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DEGRADATION OF THE PETROLEUM COMPONENTS MONOMETHYLBENZOTHIOPHENES ON EXPOSURE TO LIGHT[1]

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Abstract

The photochemical degradation of monomethylated benzo[*b*]thiophenes in aqueous solution was studied to elucidate the fate of crude oil components after an oil spill. One principal reaction pathway involves oxidation of the methyl group(s) to the carboxylic acids via aldehydes. Another pathway leads via oxidation of the thiophene ring to the quinone and then, after ring opening, to 2-sulfobenzoic acids as the ultimate products for all compounds. Opening of the benzo ring is also seen in which case thiophene aldehydes or ketones are formed. ©1998 Elsevier Science Ltd. All rights reserved

Introduction

Large amounts of crude oil and petroleum products are introduced into the environment every year. Physical processes like evaporation, dissolution and adsorption move the compounds from the site of introduction but only microbial and photochemical processes alter them chemically, ultimately leading to a mineralization and thus removing them from the environment. For the Exxon Valdez accident in Alaska in 1989, the mass balance showed that 50 % of the oil was removed through aqueous biodegradation and photolysis and a further 20 % through atmospheric photolysis. The remaining 30 % were beached, recovered by man or deposited on sediments [1].

Many of the compounds of crude oil are known to be toxic, in particular various polycyclic aromatic compounds. Much less is known about the ecotoxicological properties of the various products formed on

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[1] Polycyclic Aromatic Sulfur Heterocycles VII. For part VI, see Ref. 7

photochemical or microbial oxidation under environmental conditions. It has been shown that if crude oil is allowed to equilibrate with water and the water then is removed and various species of aquatic organisms like shrimp and fish exposed to it, no toxicity can be established [2]. However, if the crude oil was illuminated for 24, 72 or 144 hours while floating on the water, highly toxic water-soluble products were obviously formed since death was recorded for all species within minutes to a few hours in the water. Plants also suffer from exposure to diesel oil that was photooxidized for as little as four hours as was shown following a spill in the ocean in 1991 [3].

Relatively few studies have investigated the products from such photochemical experiments, and it is an open question which compounds cause this toxicity. Alkanes yield a wide range of oxygenated products such as alcohols, ketones, aldehydes, lactones and carboxylic acids [4]. Studies on the aromatics show quinones and phenols [5].

The polycyclic aromatic sulfur heterocycles (PASH) can make up a surprisingly large part of the polycyclic aromatic compounds as is readily obvious from the gas chromatogram of a crude oil in Fig 1. The aromatic fraction shown was isolated through column chromatography and both the carbon and the sulfur selective traces were obtained from the atomic emission detector (AED).

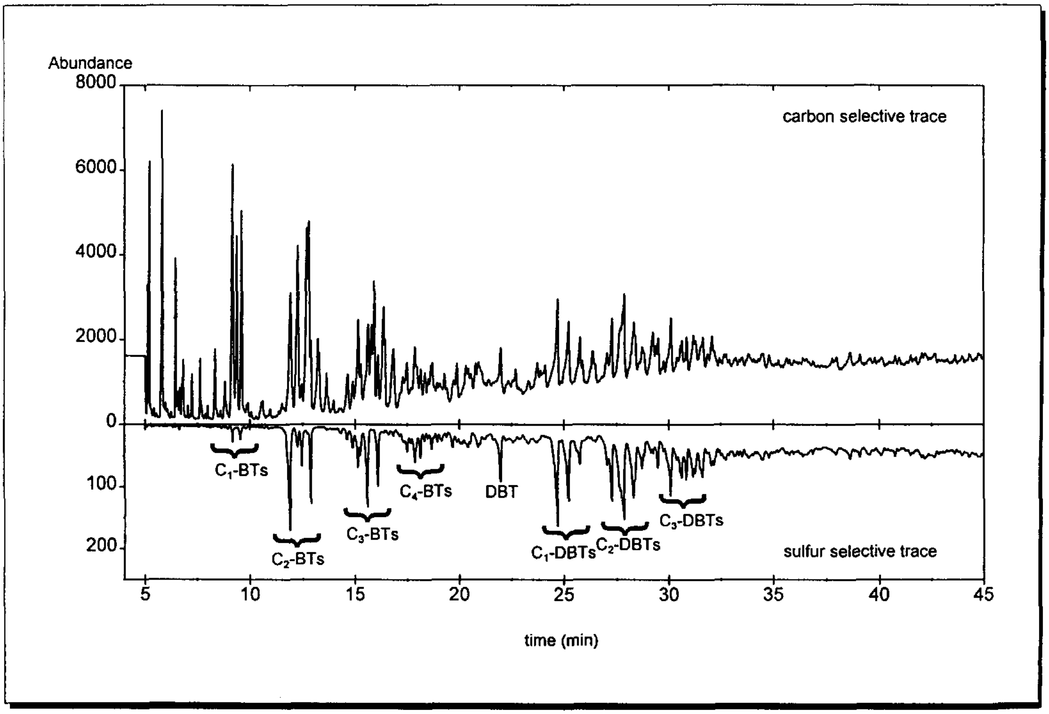

Fig. 1: AED chromatogram of the aromatic fraction of crude oil from the Kirkuk field.
BT = Benzo[*b*]thiophene; DBT = Dibenzothiophene

We have previously looked into the products formed on photolysis in aqueous solution of simple members of this class, namely benzo[*b*]thiophene [6] and the three derivatives methylated in the thiophenic ring [7]. In this work we report on a more detailed investigation of the products of all the monomethylated benzo[*b*]thiophenes.

Experimental

0.5 mg substrate was dissolved in 25 ml of a mixture of methanol/water (1:4) and irradiated with sunlight or with a mercury middle pressure lamp (TQ150, 250 W, Heraeus, Germany). The Duran glass vessels cut off all wavelengths below 300 nm. All experiments were carried out in closed vessels to prevent vaporization and to maximize the photolysis yields.

The resulting products were examined with high performance liquid chromatography and ion pair chromatography (HPLC-System Hewlett Packard HP 1050 with a variable wavelength detector; column: 25 cm * 4 mm ID Nucleosil-100 C18, 7 µm; ion pair reagent: tetrabutylammonium dihydrogen phosphate (5 mM) adjusted with phosphoric acid to pH 7 (Fluka, Germany).

Further information on products of medium polarity was obtained using gas chromatography after liquid-liquid extraction with dichloromethane. The very polar products were analyzed after removal of the solvent of the extracted aqueous solution on a rotary evaporator and derivatization of the residue with diazomethane in diethyl ether. Both an atomic emission and a mass selective detector were used (GC: HP 5890 II with AED HP 5921A or MSD HP 5970; column HP5 25 m * 0,32 mm ID, 0.17 µm). The products were identified through comparison of mass spectra and/or retention data of synthesized reference compounds.

The methylbenzo[*b*]thiophenes are commercially available from Astec, D-48161 Münster, Germany.

The product reference compounds were obtained as follows:

- 2-formylbenzo[*b*]thiophene: by oxidation of 2-methylbenzo[*b*]thiophene with $Ce(SO_4)_2$ in acetic acid [8]
- benzo[*b*]thiophene-2-carboxylic acid: by reaction of benzo[*b*]thiophene with butyl lithium, followed by addition of carbon dioxide [9]
- benzo[*b*]thiophene-2,3-quinone: by reaction of thiophenol with oxalyl chloride followed by cyclization with $AlCl_3$ (Friedel-Crafts reaction) [10]
- 5-methylbenzo[*b*]thiophene-2,3-quinone: by reaction of p-thiocresol with oxalyl chloride followed by cyclization with $AlCl_3$ (Friedel-Crafts reaction) [11]
- 2-sulfobenzoic acid dimethylester: by derivatization of an aqueous solution of anhydrous 2-sulfobenzoic acid (from Fluka, Germany) with an etheral solution of diazomethane
- benzenesulfinic acid methyl ester: by derivatization of an aqueous solution of sodium benzenesulfinate (from Aldrich, Germany) with an etheral solution of diazomethane

Results and Discussion

The photochemical oxidations were carried out in aqueous solution with 20 % methanol added in to achieve a sufficiently high concentration of the benzo[*b*]thiophenes. It was ascertained in preliminary experiments that th methanol did not influence the product distribution. Occasionally methyl esters of carboxylic acids (and hemi ketals or hemiacetals of formyl or acetyl compounds) could be found. They were obviously formed through esterification (or aldol reaction) under catalysis of the strong acids produced from the benzothiophenes on illumination Other control experiments included illumination with sunlight; again, only the same products were found as with the mercury lamp. Since the simulated photooxidation could be carried out in much shorter time due to the higher light intensity possible, the sunlight experiments were only used to verify the agreement between the two modes of illumination. Thus the simulations reported have a high relevance for the situation in the environment.

2-Methylbenzo[*b*]thiophene

The major product from 2-methylbenzo[*b*]thiophene was previously identified as 2-sulfobenzoic acid [7] with benzo[*b*]thiophene-2-carbaldehyde and benzo[*b*]thiophene-2-carboxylic acid as minor products. Traces of benzenesulfonic acid were also found. A thorough search among the minor products has now revealed that the precursor of the aldehyde presumably is the corresponding alcohol, 2-hydroxymethylbenzo[*b*]thiophene. Its mass spectrum is depicted in Fig. 2 and displays the parent peak at m/z 164 and loss of 17 mass units to give the benzothiopyrylium ion (147 m/z). This mass spectrum is in good agreement with the literature spectrum of 3-hydroxymethylbenzo[*b*]thiophene [12].

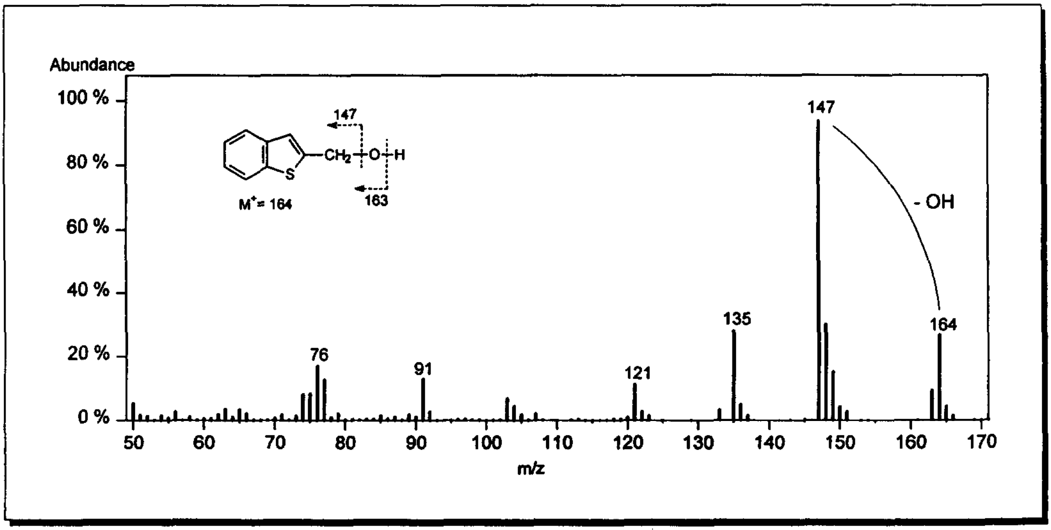

Fig. 2: Mass spectrum of 2-hydroxymethylbenzo[*b*]thiophene

A minor product was identified as 2,3-diformylbenzo[*b*]thiophene from its mass spectrum (Fig. 3). The heaviest ion at 190 indicates the molecular ion, and the prominent fragments at 161, 133 and 89 reflect consecutive losses of CHO, CO, and CS. Since this compound contains one carbon atom more than the starting compound, it must be formed in a completely different reaction. We presume it is formed through cleavage of a photochemical dimer. We have previously observed benzo[*b*]naptho[2,1-*d*]thiophene when benzo[*b*]thiophene was illuminated in a higher-concentrated tetradecane solution (2 - 3 mg benzo[*b*]thiophene in 0.5 ml tetradecane) floating on water [6].

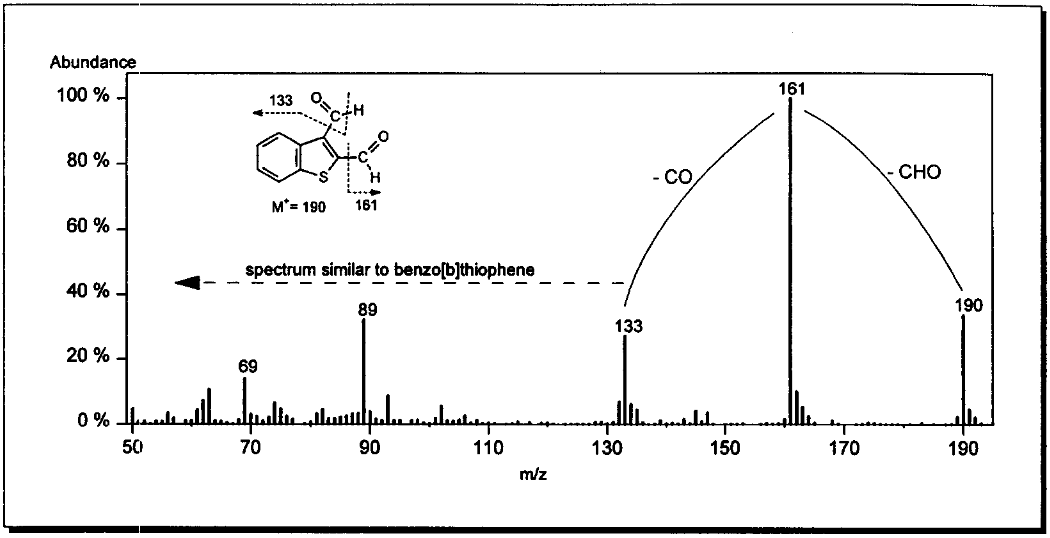

Fig. 3: Mass spectrum of 2,3-diformylbenzo[*b*]thiophene

3-Methylbenzo[*b*]thiophene

In the neutral fraction from the photooxidation of 3-methylbenzo[*b*]thiophene, the carbaldehyde emerged as the major product with very low amounts of hydroxylated methylbenzo[*b*]thiophene present [7]. In addition to this compound, very small amounts of three products with M^+ of 196, 168 and 214, respectively, have now been found but no identification seems possible at this stage using only mass spectrometry.

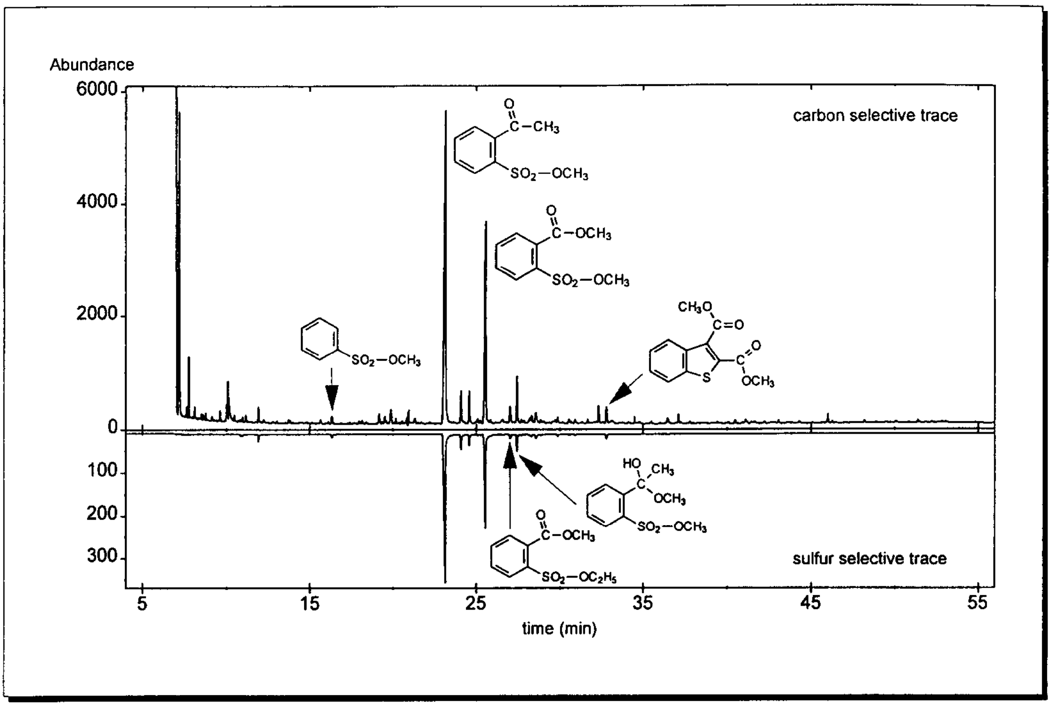

Fig. 4: Acidic fraction of 3-methylbenzo[*b*]thiophene degradation experiment after derivatization with diazomethane

After methylation of the acidic fraction, 2-sulfobenzoic acid was one of the major products (similar spectrum and retention time as for the main product in 2-methylbenzo[*b*]thiophene degradation and as for the reference compound). The other main product, present in about twice the concentration and showing a molecular mass of 16 units less, namely, 214, was not identified previously. Now this compound has been found to be 2-acetylbenzenesulfonic acid whose mass spectrum is depicted in Fig. 5. The identification is based on the mass spectrum which is very similar to the spectrum of dimethyl 2-sulfobenzoate (MW 230) with only one exception: the molecular ion is 214. This m/z value would be given by a molecule with one oxygen atom less. So there are two possible suggestions: dimethyl 2-sulfinobenzoate and methyl 2-acetylbenzenesulfonate. Aromatic sulfinic acid esters do not yield an SO_2 fragment, as we ascertained from a sample of methyl benzenesulfinate. Methyl 2-acetylbenzenesulfonate cannot loose SO_2 (64 mu) and $COOCH_2$ (58 mu) **successively** as is required from the product spectrum. Therefore we suggest a cyclic intermediate as shown in Fig. 5 with an m/z of 199 which can loose a 64 and 58 fragment in this way. 2-Acetylbenzenesulfonic acid in remarkable concentrations is also observed in other degradation experiments if the illuminated benzo[*b*]thiophene contains a methyl group in the 3 position. Such a group seems to be quite resilient to photooxidation. It therefore appears that a possible reaction pathway to the opening of the thiophenic ring is oxidation and opening of the S-C bond and a very early oxidation to the sulfonic acid group.

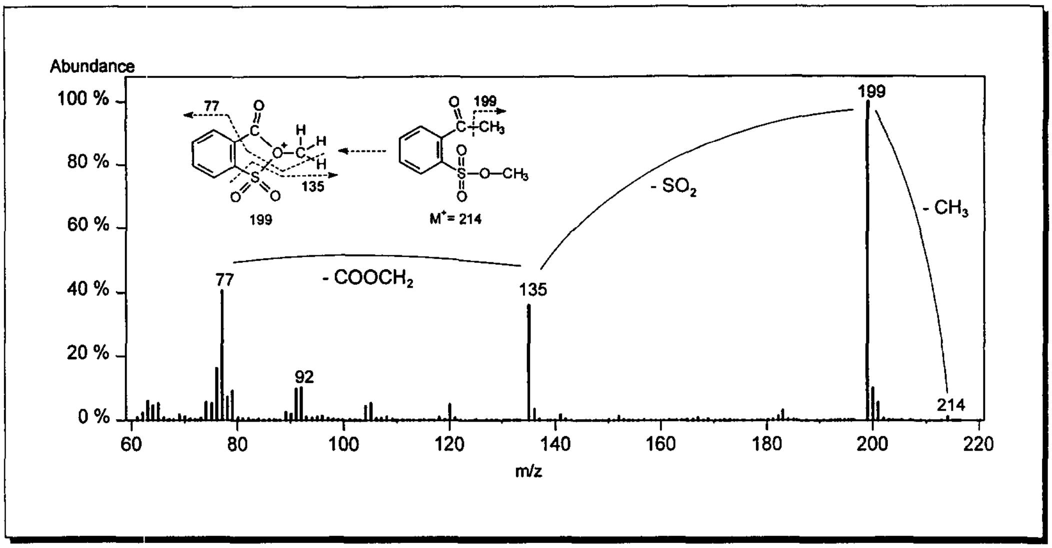

Fig. 5: Mass spectrum of methyl 2-acetylbenzenesulfonate

As one of the several minor products benzenesulfonic acid was identified. In addition, benzo[*b*]thiophene-2,3-dicarboxylic acid (see Fig. 4: as dimethyl ester) was also found in small amounts but cannot be a primary product since it contains one carbon atom more than the starting molecule. Thus we believe that this is a secondary product resulting from photochemical cleavage of a dimer as was the case for 2,3-diformylbenzo[*b*]thiophene from 2-methylbenzo[*b*]thiophene. Other sulfur containing degradation products in Fig. 4 originate at least partially from methylation with diazomethane (ethyl ester) or from reaction with methanol (hemiketals etc.).

4-Methylbenzo[*b*]thiophene

The major products in the neutral fraction were 4-methylbenzo[*b*]thiophene-2,3-quinone and 4-formylbenzo[*b*]thiophene. The first one showed a similar mass spectrum as for the synthesized reference compound 5-methylbenzo[*b*]thiophene-2,3-quinone. The latter compound exhibited a mass spectrum practically identical to the analogous derivative from 3-methylbenzo[*b*]thiophene but with slightly longer retention time; this is in agreement with the relative retention times of the 3- and 4-methyl and ethyl derivatives [13].

A minor product is suggested to be 3-acetyl-2-formylthiophene (fragmentation pattern: 154-139-111-83) which arises through oxidative ring opening of the benzo ring and retention of the 4-methyl group. Several other very small gas chromatographic peaks were visible but no plausible structure can be suggested.

The acidic fraction contained the main product 2-methyl-6-sulfobenzoic acid. Minor products are the result of further oxidation of the methyl group to yield 2-formyl-6-sulfobenzoic acid and 3-sulfophthalic acid.

5-Methylbenzo[*b*]thiophene

Extraction with dichloromethane isolated the neutral products which were dominated by 5-methylbenzo[*b*]thiophene-2,3-quinone, as established by comparison with the mass spectrum from other isomeric quinones and also through independent synthesis of the compound. Small amounts of products whose mass spectra indicate thiophenecarboxylic acid and 5-formylbenzo[*b*]thiophene were also detected.

5-Methyl-2-sulfobenzoic acid stood out among the acidic products. Its precursor, 5-methyl-2-sulfobenzaldehyde, was detected as a trace product. However, this was not the only compound formed through opening of the thiophene ring. Among the several minor products, 4-methylbenzenesulfonic acid was identified as well as 4-sulfoisophthalic acid, formed through oxidation of the 5-methyl group to a carboxylic acid. Another compound exhibited a mass of 228 with the typical mass spectrometric fragmentation associated with the acetyl (loss of CH_3 by α-cleavage) and sulfur dioxide (loss of a 64 mu fragment) groups and is thus suggested to be 2-acetyl-5-methylbenzenesulfonic acid (chromatographed as the ester after methylation). This mass spectrum is identical to that of methyl 2-acetylbenzenesulfonate (see Fig. 5) but all important fragments are positioned at values of 14 mu higher. It is possible, that this compound is not a direct photooxidation product but derived from a reaction of the previously called product 5-methyl-2-sulfobenzaldehyde with diazomethane.

The first eluting product was identified as thiophene-2,3-dicarboxylic acid, showing the possibility that the benzo ring can also be degraded.

Similar to the 3-methylbenzo[*b*]thiophene degradation experiment, 5-methylbenzo[*b*]thiophene-2,3-dicarboxylic acid (see Fig. 6: as dimethylester) was also found in small amounts. Again, the two additional carbon atoms suggest a dimeric precursor.

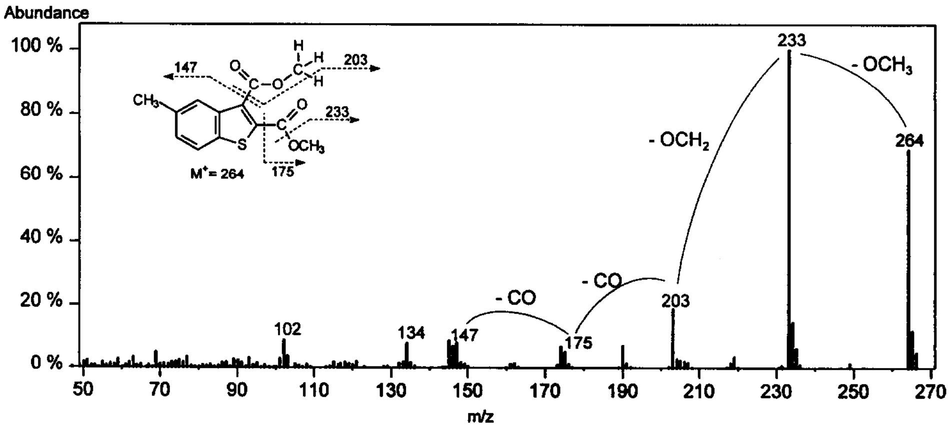

Fig. 6: Mass spectrum of dimethyl 5-methylbenzo[*b*]thiophene-2,3-dicarboxylate

6-Methylbenzo[*b*]thiophene

This compound was available only in a mixture with the 4-methyl isomer but since the products from this latter isomer are known, the ones derived from the 6-methyl isomer can be identified. The neutral products were 6-methylbenzo[*b*]thiophene-2,3-quinone and 6-formylbenzo[*b*]thiophene in agreement with several of the other isomers.

Acidic products were 4-methyl-6-sulfobenzoic acid and a small amount of 3-toluenesulfonic acid.

7-Methylbenzo[*b*]thiophene

This compound led to 7-formylbenzo[*b*]thiophene and 2-acetyl-3-formylthiophene as neutral compounds. The acidic products were 3-methyl-2-sulfobenzoic acid and 2-toluenesulfonic acid. There are also trace amounts of what we suggest to be thiophene-2,3-dicarboxylic acid, 2-formyl-6-methylbenzenesulfonic acid and 3-formyl-2-sulfobenzoic acid. The presence of 2-toluenesulfonic acid indicates loss of the carboxylic acid functionality of the main product as was previously shown for benzothiophene itself [6].

Discussion

The products obtained from the monomethylbenzothiophenes can be divided into three groups ultimately depending on the point of oxidation: those with an intact benzothiophene skeleton, those containing a benzene ring and finally those retaining the thiophene ring.

Similar to benzo[*b*]thiophene itself, in all cases the major product was a sulfobenzoic acid that is the result of cleavage of the heterocyclic ring. This is quite relevant for an ecotoxicological estimation of the toxic potential of the compounds that result from the photochemical oxidation of petroleum products since living organisms are highly susceptible to changes in pH. Sulfonic acids are strong acids and indeed the pH value of the illuminated solutions sank drastically as a consequence of this acid formation [6].

Methyl groups attached to the thiophene ring do not inhibit the opening of this ring. In several cases products were found that contain an oxidized methyl group (hydroxymethyl, formyl, carboxylic acid). Although we have not rigorously proved it, we assume that these are the first stages involved in the removal of the methyl carbons and thus precursors of the sulfobenzoic acids. For 3-methylbenzo[*b*]thiophene, the sequence of reactions leading to this stable product is indicated in Fig. 7.

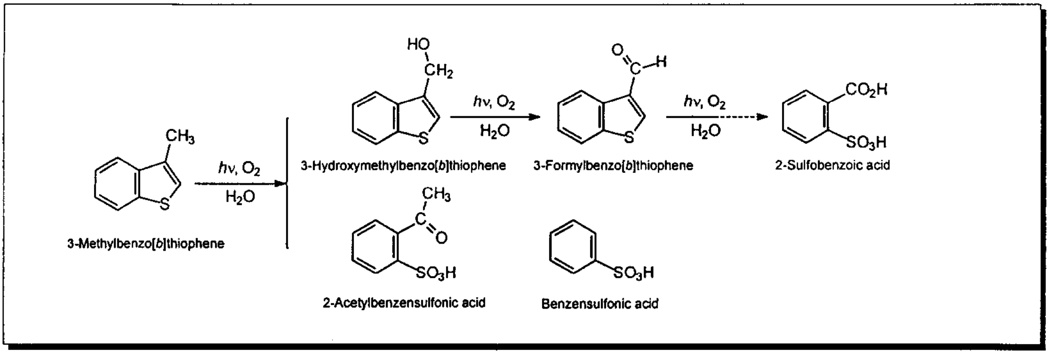

Fig. 7: Degradation pathway of 3-methylbenzo[*b*]thiophene

Methyl groups attached to the benzo ring are also oxidized but the ring does not seem to be opened through such initial reactions. In several cases the formylbenzo[*b*]thiophenes were found but also formylsulfobenzoic acids in which the thiophene ring was opened and the methyl group on the benzo ring oxidized to an aldehyde functionality. For 4-, 5- and 6-methylbenzo[*b*]thiophene, the oxidation proceeded one step further and the benzenesulfodicarboxylic acids were identified.

Opening of the benzo ring was demonstrated for 2-, 4-, 5- and 7-methylbenzo[*b*]thiophene. The carbon atoms next to the ring junctions are oxidized to a carbonyl group and the 5- and 6-carbon atoms lost. An unsubstituted 4- or 7-carbon atom therefore ends up as a formyl group and a methylated 4- or 7-carbon atom is found as the carbonyl carbon atom of an acetyl group. Further oxidation of these two carbonyl functionalities leads to thiophene-2,3-dicarboxylic acid.

The spectrum of products is depicted in Fig. 8 with 7-methylbenzo[*b*]thiophene as an example.

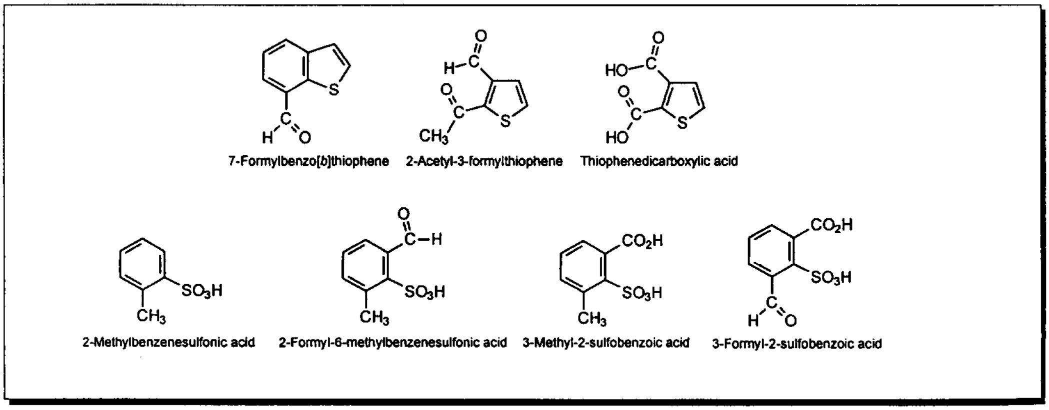

Fig. 8: Product spectrum of 7-methylbenzo[*b*]thiophene degradation

The products presented here differ considerably from the products obtained from a bacterial oxidation which has been studied for the same compounds using *Pseudomonas* sp.. The 2,3-quinone is the common intermediate in the two oxidative degradation pathways but microbial oxidation also favors sulfur oxidation to the sulfoxide and the sulfone [12]. These compounds are not seen under the photochemical conditions. Carboxylic acids resulted from microbial oxidation of methyl groups but the benzothiophene ring system remained intact [14].

Some products seem to be derived from initial photodimers. Such dimers obviously are of great interest since larger polycyclic aromatic systems are known to possess mutagenic properties that are not found for two ring aromatics.

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