

THE CHEMISTRY OF SULFUR DURING HYDROPYROLYSIS OF COALS

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Sulfur K-edge X-Ray Absorption Near Edge Structure Spectroscopy (XANES) and sulfur 2p X-Ray Photoelectron Spectroscopy have been used to identify organically bound sulfur forms in coals (1-3), and to follow the chemistry of organic sulfur during various treatments including mild oxidation (4), pyrolysis (5-7) and chemical reductions (8). This paper focuses on the changes which take place with organically bound sulfur functionalities in coals of various ranks when they are subjected to hydropyrolysis conditions. Data from both X-Ray techniques and temperature programmed decomposition-mass spectrometry were used in tandem.

Experimental Section

Most coal samples used in this study were obtained from the Argonne Premium Coal Program (9). The sample of Rasa coal was obtained from Dr. C. M. White of PETC. The procedures for obtaining and interpreting XPS and XANES spectra of coals have been reported and discussed previously (1, 2). XPS spectra were obtained on a Vacuum Generators (VG) ESCA lab system using Mg K_{α} non-monochromatic radiation using a five channel detection system. XANES spectra were recorded at the National Synchrotron Light Source at Brookhaven National Laboratory on beam line X-10C. Fluorescence spectra were recorded using a Stern-Heald-Lytle detector. Hydropyrolysis char thermal reactivity data were obtained using a temperature programmed decomposition (TPD) apparatus, the design and use of which are described elsewhere (5, 6). Samples were heated under ultrahigh vacuum from room temperature to 750 °C at a rate of 0.5 °C/s, while the off gases were monitored by a mass spectrometer. Hydropyrolysis experiments were carried out in a closed reactor pressurized at room temperature to 70 atm with a 95% hydrogen - 5% helium gas mixture. Pyrolysis was done in helium, at 1 atm in a quartz lined reactor (5). For pyrolysis experiments, the samples were heated at a linear heating rate of 0.5 °C/s to 400 °C followed by holding at that temperature for 5 minutes. The reactor temperature program for hydropyrolysis was similar except that the maximum temperature was 427 °C and the samples were held for 30 minutes under isothermal conditions. Samples were analyzed after the linear heatup and isothermal stages. These kinetic conditions favored the retention of coal liquid products in the pyrolysis and hydropyrolysis residues.

Results and Discussion

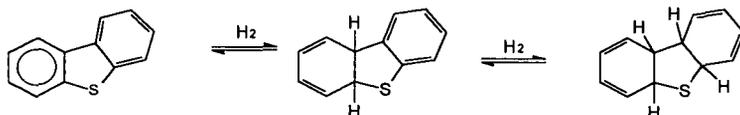
The coals were subjected to hydropyrolysis conditions and the hydropyrolysis residues were collected and examined by elemental analysis to determine sulfur loss, by XPS and XANES to determine the forms of bound sulfur remaining, and by TPD to determine the thermal reactivity of the residues. Table 1 shows the sulfur to carbon atomic ratios for samples of starting Rasa and Illinois No. 6 coals, as well as those for the residues from heating to 400 °C under helium pyrolysis and hydropyrolysis after heating to 427 °C as determined from bulk elemental analysis and from XPS by integration of the areas for sulfur and carbon (1). The bulk and XPS elemental analyses are in good agreement for Rasa coal, which contains virtually no pyrite, and are not in agreement for Illinois No. 6. The discrepancy between the bulk elemental and XPS data for Illinois No. 6 coal is due to the fact that the surface concentration of pyrite and its oxidation products are different on this coal's surface relative to that in the bulk(10). However, both analyses indicate that more sulfur was lost during hydropyrolysis than pyrolysis under nitrogen. The bulk elemental analyses indicate that about 22% of the sulfur was lost from Rasa and 32% from Illinois No. 6 under these hydropyrolysis conditions. XPS sulfur 2p spectra of the 427 °C hydropyrolysis residues from Rasa and Illinois No. 6 coal are shown in Figure 1. Included in the figure are the actual spectra and the curve resolved aromatic and aliphatic sulfur components. The results of the curve resolution analysis (1, 2) of these

spectra are shown in Table 2. The table shows the XPS results for aliphatic sulfur for the initial coals, hydropyrolysis residues obtained at 200, 350 and 427 °C, and previously obtained data (5) on helium pyrolysis chars. The results indicate that the hydropyrolysis chars contain the same ratio of aliphatic to aromatic sulfur as the starting coals, and considerably more than that contained in the pyrolysis residues. XANES data on the same samples confirm these findings. In addition, the feature attributed to pyrite in the fresh Illinois No. 6 coal and its 200 °C hydropyrolysis residue largely disappears in the 350 °C residues and is replaced by a feature attributed to pyrrhotite.

The effect of temperature on the reactivity of bound sulfur on the hydropyrolysis residues was examined by TPD. Traces of the relative intensities of the $m/e = 34$ mass spectra of the initial Rasa and Illinois No. 6 coals and their hydropyrolysis residues prepared at 200, 350 and 427 °C are plotted as a function of temperature in Figure 2. These were normalized so that the data for a given coal appear on the same relative intensity scale. Up to 350 °C, Rasa coal continues to evolve H_2S , but at 427 °C the amount released is considerably diminished. The TPD traces for fresh Illinois No. 6 coal and its 200 °C hydropyrolysis residue show evolution of H_2S from both aliphatic sulfur and pyrite, but the total amount of H_2S released from the 350 °C residue is diminished, and that from pyrite is virtually gone. There is even less H_2S evolution from the 427 °C hydropyrolysis residue.

Taken together the data present an apparent discrepancy. It is known that on pyrolysis in an inert environment at 400 °C, aliphatic sulfur is lost from the coal as H_2S (5, 6). Aromatic sulfur does not evolve at these temperatures (11). Somewhat more sulfur is lost during hydropyrolysis than pyrolysis, but the differences are not great. TPD data indicate that most of the reactive sulfur in the hydropyrolysis residues had evolved at 427 °C. Nevertheless, XPS and XANES analyses indicate that the hydropyrolysis residues contain about as much aliphatic sulfur as the starting coals; the ratio of aliphatic to aromatic sulfur is about the same, even though significant amounts of H_2S evolved during the hydropyrolysis.

To account for these observations, we postulate that molecules containing aromatic sulfur forms are partially hydrogenated under hydropyrolysis conditions as follows:



To the XPS and XANES probes, the sulfur in the hydrogenated molecules appear as aliphatic sulfurs. However, during heating, carbon sulfur bonds are not cleaved; rather the molecules lose hydrogen to regain their aromaticity.

Conclusions

Unlike pyrolysis under inert gas, pyrite in coals is converted to pyrrhotite during hydropyrolysis, and significant quantities of aliphatic sulfur are detected in the residues. It is believed that these aliphatic sulfur forms result from partial hydrogenation of aromatic sulfur species. While these sulfur species appear to be aliphatic to the X-ray probes, they are not, and do not behave thermally as aliphatic species.

References

- Kelemen, S. R.; Gorbaty, M. L.; George, G. N. *Fuel*, **1990**, *69*, 939, 945.
- George, G. N.; Gorbaty, M. L.; Kelemen, S. R.; Sansone, M. *Energy Fuels*, **1991**, *5*, 93.
- Huffman, G. P.; Mitra, S.; Huggins, F. E.; Shah, N.; Vaidya, S.; Lu, F. *Energy Fuels*, **1991**, *5*, 574.
- Gorbaty, M. L.; Kelemen, S. R.; George, G. N.; Kwiatek, P. J. *Fuel*, **1992**, *71*, 1255.
- Kelemen, S. R.; Gorbaty, M. L.; George, G. N.; Kwiatek P. J.; Sansone, M. *Fuel*, **1991**, *70*, 396.

6. Kelemen, S. R.; Vaughn, S. N.; Gorbaty, M. L.; Kwiatek, P. J. *Fuel*, **1993**, 72, 645.
7. Taghiei, M. M.; Huggins, F. E.; Shah, N.; Huffman, G. P. *Energy Fuels*, **1992**, 6, 293.
8. Chatterjee, K.; Stock, L. M.; Gorbaty, M. L.; George, G. N.; Kelemen, S. R. *Energy Fuels*, **1991**, 5, 773.
9. Vorres, K. *Energy Fuels*, **1990**, 4, 420.
10. Kelemen, S. R.; Gorbaty, M. L.; George, G. N.; Kwiatek, P. J. *Energy Fuels*, **1991**, 5, 720.
11. Calkins, W.H.; Torres-Ordonez, R. J.; Jung, B.; Gorbaty, M. L.; George, G. N.; Kelemen, S. R. *Energy Fuels*, **1992**, 6, 411.

TABLE 1

<u>RASA</u>	SULFUR/CARBON ATOM RATIO (x100)	
	<u>XPS</u>	<u>BULK</u>
INITIAL	6.20	6.10
PYROLYSIS	4.70	5.30
HYDROLYSIS	4.51	4.82
<u>ILLINOIS #6</u>		
INITIAL	1.25	2.32
PYROLYSIS	0.98	2.25
HYDROLYSIS	0.96	1.58

TABLE 2

	XPS MOLE PERCENT SULFIDIC SULFUR	
	<u>RASA</u>	<u>ILLINOIS #6</u>
INITIAL	26	29
HYDROLYSIS (200 °C)	25	30
HYDROLYSIS (350 °C)	26	--
HYDROLYSIS (427 °C)	25	26
PYROLYSIS (400 °C)	8	13

FIGURE 1

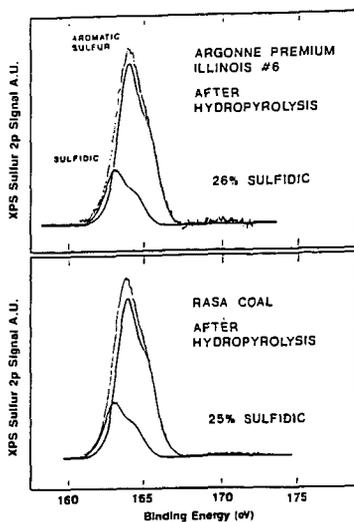


FIGURE 2

