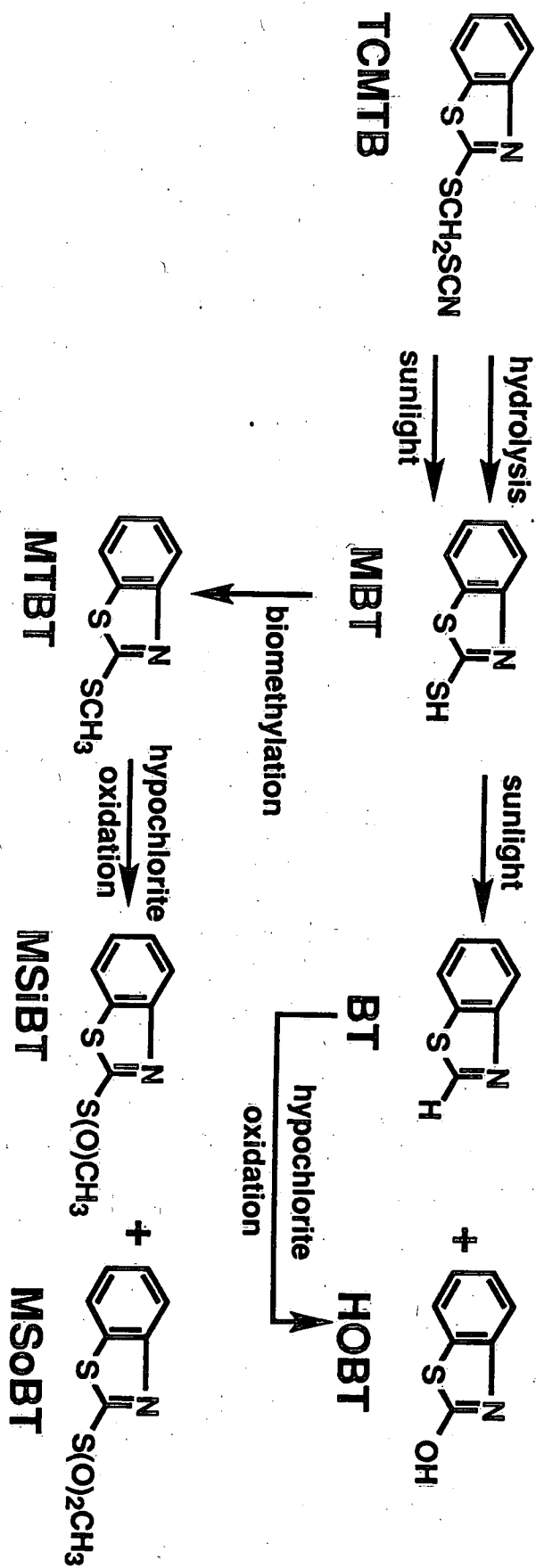


Figure 3.



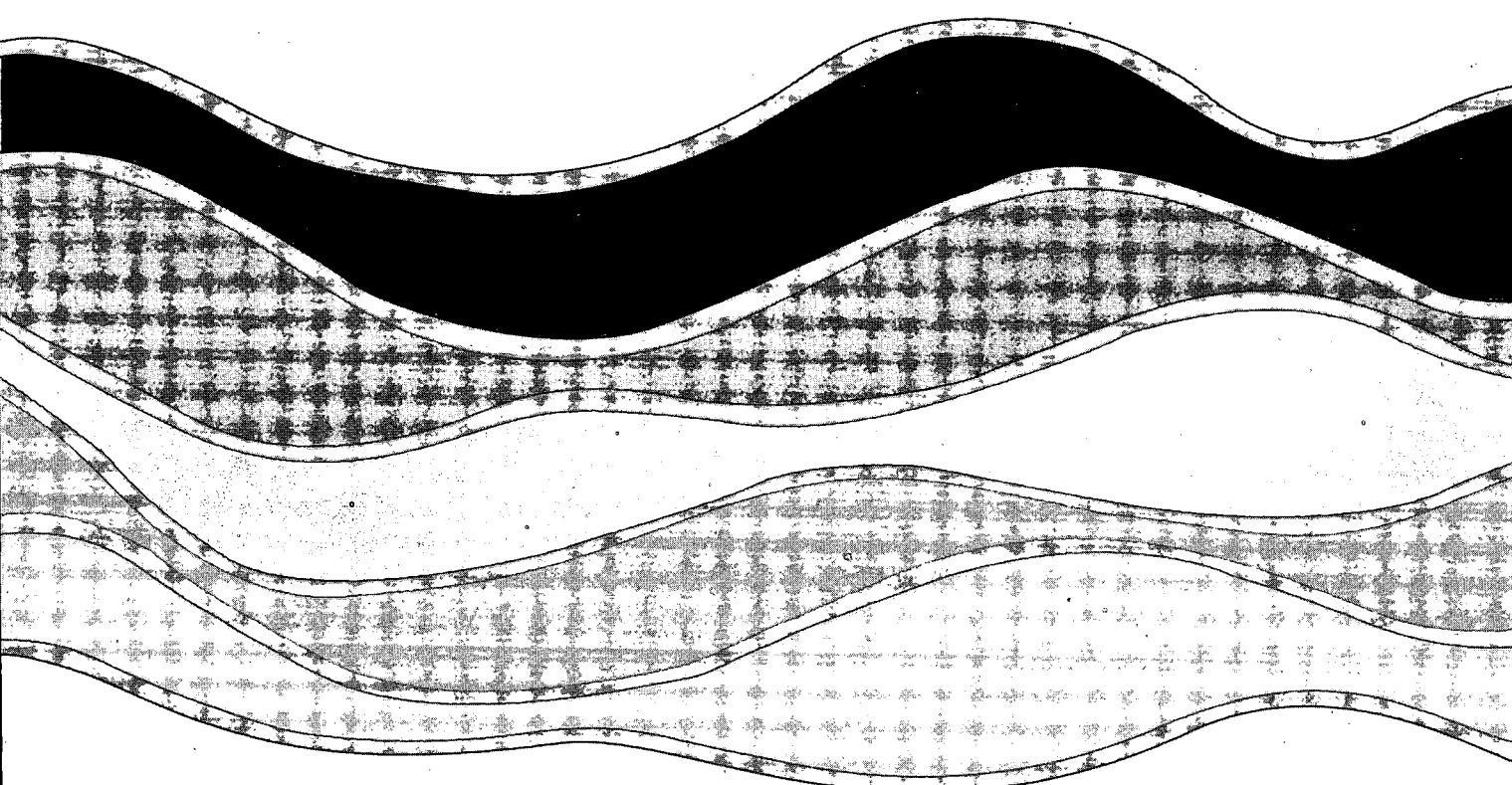
Scheme 1.







3 9055 1017 0346 9



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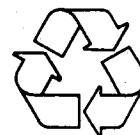


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