TOWARD ORGANIC DESULFURIZATION

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INTRODUCTION

Advances in the organic desulfurization of coals and resids depend upon the discovery of methods for the secure definition of the sulfur forms in fossil fuel materials as well as upon the discovery of innovative chemical desulfurization strategies. This report deals with the coupling of selective chemical methods with XANES in an investigation of the desulfurization of Illinois No. 6 bituminous coal and Rasa subbituminous coal.

EXPERIMENTAL PART

The Argonne National Laboratory Premium sample of Illinois No. 6 bituminous coal and a sample of Rasa subbituminous coal that was provided by Ljiljana Ruscic were used in these experiments. The Illinois No. 6 coal contains 81% C (maf) with 2.0%S in organic compounds and 2.8%S in pyrite. The Rasa coal contains 73%C (maf) with 11.7%S in organic compounds.

The procedures that we used for selective desulfurization with lithium aluminum hydride (1-3), potassium naphthalene (-1), (3), and n-butyllithium-potassium t-butoxide (4) have been described previously. Conventional isolation procedures were used in most experiments, however, the facility with which some of the residual sulfur-containing compounds underwent air oxidation prompted us to protect the reaction products from oxygen in certain experiments.

All of the sulfur analyses were performed by Commercial Testing and Engineering of South Holland, IL.

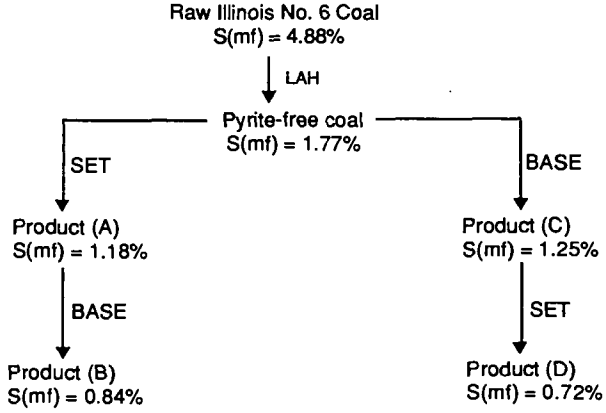
The XANES measurements were carried out by Gorbaty and his associates (5).

RESULTS AND DISCUSSION

The Illinois No. 6 coal was treated with lithium aluminum hydride to remove pyrite (1-3). As already reported, this method reduces the iron content of this coal to less than 0.1% by weight without altering the organic sulfur content. Several lines of evidence secure this point. First, pyrite reflections are absent in X-ray spectrum. Second, the XANES spectra of the product and the starting material indicate that the distribution of the sulfur forms is unchanged.

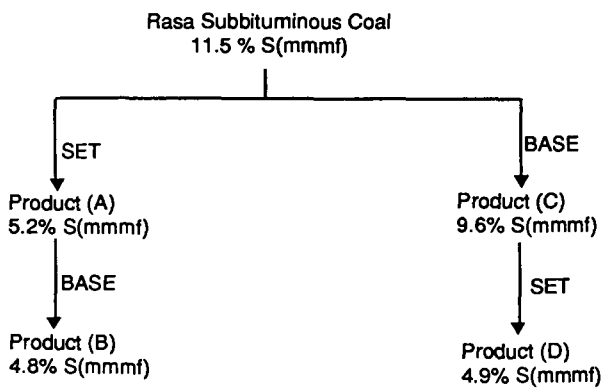
The pyrite-free coal was then treated with a single electron transfer reagent (SET) to react selectively with aromatic sulfur compounds including the sulfur heterocycles (3). We used potassium naphthalene(-1) in tetrahydrofuran at 67°C for 24 hours in most experiments. In an attempt to remove sulfidic sulfur, we used Lochmann's base (BASE), a very reactive mixture of n-butyllithium and potassium t-butoxide, in heptane at 98°C for six hours (4).

The results of the desulfurization experiments, which have been reported elsewhere (6), are summarized in the equation.



The XANES spectra of each product were recorded by Gorbaty and his colleagues at the Exxon beamline at National Synchrotron Light Source at Brookhaven National Laboratory (6). In brief, Gorbaty has shown that the sulfur XANES spectra of pyrite-free, unoxidized coals exhibit key features near 2469.6 and 2470.5 ev. The feature at 2469.6 ev arises from sulfidic sulfur compounds such as aromatic and aliphatic thiols, aliphatic sulfides, and aryl alkyl sulfides. The feature near 2470.5 ev is dominated by sulfur bound to sp^2 hybridized carbon atoms. The sulfur heterocycles and diaryl sulfides exhibit their absorptions in this region of the spectrum. The pyrite-free Illinois No. 6 coal contains 65 mole % aromatic sulfur and 35% sulfidic sulfur (7). As already reported, SET selectively reduces the aromatic sulfur content and the signal at 2470.5 ev is selectively decreased . On the other hand, BASE removes certain sulfidic forms that contribute to the intensity at 2469.6ev.

With these results in hand, we turned our attention to the Rasa coal. The work with this subbituminous coal provided the results shown in the equation.



The Rasa coal undergoes extensive desulfurization with the SET reagent. It removes 55% of the sulfur when it is used as the first reagent and 41% of the sulfur when it is used as the second reagent. BASE is much less effective. It removes only 17% of the sulfur when it is employed as the first reagent, and even less, 3%, of the sulfur when it is used after the SET reagent. We also found that when the Rasa coal was treated with BASE and SET and

then treated with SET again, the sulfur content was reduced to 2.2%. When the BASE treatment was omitted entirely, dual SET reactions again reduced the sulfur content to 2.2%.

The XANES spectra for selected products were recorded. It was found that the sulfur bonded to sp^2 carbon in diaryl sulfides and heterocycles is virtually eliminated in the dual SET reactions, but that the feature at 2469.6ev remains.

In the course of our studies with the Illinois coal, we also found that the sulfur compounds that remained after SET and BASE reactions were thermally labile, and were also decomposed by vigorous acid hydrolysis.

CONCLUSIONS

Although space limitations do not permit a full discussion of all the results, the chemical and spectroscopic observations when coupled with information about the known chemistry of SET and BASE suggest the following conclusions.

First, the SET reagent selectively removes sulfur from heterocyclic sulfur compounds and aromatic sulfides. BASE does not remove the sulfur from the heterocycles but does react with sulfur compounds such as alkyl aromatic sulfides that are susceptible to base catalyzed elimination reactions. Neither of these reagents is effective for the removal of sulfur from aliphatic thiols under the mild conditions that were used in these experiments.

Second, the sulfur compounds that remain after the treatment with SET and BASE are probably aliphatic substances including alkyl and allylic thiols.

Third, BASE can be effective for partial organic desulfurization in some coals, but, generally speaking, the SET reactions, while slow, are more effective and purge sulfur selectively from the organic compounds in these coals without appreciable loss in the heat content.

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