THE CONVERSION OF ORGANIC SULFUR IN COAL TO SULFATE USING PERCHLORIC ACID

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ABSTRACT

Based upon our previous research in which the variable oxidizing power of perchloric acid ($HClO_4$) was used to determine directly the organic sulfur in coal, it was hoped that this property of $HClO_4$ could be also used to determine different forms of organic sulfur in coal. This preliminary investigation into the usage of $HClO_4$ to delineate between various organic sulfur forms was based on model compounds. Dibenzothiophene, benzothiophene, diphenyl sulfide, 2-naphthalenethiol, dibenzyl disulfide, and dioctyl sulfide were oxidized in a Bethge apparatus with $HClO_4$ of varying concentration and boiling point. To insure complete sulfur recovery, gases produced during the reaction were captured in a trap containing hydrogen peroxide. Sulfate was then measured nephelometrically, after precipitation as barium sulfate, in the residual $HClO_4$ solution and in the peroxide trap. No appreciable amount of sulfate was measured for the aromatic compounds until a temperature of 170°C or higher was reached. However, for dibenzyl disulfide and dioctyl sulfide, large amounts of sulfate were measured in the trap, even at lower temperatures. The volatility of these two compounds may be a contributing factor in their high conversion to sulfate.

INTRODUCTION

A method for the direct determination of the sulfur forms in coal has been developed which takes advantage of the selective oxidizing ability of perchloric acid (1). In that method, sulfate sulfur was extracted from a coal sample with a boiling perchloric acid solution having a boiling point of 120°C. At the boiling point of 120°C, perchloric acid is a non-oxidizing acid. If any sulfidic sulfur was present, it was converted to hydrogen sulfide and absorbed in the trap containing 15 percent hydrogen peroxide. The residue from the 120°C reaction was reacted with a perchloric acid solution at a boiling point of 155°C. At this temperature, perchloric acid begins to have some oxidizing power (2). Thus, pyritic sulfur was converted to sulfate and a sulfur-containing gas which was trapped in hydrogen peroxide. The residue from the 155°C reaction was reacted with a 9:1 mixture of concentrated perchloric and phosphoric acids boiling at 205°C. At this temperature, perchloric acid is a powerful oxidizing agent (2), converting organic sulfur to sulfate and a sulfur-containing gas which was trapped in hydrogen peroxide. Total sulfur was determined by reacting another coal sample with the 9:1 mixture of perchloric and phosphoric acids. Sulfate was determined turbidimetrically in the perchloric acid solution and in the peroxide trap after precipitation as barium sulfate. Sulfur recoveries were good and the results for sulfur forms compared well with the results obtained using the ASTM procedure (3) on the same coals. The development of this method was

based on a series of perchloric acid oxidations performed on coal-derived pyrite and the Charming Creek coal from New Zealand in which almost all of the sulfur was organic (4).

The present study was undertaken for two reasons. The first was to further validate that organic sulfur was not oxidized appreciably at 155°C. The second reason was to investigate the possibility of delineating between various organic sulfur forms by taking advantage of the considerable variation in the oxidizing ability of perchloric acid. It was hoped that different sulfur functionalities would react at different temperatures above 155°C to produce sulfate and/or sulfur-containing gases. To attain these objectives, several sulfur-containing organic compounds were oxidized with perchloric acid solutions ranging in boiling point from 155°C to 203°C (concentrated perchloric acid). The model compounds subjected to oxidation were dibenzothiophene, benzothiophene, diphenyl sulfide, 2-naphthalene-thiol, dibenzyl disulfide, and dioctyl sulfide.

EXPERIMENTAL

Dibenzothiophene, benzothiophene, diphenyl sulfide, 2-naphthalene thiol, and dioctyl sulfide were obtained from Aldrich Chemical Company. Dibenzyl disulfide was obtained from Columbia Chemical Company. All reagents were used as received. All reactions were run in a modified Bethge apparatus described previously by McGowan and Markuszewski (4). The Bethge apparatus was designed to maintain a constant boiling mixture. The system was fitted with a trap containing 15 percent hydrogen peroxide to collect sulfur-containing gases and convert them to sulfate.

A Note on Safety. The use of perchloric acid alone as an oxidizing agent for organic materials always poses a hazard. In this study, all reactions were performed in a hood and behind an explosion shield. For each sample, reactions were performed at the lower temperatures first. For reactions at 203°C, small samples were reacted to minimize the possibility of an explosion. In the course of this study, a small fire occurred during the reaction of a 0.3-mL sample of dioctyl sulfide at 190°C and for a 0.1-mL sample of dioctyl sulfide reacted at 203°C. The fires were contained in the reaction vessel and no glassware was broken. The authors recommend that extreme care be taken any time perchloric acid alone is used as an oxidizing agent for organic materials.

Reaction Procedure. For the oxidations, the following procedure was followed. A perchloric acid solution was added to the Bethge apparatus and the boiling point adjusted to the desired temperature. By varying the initial amount of perchloric acid solution added, a final volume of approximately 50 mL was obtained. The perchloric acid solution was allowed to cool. In the case of dibenzyl disulfide and dioctyl sulfide, the 9:1 mixture of perchloric acid and phosphoric acid was used instead of only concentrated perchloric acid for the reaction at 205°C. A weighed sample of the solids or a pipetted sample of the liquids was placed in the Bethge apparatus. The mass of the liquid

samples was calculated by using handbook densities. A gas absorption bottle containing 100 mL of 15 percent hydrogen peroxide was attached to the top of the Bethge apparatus. Nitrogen was used as the purge gas. The reaction vessel was heated to the stable reaction temperature, and the reaction was allowed to proceed for 1.5 hrs. After the heat was removed, the system was purged for an additional 30 min. with nitrogen. The solution in the absorption bottle was boiled to insure oxidation of all the sulfur to sulfate and to reduce the volume to approximately 25 mL. The solution was transferred to a 50-mL volumetric flask and diluted to mark. After cooling, the perchloric acid reaction mixture was filtered. The filtrate was transferred to a 250-mL volumetric flask and diluted to mark.

Sulfate in the trap and the filtrate was determined by precipitation with barium and spectrophotometric measurement of the turbidity of the resultant barium sulfate suspension. The procedure used was described by Markuszewski et al. (5) and modified by McGowan and Markuszewski (4). Since some of the filtrates contained a solid material, the solutions were allowed to sit at least overnight and the sample used in the analysis was pipetted from the supernatant liquid. Since most of the filtrates were also colored, the absorbance of the sample without barium chloride added was measured and subtracted from the absorbance of the test solutions. In the case of analysis of the filtrates, perchloric acid was added to the standards to approximate the acid concentration of the filtrates.

RESULTS AND DISCUSSION

The results for the oxidation of model compounds in which the sulfur is attached directly to an aromatic ring appear in Tables 1-4. The results were very similar. Only insignificant amounts of sulfate were measured in products from the reactions carried out at 155°C. For the reactions at 170°C, a significant amount of sulfate was measured for 2-naphthalenethiol, while the remaining aromatic compounds still produced only insignificant amounts. With increasing temperature, the amount of measured sulfate increased linearly, and sulfur recovery was complete for the reactions carried out at 203°C. For the aromatic materials, most of the sulfate was found in the filtrate as the temperature increased above 170°C.

Table 1. Results for the oxidation of dibenzothiophene (Theoretical=17.4% sulfur)

Boiling Point (°C)	Sample Weight (g)	Sulfur in Trap (% Samp.)	Sulfur in Filtrate (% Samp.)	Total Sulfur (% Samp.)	Sulfur Recovered (% of Theor.)
155	0.3062	0.09	0.30	0.39	2.2
170	0.3095	0.00	0.00	0.00	0.0
180	0.3129	2.23	0.18	2.41	13.8
190	0.2956	1.43	7.05	8.48	48.7
203	0.2956	2.21	15.29	17.50	100.5

Table 2. Results for the oxidation of benzothiophene (Theoretical=23.9% sulfur)

Boiling Point (°C)	Sample Weight (g)	Sulfur in Trap (% Samp.)	Sulfur in Filtrate (% Samp.)	Total Sulfur (% Samp.)	Sulfur Recoverd (% of Theor.)
150	0.5024	0.46	0.27	0.73	3.1
155	0.4993	0.59	0.34	0.93	3.9
170	0.5000	0.16	0.44	0.60	2.5
180	0.5065	1.21	6.07	7.28	30.4
190	0.5000	2.53	11.80	14.33	60.0
203	0.0623	3.68	19.70	23.38	97.9

Table 3. Results for the oxidation of diphenyl sulfide (Theoretical=17.2% sulfur)

Boiling Point (°C)	Sample Weight (g)	Sulfur in Trap (% Samp.)	Sulfur in Filtrate (% Samp.)	Total Sulfur (% Samp.)	Sulfur Recovered (% of Theor.)
150	0.3354	0.34	0.28	0.62	3.6
155	0.3354	0.09	0.44	0.53	3.1
170	0.3354	0.00	0.00	0.00	0.0
180	0.3354	1.91	1.55	3.46	20.1
190	0.3354	2.12	6.86	8.98	52.2
203	0.1115	1.40	14.60	16.00	92.9

Table 4. Results for the oxidation of 2-naphthalenethiol (Theoretical=20.0% sulfur)

Boiling Point (°C)	Sample Weight (g)	Sulfur in Trap (% Samp.)	Sulfur in Filtrate (% Samp.)	Total Sulfur (% Samp.)	Sulfur Recovered (% of Theor.)
155	0.3118	0.13	0.00	0.13	0.7
171	0.3022	1.67	0.80	2.40	12.0
180	0.3138	2.63	8.52	11.15	55.8
190	0.2961	1.98	11.74	13.72	68.6
203	0.0996	1.24	20.67	21.91	109.6

The results for the oxidation of compounds in which the sulfur was attached to an aliphatic carbon appear in Tables 5 and 6. For these compounds, significant amounts of sulfate were found in the peroxide traps for reactions at all the temperatures tested. For dibenzyl disulfide, 87-108% of the theoretical amount of sulfur was recovered at

155-205°C. Over 80 percent of the sulfur contained in dibenzyl disulfide was found in the gas trap for every reaction except that at 205°C. Lesser amounts of sulfate were measured for reaction products from dioctyl sulfide. For the reactions at 155°C and 170°C, the peroxide traps had foul, nauseating odors. This suggested that the sulfur-containing gases trapped were thiolic in nature and did not exist as an oxidized form of sulfur. The implication is that oxidation occurred on the carbon portion of the molecule, forming smaller, more volatile organosulfur compounds which escaped and were subsequently trapped. This was especially true for dibenzyl disulfide, containing the reactive benzyl carbon. The amounts of sulfate measured in the filtrates for dioctyl sulfide were similar to the amounts measured for the aromatic compounds. For dibenzyl disulfide, lesser amounts of sulfate were measured in the filtrate.

Table 5. Results for the oxidation of dibenzyl disulfide (Theoretical=26.0% sulfur)

Boiling Point (°C)	Sample Weight (g)	Sulfur in Trap (% Samp.)	Sulfur in Filtrate (% Samp.)	Total Sulfur (% Samp.)	Sulfur Recovered (% of Theor.)
155	0.3099	21.78	0.86	22.64	87.3
170	0.3068	22.16	1.17	23.90	90.0
181	0.3050	22.20	2.18	24.38	93.8
190	0.3000	22.33	3.43	25.76	98.8
205	0.1090	9.48	18.82	28.30	108.8

Table 6. Results for the oxidation of dioctyl sulfide (Theoretical=12.4% sulfur)

Boiling Point (°C)	Sample Weight (g)	Sulfur in Trap (% Samp.)	Sulfur in Filtrate (% Samp.)	Total Sulfur (% Samp.)	Sulfur Recovered (% of Theor.)
155	0.2526	3.72	0.00	3.72	30.0
170	0.2526	4.08	0.00	4.08	32.9
181	0.2526	6.02	2.97	8.99	72.5
190	0.2526	7.24	4.34	11.56	93.2
205	0.0842	1.41	12.56	13.97	112.6

Benzothiophene, diphenyl sulfide, and 2-naphthalenethiol were soluble in perchloric acid, giving clear solutions. Only very small amounts of char formed during the reactions at 170°C to 190°C. The odor of naphthalene was noted in the filtrates of the reaction of 2-naphthalene-thiol at 170°C and 180°C. A black char formed during the reaction of dioctyl sulfide at 155°C, 170°C, and 180°C. The color of the filtrates from the above reactions ranged from yellow at 155°C to orange and brown at 170°C and 180°C, respectively, and back to clear at 203°C.

During the oxidation of dibenzyl disulfide, a purplish-black, gummy solid, representing from 60 to 90 percent of the sample mass, formed at temperatures from 155°C to 190°C. The color of the filtrates indicated that some new compounds were formed at temperatures below 203°C. The filtrate was orange-pink at 155°C, light orange at 170°C, orange with a green tint at 181°C, dark brown at 190°C, and colorless at 203°C.

Dibenzothiophene was insoluble in perchloric acid, and unreacted dibenzothiophene was recovered from reactions carried out at 180°C and below. A different, yellow solid was formed at 190°C. This solid material was analyzed by Fourier transform infrared spectroscopy and mass spectrometry. Three series of compounds were identified in the solid. The major series consisted of chlorinated dibenzothiophene sulfones containing from one to seven chlorine atoms. A second series consisted of chlorinated dibenzothiophenes containing from one to eight chlorine atoms. A minor series of chlorinated compounds for which the base was dibenzothiophene plus three oxygen atoms was also indicated. No solid was recovered from the reaction carried out at 203°C.

CONCLUSIONS

Aromatic sulfur compounds are not oxidized to sulfate or a sulfur-containing gas by perchloric acid having boiling points of 170°C or lower. At higher temperatures, aromatic sulfur compounds apparently are oxidized by perchloric acid first to sulfones and chlorinated sulfones, then to sulfonic acids and finally to sulfate. Volatile sulfur-containing gases are not produced by this oxidation sequence. However, for aliphatic sulfur compounds, the carbon portion is apparently oxidized at lower temperatures, resulting in the formation of volatile sulfur-containing compounds which are trapped in hydrogen peroxide.

For analysis of a coal containing aliphatic sulfur near the end of a chain, it is possible that some of the sulfur measured after reacting the coal at 155°C could be due to organic sulfur, thus causing a positive error in the measurement of pyritic sulfur. However, during previous oxidation reactions of several different coals, no odor has ever been noted around the trap of the reaction carried out at 155°C, indicating that this possibility is probably low. Since a difference has been noted in the oxidation of aromatic sulfur and aliphatic sulfur compounds, the possibility of distinguishing between the two forms exists, and further investigation is warranted.

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