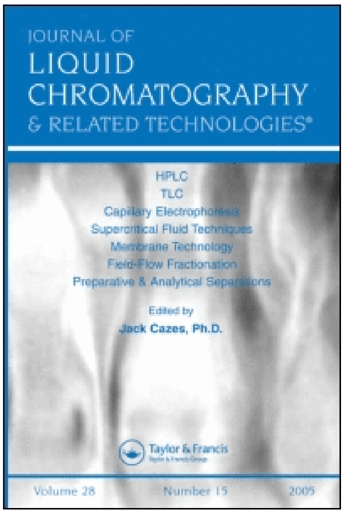

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Monitoring of Photodegradation Process of Various Benzothiazoles by HPLC and UV Spectrometry: Application of LC-MS in Photoproduct Identification

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Abstract: A simple gradient elution reverse-phase liquid chromatography method, together with UV spectrometry, was used for monitoring of the photodegradation process of various benzothiazoles. A combination of liquid chromatography (LC) with a photodiode array detector (PDA) and an electrospray ionization mass spectrometry detector (ESI-MS) was further used for identification of photoproducts. Separation was accomplished on a Hypersil ODS column with acetonitrile-water gradient at detection wavelength of 255 nm. Formic acid or ammonium acetate were used as additives in the positive or negative mode of ionization with the ESI-MS detector.

Keywords: Benzothiazoles, HPLC, Mass spectrometry, UV spectrometry

INTRODUCTION

Benzothiazoles have a wide range of applications and uses. Their major application is as rubber vulcanization accelerators. Rubber vulcanization accelerators are chemicals of a highly reactive nature. They are used to increase both the rate and "state" of curing, and function by attacking

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the sulfhydryl end groups in rubber.[1] Benzothiazole (BT), together with 2-hydroxybenzothiazole (HBT), is produced as a by-product from the industrial production of rubber vulcanization accelerators[1] and is used as a pesticide.[2] Both compounds are present in antifreeze[3] to which they could have been added as corrosion inhibitors or by leaching out from the rubber hoses in cooling systems.[4] 2-Mercaptobenzothiazole (MBT) is the most important and most widely used member of the benzothiazole family. It has found a broad application as a rubber vulcanization accelerator,[1] a corrosion inhibitor in paper production,[5] an antifungal drug in medical applications,[6] and a coating agent of metallic surfaces.[7]

Sodium and zinc salts of MBT are used as fungicides, microbicides, and bactericides.[8] 2-Mercaptobenzothiazole disulfide (MBTS) is known for its use as a vulcanization accelerator in the rubber industry[9] and as a fungicide, microbicide, and insecticide.[10]

Sources of benzothiazoles released into the environment are the various industrial applications as mentioned above. Their presence can be detected in various environmental and other types of samples. Currently, there is a growing interest in the studies of degradation pathways of organic contaminants.

Benzothiazoles represent compounds of a wide range of polarities. They range from the most polar 2-benzothiazolesulfonic acid (BTSA) to the nonpolar dimer 2-mercaptobenzothiazole disulfide (MBTS). Therefore, reverse-phase high-performance liquid chromatography seems to be a good choice for their separation. Liquid chromatography, coupled to a UV detector, has been shown to be a well-suited detection technique for the BTs in activated sludge,[11,12] wastewater,[13–17] and river water.[3] LC-UV was also used as a technique to follow the photolysis process of MBT in water,[18] oxidation process of BT, MBT, and HBT,[19] or to follow kinetic studies between BT and ozone in water.[20] Fiehn et al.[21] combined three techniques – LC-PDA, GC-MS, and capillary electrophoresis – for the analysis of the ozonization products of 2-mercaptobenzothiazole in water.

Coupling of liquid chromatography with atmospheric pressure chemical ionization mass spectrometry was applied to analysis of food and drinks for residues of MBT, BT, MBTS, and N-cyclohexyl-2-benzothiazole sulfenamide[22] and to the analysis of seawater samples after off-line solid phase extraction.[23] Reemtsma[24] published the use of liquid chromatography/electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS) as a successful technique for the analysis of a mixture of benzothiazoles in the wastewaters. Mixtures of benzothiazole (BT), 2-aminobenzothiazole (ABT), 2-methylbenzothiazole (MeBT), 2-thiocyanatomethylthiobenzothiazole (TCMTB), and 2-methylthiobenzothiazole (MTBT) were analyzed in the positive mode of ionization. 2-Benzothiazolesulfonic acid (BTSA), 2-mercaptobenzothiazole (MBT), and

2-hydroxybenzothiazole (HBT) were analyzed in the negative ionization mode.

The detailed description of the process of photodegradation of the three benzothiazoles (BT, MBT, and MBTS) in various solvents is described elsewhere.[25] The aim of this paper is to show the potential of LC-PDA, in combination with LC-ESI-MS, as a valuable tool for the detection and identification of photodegradation products of various benzothiazoles under laboratory conditions. Monitoring of degradation processes requires a technique which would permit detection of fast occurring changes. Due to the very good electronic absorption properties of BTs, UV spectrometry is often the method of choice.[18,26–30] However, one should not rely solely on this source of information because certain benzothiazoles possess very similar to identical chromophores and, consequently, similar spectra. Another analytical technique should be used as well and, therefore in addition, liquid chromatography was used as monitoring tool for slow degradation changes.

EXPERIMENTAL

Materials and Reagents

2-Mercaptobenzothiazole disulfide (99%), 2-hydroxybenzothiazole (98%), 2-benzothiazolyl sulfide, 2,2′-bibenzothiazole, 2-methylbenzothiazole (99%), *p*-toluenesulfonyl cyanide (95%), ammonium acetate (>98%), and formic acid (~98%, Fluka brand) were purchased from Sigma-Aldrich and 2-mercaptobenzothiazole (95%), and benzothiazole (97%) from Acros Chemical Co. Benzothiazolesulfonic acid and 2-thiocyanatobenzothiazole were synthesized by following the procedure described by Brown et al.[31] and Miyashita et al.[32] Methanol, acetonitrile, water, ethanol, and cyclohexane were HPLC grade from Fisher Scientific, Suwanee, GA. Ultra-high purity nitrogen and helium were from Airgas Inc., Radnor, PA.

Irradiation Conditions

For irradiations at $\lambda > 290\,\text{nm}$, a Rayonet-Srinivasan-Griffin photochemical reactor (The Southern N.E. Ultraviolet Co.) was used. It was equipped with 16 high pressure mercury lamps RPR-2537A. A Pyrex glass vessel (Rayonet-RPV-8, 18 mL) is used as a filter with emission cut-off at $\lambda > 290\,\text{nm}$. For the dark studies, a sample wrapped in aluminum foil was irradiated simultaneously with unwrapped solution and the temperature inside the reactor was monitored.

For irradiations at 253.7 nm, an Ace Glass (Ace Glass Inc., Vineland, NJ) microscale photochemical reactor equipped with a Pen-Ray 5.5 watt low pressure mercury lamp (TM UVP, Inc., San Gabriel, CA) was used. The immersion well (15 mL) with a water jacket is of quartz glass; the cooling of the system was obtained by circulating water through the water jacket of the immersion well. Since quartz glass is transparent in the entire UV region, the sample was exposed to peak emission of the UV lamp at 253.7 nm.

Solutions of 2-mercaptobenzothiazole disulfide were prepared in methanol, ethanol, acetonitrile, and cyclohexane (1×10^{-4} M or 1×10^{-5} M), with a precaution that the solutions were never heated above 45°C and were always kept in total darkness. Each solution was purged with N_2 or air for 10 minutes before and during the time of irradiation. At given time intervals, analytical samples were taken from the irradiated solution and analyzed by HPLC and/or UV. The changes in the UV spectra were measured with a Cary 3 UV-Vis spectrophotometer (Varian Inc.) using 1 cm quartz cells. Irradiation was stopped after no changes in the UV or HPLC were observed. For HPLC analysis, the irradiated solution was directly injected into the HPLC system. In the case of UV measurements, 200 μL of irradiated solution was diluted into 5 mL volumetric flask with the appropriate solvent. For 1×10^{-5} M starting concentration of MBTS, the UV spectrum of irradiated samples was measured directly without the dilution step. The same procedure was applied to photodegradation studies of benzothiazole and 2-mercaptobenzothiazole.

Chromatographic Conditions

Chromatographic analyses were performed using an LC pump, Series 410 (Perkin Elmer) coupled to a diode array detector, Series 235 C (Perkin Elmer) and PeakSimple chromatography data system, Model 203 (SRI Instruments).

Hypersil ODS 5 μm column (250 × 4.6 mm) (Thermo Electron Corporation) was used as the stationary phase and water and acetonitrile (MeCN) as the mobile phase at a flow of 1 mL/min. Elution started with a 5 minute isocratic period of 30% of MeCN followed by a linear gradient to 100% MeCN in 25 minutes and an isocratic period of 100% of MeCN for 10 minutes. The single wavelength UV detector was set to 255 nm and the sample was injected with a 20 μL loop.

Absorption spectra of individually eluted peaks were observed using liquid chromatography coupled to a photodiode array detector (LC-PDA), Series 1100 (Hewlett Packard/Agilent, Inc.). Chromatograms were detected at three wavelengths: 220 nm, 255 nm, and 280 nm. A mixture of standards for LC-UV, LC-PDA, and LC-MS measurements was prepared by recombination of 50 μL of each standard (9 total) from their stock solution (1 mg/1 mL in acetonitrile).

Mass Spectrometric Conditions

A Hitachi mass spectrometer, M-8000, was equipped with electron spray ionization (ESI) source and ion trap mass analyzer. ESI parameters were as follows: source temperature 150°C, assistant gas temperature 120°C, apertures 1 and 2 temperature 180°C, detector 400 V, focus 30 V drift 60 V and the capillary voltage was set to 3.5 kV in positive and 4.0 kV in negative mode. 0.1% Formic acid or 10 mM ammonium acetate were used as additives to water mobile phase in the positive or negative mode to help ion formation. Direct injections of standards (1 mg/1 mL in acetonitrile) were performed using a syringe pump Model 355 (Sage Instruments) with mobile phase 70:30% of MeCN:H_2O (water with additives) and flow 0.2 mL/min.

RESULTS AND DISCUSSION

Chromatographic Separation

At first, chromatographic conditions were developed in order to separate a mixture of standard benzothiazoles with structures summarized in Figure 1. The type of substituent in the position 2 of benzothiazole ring

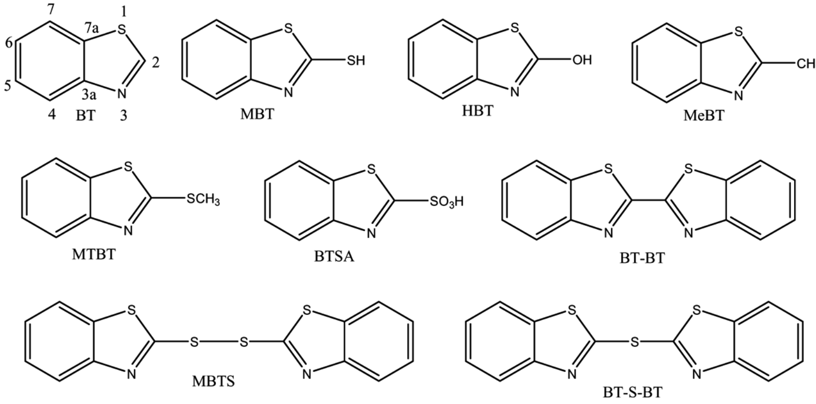

Figure 1. Chemical structures of standard benzothiazoles.

and the symmetry of the benzothiazoles can serve as good predictors of the polarities of compounds under investigation. It can be concluded that benzothiazoles cover a wide range of polarities and, therefore, reverse-phase high-performance liquid chromatography seems to be a good choice for their separation. The most polar compound, 2-benzothiazolesulfonic acid, with the acidic functional group, is expected to elute from the column first and the least polar and the most symmetrical MBTS should be eluted last.

The separation was performed using a Hypersil ODS column with C_{18} non-polar stationary phase. An acetonitrile – water gradient was used as a mobile phase medium. Increasing the strength of the mobile phase by increasing the amount of organic solvent helps the elution of the nonpolar analytes. A single wavelength of 255 nm was chosen for the detector in the single wavelength LC-UV analysis to ensure that all benzothiazoles can be detected at this wavelength.

The developed chromatographic conditions were further adjusted and applied for the separation of photodegradation products in the irradiated solutions of BT, MBT, and MBTS. Liquid chromatography, in addition to UV spectrometry, was used to follow the degradation process for irradiation of solutions at $\lambda > 290$ nm. Irradiation was stopped when there were no further changes observed in the chromatograms or the UV spectra.

The changes in the chromatogram during the course of irradiation of aerated methanolic solution of 2-mercaptobenzothiazole disulfide (MBTS) at $\lambda > 290$ nm are shown in Figure 2. After 30 minutes of irradiation, there was no MBTS left in the solution. MBTS is degraded to 2-mercaptobenzothiazole (MBT) and unsymmetrical 2,x′-thiobisbenzothiazole (2,x′-BT-S-BT) in a ratio 1.4:1. After 14 hours, oxygenated photoproducts, 2-benzothiazolesulfonic acid (BTSA) and benzothiazole (BT), are the major products detected (1.3:1). In a much smaller amount, the presence of 2-hydroxybenzothiazole (HBT) and 2-methylbenzothiazole (MeBT) can be detected in the chromatogram.

UV Spectrometry

Photodegradation of the starting material in irradiated solutions at 253.7 nm occurs within a few minutes, unlike irradiation at $\lambda > 290$ nm, which can be monitored at hourly intervals. Therefore, a technique is needed which would allow for a fast detection of such changes. In this case, UV spectrometry is the best choice, considering the fact that all benzothiazole compounds are UV active and scanning of spectra takes only few seconds. Changes in the UV profile of the methanolic solution of 2-mercaptobenzothiazole disulfide (MBTS) upon irradiation at 253.7 nm

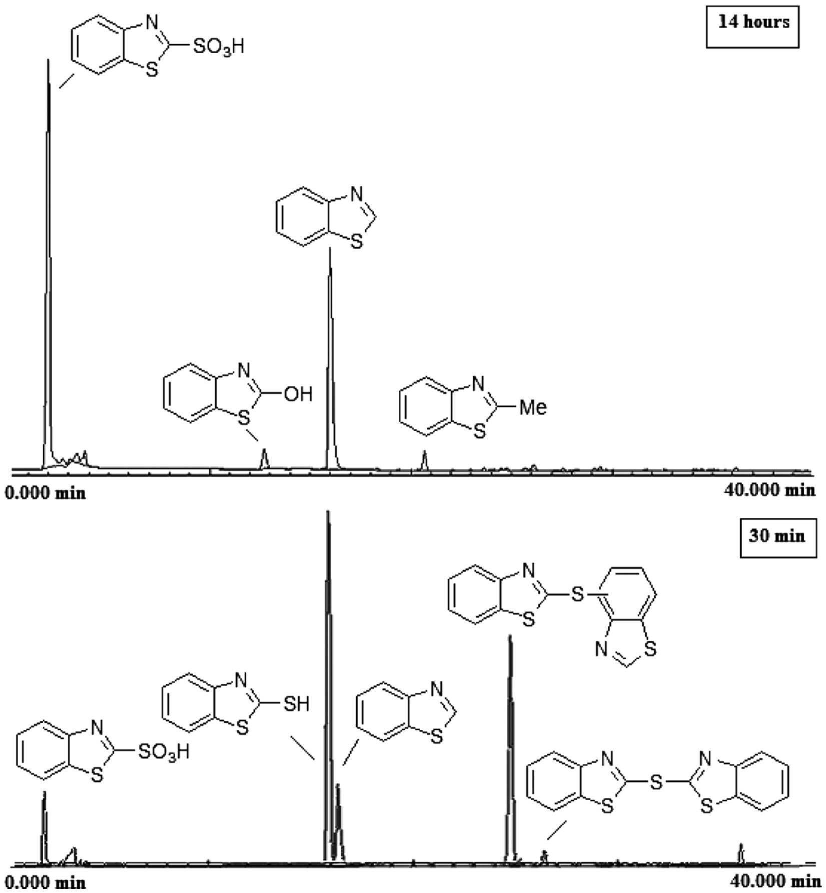

Figure 2. Chromatogram after 30 minutes and 14 hours of irradiation of an aerated methanolic solution of MBTS at $\lambda > 290\,\mathrm{nm}$.

in the presence of oxygen are shown in Figure 3. The spectra show a decrease of the intensity of the absorption wavelength of the starting material (MBTS, 272 nm) and an increase of the absorption band of 2-mercaptobenzothiazole (MBT, 325 nm) after 4 minutes. After 35 minutes, MBT has further decomposed into benzothiazole (BT, 251 nm) and 2-benzothiazolesulfonic acid (BTSA, 260 nm). The analysis of the chromatogram of the finally decomposed solution confirms the presence of major photoproducts BT and BTSA in a ratio 2.5:1. UV spectrometry is a great technique to be used to follow degradation processes, but an additional technique, such as liquid chromatography is essential for further clarification.

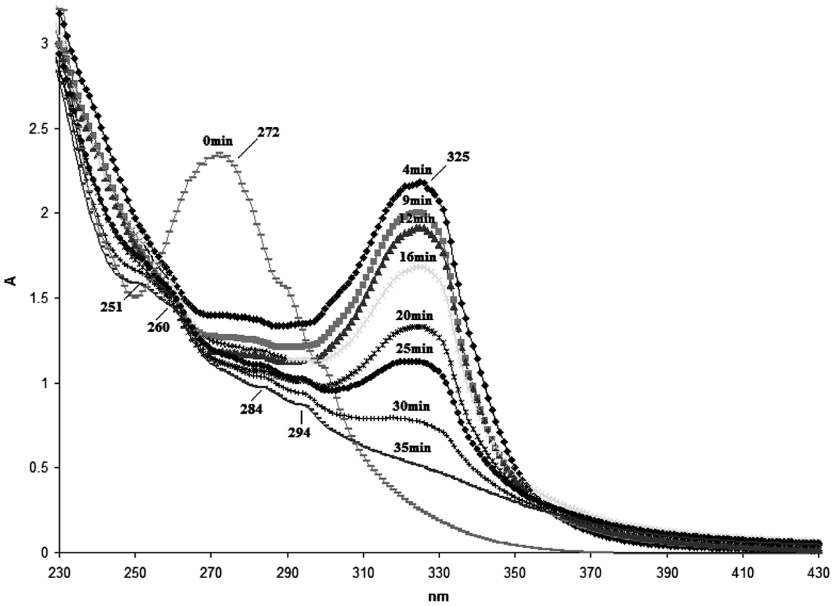

Figure 3. UV absorbance changes in the course of the irradiation of an aerated methanolic solution of MBTS (1×10^{-4} M) at 253.7 nm.

Compound Identification

Identification data, such as the retention time, absorption profile, and base peak of individual benzothiazole standards are summarized in Table 1. These data were acquired utilizing liquid chromatography, UV spectrometry, and direct injection mass spectrometry. If the relative retention time, UV spectrum, and mass spectrum of the unknown compound agree with that of a standard compound run under identical LC-PDA and LC-MS conditions, it can be accepted as a positive identification. The assignment of 2,x′-thiobisbenzothiazole (where x = 4, 5, 6, 7 and refers to the position on the benzothiazole ring) was only tentative, since an authentic standard or the starting material for its synthesis was not available nor was there a spectrum in the computer databases or the literature. The proposed photolysis pathway for the photodegradation of three benzothiazoles BT, MBT, and MBTS is described in detail in our previous publication.[25]

Reemtsma[24] published suitable LC-ESI-MS/MS conditions for the determination of 2-substituted BTs in water. In agreement with Reemtsma's paper, the three benzothiazoles, BTSA, HBT, and MBT, gave a positive response in the negative mode of ion formation. HBT and

Table 1. Retention time, UV profile and base peak of standard benzothiazoles

Retention time (min)	UV (nm) (log[Io/I])	Base peak[a]	Average mass	Name
2.15	202 (0.829); 219 (0.732); 262 (0.435); 292 (0.104)	(−) 214.07	215.25	BTSA
12.33	213 (0.9258); 237 (0.1502); 281 (0.0799); 289 (0.0790)	(−) 150.31	151.19	HBT
15.38	208 (0.5033); 230 (0.4623); 237 (0.466); 325 (0.9741)	(−) 166.24 (+) 167.88	167.25	MBT
15.82	201 (0.8019); 217 (0.8512); 251 (0.2766); 284 (0.1041); 294 (0.0936)	(+) 135.88	135.19	BT
20.18	201 (0.8019); 217 (0.8512); 251 (0.2766); 283 (0.0675); 293 (0.0555)	(+) 149.95	149.21	MeBT
22.63	202 (0.8173); 219 (0.7627); 277 (0.3805); 288 (0.3244); 299 (0.2431)	(+) 181.88	181.28	MTBT
29.60	203 (0.9775); 219 (0.9392); 278 (0.4359); 300 (0.3861)	(+) 301.05	300.42	BT-S-BT
29.97	215 (1.0232); 253 (0.2008); 327 (0.4854); 343 (0.5579); 362 (0.4063)	(+) 269.05	268.36	BT-BT
31.17	221 (0.7778); 272 (0.4079)	(+) 333.15	332.49	MBTS

[a] (−) negative and (+) positive mode of ionization.

MBT were two closely coeluting peaks, but they could be clearly resolved from each other on the basis of their base peaks. MBT, BT, MeBT, MTBT, and the dimers BT-BT, BT-S-BT, and MBTS gave a response in the positive mode of ionization. We were not able to detect 2-thiocynatobenzothiazole in either positive or negative mode; therefore, it was removed from the mixture of standard benzothiazoles suitable for LC-ESI-MS analysis. 2-Mercaptobenzothiazole (MBT) is the only compound which has given positive response in positive *and* negative modes of ionization.

CONCLUSIONS

UV spectrometry, together with liquid chromatography, was utilized to monitor the photodegradation process of benzothiazoles under laboratory conditions. Collected data such as retention time, UV profile, and base peak of standard benzothiazoles were used for the identification and characterization of photodegradation products.

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