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Determination of Hydroxylated Thiophenic Compounds in a Coal Liquid

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Hydroxylated thiophenic compounds in a coal liquid were determined by capillary column gas chromatography and gas chromatography/mass spectrometry. Capillary column gas chromatography with two new selective stationary phases, a biphenyl polysiloxane and a smectic liquid crystalline polysiloxane, were used. Several compounds were positively identified by comparison of their retention times with those of newly synthesized standard compounds. Sulfur-selective flame photometric detection and mass spectrometry were used to verify compound identifications. Two groupings of hydroxylated thiophenic compounds were observed in this sample. The first group is composed of hydroxybenzothiophenes and (hydroxyphenyl)thiophenes, while the second group contains hydroxydibenzothiophenes and (hydroxyphenyl)benzothiophenes.

Polycyclic aromatic compounds (PAC) are abundant in coal liquids and tars as well as in other heavy oils derived from fossil fuels. While the polycyclic aromatic hydrocarbons (PAH) are usually the most abundant PAC, nitrogen-, sulfur-, and oxygen-containing compounds are also usually present in significant concentrations. These heteroatom-containing PAC are undesirable for the upgrading process and coking process and for human health. They can poison the catalyst used for catalytic cracking and are resistant to aromatic condensation and crystallization which leads to the formation of the graphitic structure. In addition, many of these compounds are suspected mutagens and/or carcinogens.

Numerous studies have been undertaken in the past to identify the heterocyclic compounds in coal-derived products, the most successful utilizing capillary column gas chromatography and gas chromatography/mass spectrometry (GC/MS) (1, 2). Considerable information is presently available with respect to speciation of nitrogen-containing (1–4), sulfur-containing (5, 6), and oxygen-containing (7, 8) PAC as a result of these studies. In most cases, compounds containing only one heteroatom were considered. However, there is some evidence for the existence in coal derived products of PAC containing two heteroatoms (9–13), but compounds were usually only tentatively identified by high-resolution mass spectrometry.

In this study, PAC containing both a sulfur and an oxygen heteroatom as hydroxylated thiophenic compounds were determined in a coal liquid. Although previous studies have detected the presence of this compound type in coal-derived products (14, 15), positive identification and quantitation of individual species have not been reported. Capillary column gas chromatography with two new selective stationary phases, a biphenyl polysiloxane (16) and a smectic liquid crystalline polysiloxane (17), and a sulfur-selective flame photometric detector (FPD) were used. Complementary information for identification was provided by GC/MS.

EXPERIMENTAL SECTION

Materials. The solvent-refined coal heavy distillate (SRC II HD, 260–450 °C boiling point range) was collected during the processing of a West Virginia coal from the Pittsburgh seam and obtained from the Fort Lewis, Washington, pilot plant which was operated by the Pittsburgh and Midway Coal Mining Co. This material is of pilot plant origin and should not necessarily be considered as representative of products that may eventually be produced on a commercial scale. The hydroxylated thiophenic reference compounds used in this study were synthesized in our laboratories (18).

Fractionation and Derivatization Procedures. The SRC II HD was fractionated into chemical classes by column adsorption chromatography on neutral alumina as previously described (19). The A-4 fraction (hydroxylated PAC) was selected for analysis in this study. Half of the A-4 fraction (20 mg from 0.3 g of original SRC II HD) was dried under a gentle nitrogen gas purge, dissolved in 0.5 mL of benzene, and derivatized with (trimethylsilyl)-imidazole (TMSI, Regis Chemical Co.). For derivatization, 15 μL of TMSI was added to the sample in a reaction vial, and the vial was sealed and heated at 80 °C for 20 min in an oil bath. Approximately 50 μg of each the four hydroxydibenzothiophene standard compounds was dissolved in 0.5 mL of benzene and derivatized using 20 μL of TMSI as described above.

Gas Chromatography and GC/MS. A Hewlett-Packard Model 5880 gas chromatograph equipped with an FPD was used for all gas chromatographic analyses in this study. Sample injection was made in the splitless mode, the hydrogen carrier gas was set at a linear velocity of 90–100 cm s^{-1}, and the detector sensitivity was set to give a full-scale response for 60 ng of benzo[b]naphtho[1,2-d]thiophene.

Capillary columns were prepared by statically coating fused silica capillary tubing (0.32 mm i.d., Hewlett-Packard, Avondale, PA) with a 25% biphenyl methylpolysiloxane (20 m length) (16) or a mesogenic polysiloxane (10 m length) (17) (0.25 μm film thickness). The biphenyl stationary phase was cross-linked using azo-t-butane (20). Both columns were conditioned overnight at 280 °C under nitrogen gas flow.

Compounds were identified by comparison of relative retention times (relative to phenanthrene) of the pure standards with the

Table I. Identification and Relative Retention Times of Hydroxylated Thiophenes in an SRC II Heavy Distillate Coal Liquid

peak no.	compound[a]	relative retention times[b]		identification[c]
		biphenyl phase	liquid crystal phase	
1	4-hydroxybenzothiophene	0.7168	0.8075	GC, GC/MS
2	6-hydroxybenzothiophene	0.7482	0.8672	GC, GC/MS
	2-(2-hydroxyphenyl)thiophene	0.7496	0.7658	
3	C$_1$-hydroxybenzothiophene			GC/MS
4	(hydroxyphenyl)thiophene isomers			GC/MS
	2-(4-hydroxyphenyl)thiophene	0.9800	1.301	
5	2-(3-hydroxyphenyl)thiophene	0.9836	1.212	GC, GC/MS
6	3-(3-hydroxyphenyl)thiophene	0.9964	1.255	GC, GC/MS
	3-(4-hydroxyphenyl)thiophene	1.000	1.343	
	4-hydroxydibenzothiophene	1.432 (1.332)	1.833	
7	1-hydroxydibenzothiophene	1.465 (1.256)	2.055	GC, GC/MS
8	2-hydroxydibenzothiophene	1.491 (1.302)	1.964	GC, GC/MS
	3-hydroxydibenzothiophene	1.491 (1.267)	2.059	
9	C$_1$-hydroxydibenzothiophene and (hydroxyphenyl)benzothiophene			GC/MS
10	4-hydroxy-7-phenylbenzothiophene	1.621	2.040	GC, GC/MS
11	7-(4-hydroxyphenyl)benzothiophene	1.632	2.068	GC, GC/MS
12	2-(3-hydroxyphenyl)benzothiophene	1.755	2.373	GC, GC/MS
	2-(2-hydroxyphenyl)benzothiophene	1.755	>3.000[d]	
	2-(4-hydroxyphenyl)-4-phenylthiophene	>2.000[d]	>3.000[d]	
	2-(2-hydroxyphenyl)-4-phenylthiophene	>2.000[d]	>3.000[d]	

[a] Compounds which are not numbered were not found in the coal liquid. [b] Retention times relative to phenanthrene. Values in parentheses are for Me$_3$Si derivatives. [c] GC, capillary gas chromatography; GC/MS, capillary gas chromatography/mass spectrometry. [d] Compound did not elute under the chromatographic conditions used.

components in the coal liquid A-4 fraction on the two different selective stationary phases. Compound identities were confirmed by making the same retention comparison of the standards and sample after they had been derivatized with TMSI. In addition, the Me$_3$Si-derivatized fraction was analyzed by GC/MS using a Hewlett-Packard 5982A GC/MS system operated in the electron impact mode at 70 eV. Spectra were acquired and processed with an HP 5934A data system.

RESULTS AND DISCUSSION

As previously reported (19), the A-4 fraction of the SRC II HD is mainly composed of hydroxylated PAC. The main compounds identified were indanols, hydroxybiphenyls, hydroxyfluorenes, naphthylphenols, and their alkylated derivatives. In recent studies (21, 22), the sulfur-containing PAC in the A-2 and A-3 fractions were studied using capillary column gas chromatography with sulfur-selective detection. Numerous polycylic aromatic thiophenes were identified in the A-2 fraction, while the major sulfur-containing components in the A-3 fraction were the aminodibenzothiophenes. Other nitrogen/sulfur-containing heterocyclic compounds were also present in the A-3 fraction.

In this study, it was of interest to characterize the hydroxylated sulfur heterocycles in the SRC II HD. Since coal liquids are extremely complex, and the hydroxylated sulfur heterocycles were expected to be minor components in the mixture, prefractionation of the coal liquid was necessary in order to concentrate the compounds of interest. The alumina column adsorption chromatographic procedure (19) provided a fraction enriched in hydroxylated PAC. Further isolation of the thiophenic compounds from this fraction could not be accomplished. Therefore, sulfur-selective detection and column selectivity in capillary column gas chromatography were applied to the A-4 fraction without further pretreatment for identification of these compounds.

Figure 1 shows chromatograms of the A-4 and derivatized A-4 fractions on the 25% biphenyl methylpolysiloxane stationary phase. Table I lists the compounds identified, the chromatographic retention indexes, and methods used to confirm the identifications. Derivatization generally increased the volatility of the compounds, leading to decreased retention. Furthermore, blocking of the polar hydroxyl groups led to a
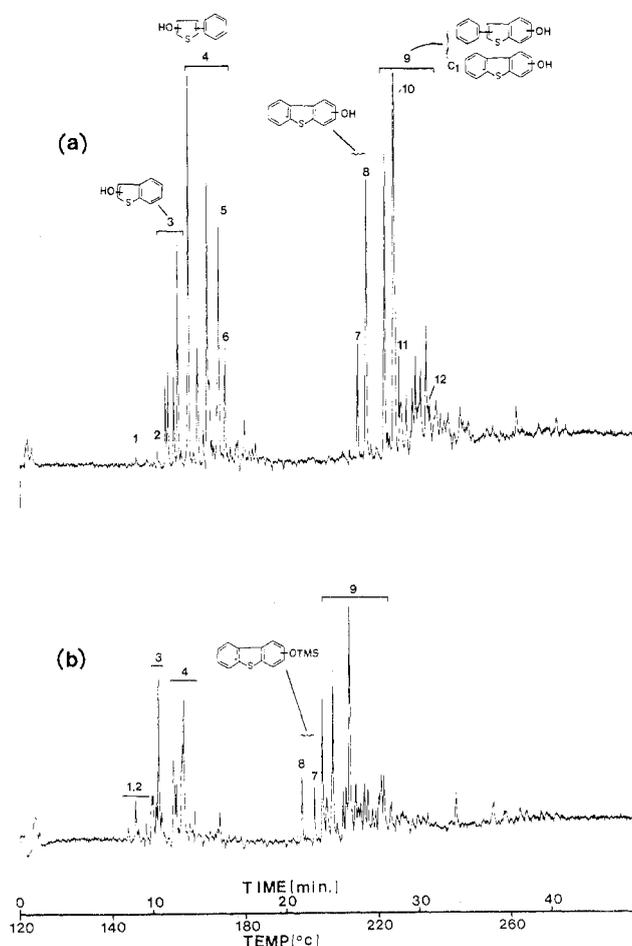

Figure 1. Chromatograms of the hydroxy-PAC fraction of an SRC II HD (a) before and (b) after derivatization with TMSI. Conditions were as follows: 20 m × 0.32 mm i.d. fused silica capillary column with a 25% biphenyl polysiloxane stationary phase (0.25 μm film); temperature programmed from 120 °C to 260 °C at 4 °C min⁻¹ after an initial 2-min isothermal period; hydrogen carrier gas at 100 cm s⁻¹; sulfur-selective flame photometric detection. Peak numbers refer to compounds listed in Table I.
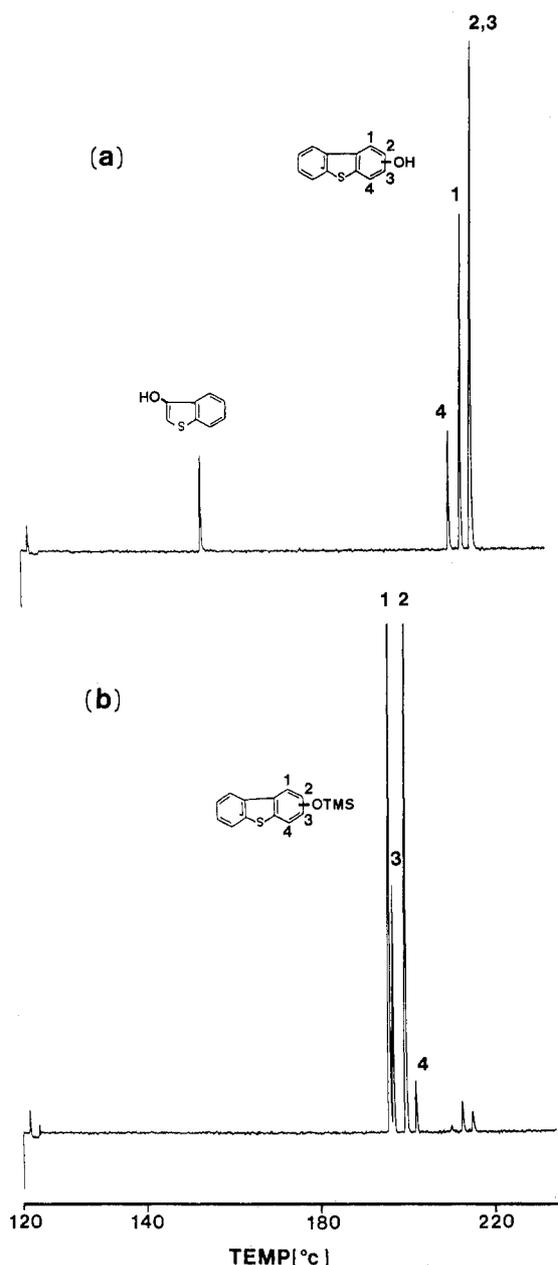
Figure 2. Chromatograms of the hydroxydibenzothiophene isomers (a) before and (b) after derivatization with TMSI. Conditions are given in Figure 1.

decrease in the dipolar-induced dipolar interactions between the solutes and stationary phase, also leading to decreased retention. However, derivatization improved the resolution of the hydroxydibenzothiophenes on the biphenyl phase as can be seen in Figure 2. The coeluting 2- and 3-hydroxy isomers in chromatogram 2(a) were completely resolved after derivatization (chromatogram 2(b)). Slight differences in molecular structures of isomers cannot be differentiated when the interactions between the solutes and stationary phase are strong and solute retention differences tend to be minimized. Reducing the polarities of the hydroxydibenzothiophenes by derivatization leads to a "softer" interaction with the polarizable biphenyl stationary phase and subsequent improved resolution. The same phenomenon was observed for the pentafluoropropyl (PFP) derivatives of the alkylated aminodibenzothiophenes (22).

Further confirmation of the identities of the hydroxylated PASH found in the SRC II HD coal liquid was obtained by gas chromatographic analysis of the A-4 fraction on a mesogenic polysiloxane which has a wide smectic range (118–300

°C). This methylpolysiloxane polymer has 25% substitution with 4-methoxyphenyl 4-(4-propoxyphenyl)benzoate and 4-methoxyphenyl 4-(4-pentoxyphenyl)benzoate side groups, and has been described in detail elsewhere (17). The relative retention values of the standard compounds and mixture constituents on this stationary phase are listed in Table I.

Since reducing the polarities by derivatization leads to improved resolution and derivatives show characteristic mass spectra, the Me₃Si-derivatized fraction was analyzed by GC/MS using the 25% biphenyl methylpolysiloxane stationary phase. Most identifications were confirmed by GC/MS (see Table I).

The distribution of hydroxylated PASH in this coal liquid is quite interesting. Two groupings of chromatographic peaks are observed in Figure 1. The first group is composed of hydroxybenzothiophenes and (hydroxyphenyl)thiophenes, while the second group contains hydroxydibenzothiophenes and (hydroxyphenyl)benzothiophenes. The difference between the two groupings of compounds is one benzene ring. This is consistent with what was earlier observed for the hydroxy-PAH fraction (19).

A number of individual hydroxy-PASH were identified in this study by comparison of chromatographic retention and mass spectral data of the SRC-II HD A-4 fraction with comparable data obtained for standard compounds. All of the reference standards are also listed in Table I. Of the four possible hydroxydibenzothiophene isomers, only the 1- and 2-hydroxy compounds were positively identified. Because of the numerous possible isomers for many of the hydroxylated PASH ring systems detected (i.e., 12 for (hydroxyphenyl)-thiophene and 48 for (hydroxyphenyl)benzothiophene) and the lack of reference standards for all of these compounds for comparison, many have only been tentatively identified. Semiquantification for 2-(3-hydroxyphenyl)thiophene and 1-hydroxydibenzothiophene was 7.5 and 3.4 μg/g in the SRC II HD, respectively.

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Solid Sorbent for Sampling of Sulfur Dioxide in Occupational Hygiene

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Sulfur dioxide is stabilized as an addition compound with ethanedial after initial hydrolysis. Reaction takes place on a partly regenerated poly(acrylic acid) weak cation exchange gel that is used as buffering carrier for the stabilizer solution. This results in high acid/base buffer capacity without release of anions to the sample solution, which permits use of both colorimetric and ion chromatographic determination. Breakthrough curves at different sampling temperatures and relative humidities are presented. An 80–95% S(IV) recovery was obtained after storing the sample on the tube for 2 weeks. If the sample was stored desorbed in a refrigerator, recovery was 100%. Stabilizing power of the sorbent was not affected by 4 months of storage prior to use. Equal concentrations were found with the sorbent and a buffered formaldehyde absorber when used in parallel in a field study. Precision of the sorbent method was, however, higher.

With widespread industrial use, documented acute (*1*) and suspected chronic (*2, 3*) toxicity of sulfur dioxide calls for a continuous development of the tools for monitoring the gas in the workplace. At the same time personal sampling devices are gaining increased popularity among occupational hygienists due to their convenience in use compared to impinger methods (*4*). A number of solid sorbents for sulfur dioxide are already described in the literature (*5–12*). As several countries have separate TLV's for sulfur species of different oxidation states, most of these (*5–11*) are, however, formally invalid, as they are unable to prevent sulfur dioxide from being oxidized after sampling. Some of them even involve an oxidation step prior to the determination of $SO_2(g)$ as sulfate ion (*10, 11*).

Passive diffusion badges (*13*) and untreated molecular sieves (*12*) have this speciation capability. The sensitivity of the diffusion badge is, however, insufficient for short-time sampling and molecular sieves demand specialized equipment for the determination of sulfur dioxide, which makes them unattractive to many users.

The reaction of carbonyl compounds with hydrogen sulfite ions has recently been used for stabilization of sulfur dioxide after sampling (*14, 15*) and for preparation of standards for ion chromatography (*16*). The sampling method was originally developed for ambient monitoring, but the buffered formaldehyde absorber should also be of use in industrial hygiene,

in both impingers and diffusion badges. Stabilization of S(IV) by formaldehyde is superior to the classical West and Gaeke method (*17*), if the absorber is buffered to a pH between 4 and 5. Reactive aldehydes are therefore the reagents of choice in this application.

A formaldehyde-based solid sorbent would permit sensitive and selective short-time sampling and make use of the same colorimetric determination as the diffusion badge, whose excellent long-time sampling characteristics it would complement. The volatility and instability of formaldehyde forced us, however, to search for another aldehyde in this application. A high buffer capacity was needed on the solid sorbent to compensate for the uneven distribution of sampled species on a sorbent tube, as compared to a solution. The water-retaining capacity of the sorbent had, furthermore, to be maximized to ensure that the initial hydrolysis of sulfur dioxide takes place. The efforts made to accomplish this are the subject of this paper.

EXPERIMENTAL SECTION

Reagents and Solutions. All chemicals were reagent grade, except 30% (w/v) aqueous ethanedial, benzaldehyde, and 3-phenylpropenal (synth.; Merck-Schuchardt, Munich, FRG), acetaldehyde (f. biochem.; Merck, Darmstadt, FRG), DL-glyceraldehyde (mp 135–138 °C; Aldrich, Beerse, Belgium), and dihydroxyacetone ("research grade"; Serva, Heidelberg, FRG). The pararosaniline ("standard grade"; Fluka, Buchs, Switzerland) was purified according to Scaringelli et al. (*18*).

The following carriers were used: Amberlite XAD-2, XAD-7, and IRC-84 (H⁺ form) (pract.; Serva), active charcoal (20–35 mesh for GC; Merck), 5-Å molecular sieves (Kebo, Stockholm), and silica gel (Grace Type 58, 0.2–0.4 mm; Darex, Bad Homburg, FRG). All carriers were crushed (if necessary), washed carefully several times with methanol and water, dried, and sieved to 20–40 mesh before use. The mixed base for sample hydrolysis contained 20 mM formaldehyde and 0.5 M NaOH and was prepared fresh every third day. The color reagent was composed of 0.8 mM pararosaniline hydrochloride in 1 M HCl. Milli-Q (Millipore, Bedford, MA) deionized water was used throughout.

WARNING: Pararosaniline and formaldehyde are suspected carcinogens and should be handled with due care.

The Sorbent. One hundred grams moist Amberlite IRC-84 was converted to the Na⁺ form by stirring with 500 mL of 1 M NaOH for 30 min. It was then rinsed twice with water and reconverted to the H⁺ form with 1 M HCl by the same procedure. The acidic resin was carefully washed with water to remove excess hydrochloric acid and slurried in a volume of water just sufficient to cover the resin. The wet bed volume of the resin was estimated, and a volume of 0.5 M NaOH 3 times the wet bed volume was