

Evaluation of Oxydesulfurization Processes for Coal  
I. The Effect of the Ames Process on Model Organosulfur Compounds

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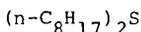
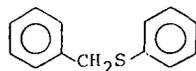
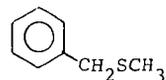
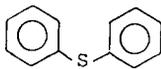
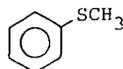
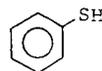
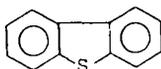
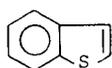
INTRODUCTION

One of the main obstacles to the use of coal as an alternate energy source is that it contains sulfur which contributes to air pollution when the coal is burned. It is estimated that only few percent of coals in the United States will be able to meet EPA SO<sub>2</sub> emission standards (1). Although some chemical procedures have been reported to be effective for desulfurization of coals, most, if not all, of the sulfur that is removed is inorganic. There is little information about what actually happens to the organic sulfur when coals are subjected to these process conditions. A major reason for this ignorance is the lack of information about the nature and distribution of the organosulfur functional groups in the coal.

Recently, several workers have reported that organic sulfur as well as inorganic sulfur can be removed by oxidative processes (2-6). Wheelock, *et. al.* (2) reported that under the following conditions: 150°C, 200 psig O<sub>2</sub>, 0.2M aq. Na<sub>2</sub>CO<sub>3</sub>, 1 hour; up to 40% of the organic sulfur can be removed from coal without significantly reducing the recovery of combustible organic matter.

In this paper we wish to report our evaluation of the effectiveness of this Ames process in the desulfurization of coal. Instead of using coal, model organosulfur compounds were subjected to Ames process conditions. Our approach is based on the assumption that a definitive knowledge of the organosulfur functional groups and their distribution in coal is not a prerequisite for investigating the viability of desulfurization processes. Thus, it is sufficient to measure the propensity of a representative spectrum of organosulfur model materials toward desulfurization under process conditions.

In our study, the following organosulfur compounds have been subjected to Ames process conditions either by themselves or in the presence of coal. For comparison, some model sulfur compounds were also run under the same conditions except that nitrogen was used in place of oxygen. The results of our study are summarized in Tables I and II.



## EXPERIMENTAL

### Reactions in the Absence of Coal

The reactions were run either in an 1 liter or a 300 ml autoclave. In a typical run, approximately 5 g (for the 1 liter autoclave) or 1 gram (for the 300 ml autoclave) of organic sulfide was placed in a glass liner of an autoclave. After adding 300 ml (1 l autoclave) or 50 ml (300 ml autoclave) of 0.2M aqueous sodium carbonate solution, the reactor was sealed, flushed with  $N_2$ , and heated as rapidly as possible to 150°C. After the reactor had equilibrated at 150°C (10-15 minutes), the system was pressurized to 200 psig with oxygen and the reactor was flushed with a slow stream of oxygen for 3 minutes. A cold trap was connected to the vent tube of the autoclave to collect the starting sulfide (usually a small amount) which escaped from the reactor during the flushing process (the collected sulfide was combined with the reaction mixture in the autoclave after the reaction). The reactor was then sealed, and temperature (150°C), stirring (1500 rpm) and pressure (200 psig) were maintained for one hour. During the initial pressurization and the first 20-30 minutes of the reaction, cooling of the reactor with water was sometimes required.

After one hour, the heater was turned off; the reactor was cooled to room temperature and the contents were poured into a beaker. The reactor and the glass liner were washed with benzene and with water. The reaction mixture and these washings were combined and extracted with benzene, and the benzene extract was dried ( $Na_2SO_4$ ) and filtered. To the reactions run in the 300 ml autoclave an internal standard was added directly to the dried benzene extract and the solution was analyzed by gas chromatography (GC) to determine the quantity of starting sulfide left and volatile compounds formed in the reaction. GC response factors for the sulfides, products and the standards were generated in the form of calibration table using standard solutions containing the sulfide, products and the standard. For the reactions run in the 1 liter autoclave, the volume of dried and filtered benzene extract was adjusted to 500 ml, and a 50 ml of aliquot of the benzene solution was withdrawn. An internal standard was added to the 50 ml solution; the solution was analyzed with GC.

The extracted aqueous layer of the benzyl phenyl sulfide or the benzyl methyl sulfide reaction mixture was acidified with concentrated hydrochloric acid, and washed with benzene. The benzene washings were dried ( $Na_2SO_4$ ) and flash evaporated to afford a residue which NMR and IR analysis showed to be benzoic acid. The remaining aqueous layer was evaporated to dryness, and the residue was analyzed by NMR, IR, and UV spectroscopy.

### Reaction in the Presence of Coal Under Oxygen or Under Nitrogen Atmosphere

The coal used was Iowa coal (Lovilia, 200 mesh) and was dried at 110°C overnight. The reactions in the presence of coal were run in a 300 ml autoclave. The reaction procedures were the same as those mentioned above except that ca 4.0 g of coal was added to the reaction mixture for each run. After the reaction, the reaction mixture and washings were combined and filtered, and the filtrate was extracted with benzene. The coal collected with filtration was washed with acetone, then benzene several times. The benzene and the acetone-benzene extracts were combined, dried ( $Na_2SO_4$ ) and analyzed with GC using internal standards.

## RESULTS AND DISCUSSION

Tables I and II demonstrate that among the model compounds that we studied, only thiophenol and compounds containing a benzylic sulfide linkage were oxidized to an appreciable extent. Thiophenol was converted to phenyl disulfide which was resistant to further oxidation. Benzyl phenyl sulfide was oxidized and cleaved to give benzaldehyde, benzoic acid and benzenesulfonic acid; benzyl methyl sulfide gave similar results. The other model compounds were unreactive under the Ames process conditions either by themselves or in the presence of coal. Even in the presence of coal, more than 70% of the starting sulfide was recovered. The reduced recoveries of starting

Table I. Reaction Results of Compounds Run Under the Ames Process Conditions in the Absence of Coal<sup>a</sup>

<u>Compound</u>	<u>Recovered Yield (%) of Starting Sulfide</u>	<u>Product</u>
Benzothiophene	87	-----
Dibenzothiophene	96	-----
Thiophenol	0	Phenyl Disulfide
Phenyl sulfide	98	-----
Phenyl methyl sulfide	89	-----
Benzyl methyl sulfide	36	Benzoic acid Benzaldehyde Methanesulfonic acid
Benzyl phenyl sulfide	29	Benzoic acid Benzaldehyde Benzenesulfonic acid
N-Octyl sulfide	90	-----

<sup>a</sup> Ames process conditions: 150°C, 200 psig O<sub>2</sub>, 0.2M aqueous Na<sub>2</sub>CO<sub>3</sub>, 1 hour.

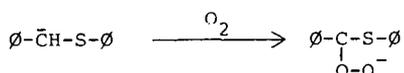
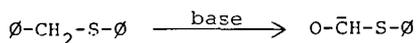
Table II. Reaction Results of Compounds Run Under the Ames Process<sup>a</sup> Condition in the Presence of Coal<sup>b</sup>

<u>Compound</u>	<u>Recovered Yield (%) of Starting Sulfide</u>	
	<u>N<sub>2</sub><sup>c</sup></u>	<u>O<sub>2</sub><sup>d</sup></u>
Dibenzothiophene	83	76
Phenyl sulfide	76	74
Benzyl methyl sulfide	75	13
N-octyl sulfide	--	82

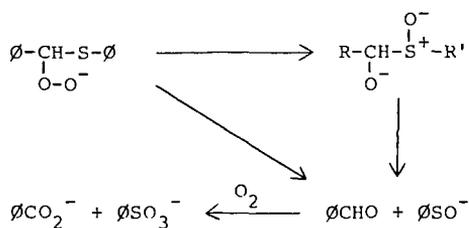
<sup>a</sup> Ames process conditions: 150°C, 200 psig O<sub>2</sub>, 0.2M aqueous Na<sub>2</sub>CO<sub>3</sub>, 1 hour. <sup>b</sup> Iowa Lovilia Coal. <sup>c</sup> Reaction run under nitrogen atmosphere. <sup>d</sup> Reaction run under oxygen atmosphere.

materials in the presence of coal (see Table II) can be attributed to absorption of the organosulfur compound by the microporous structure of coal and the mechanical loss associated with working up the reaction mixture. This hypothesis was confirmed by the correspondingly low recoveries of starting sulfides from reactions run in the presence of coal under nitrogen atmosphere--an inert atmosphere. Furthermore, no oxidation products were detected in the reaction mixtures. Clearly, of the compounds investigated thus far, only benzyl sulfides and thiophenol underwent any chemical reaction, and (the benzyl sulfides were the only compounds in which carbon sulfur bond cleavage occurred.

The base-catalyzed reaction of compounds containing a benzylic sulfide linkage with molecular oxygen has been studied under a variety of conditions. Wallace *et. al.* (7) reported that benzyl phenyl sulfide can be oxidized with molecular oxygen in 2M potassium *t*-butoxide-HMPA at 80°C to yield benzoic acid. The authors proposed that the reaction proceeded *via* the formation of an  $\alpha$ -carbanion followed by reaction between the ion and oxygen.



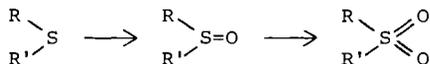
The resulting  $\alpha$ -peroxide anion can then decompose in either a stepwise or concerted manner to form benzaldehyde and benzenesulfenate which are oxidized to the corresponding carboxylic and sulfonic acids. In the first step of this mechanism, the  $\alpha$ -carbanion is stabilized by the d-orbital of the adjacent divalent sulfur atom.



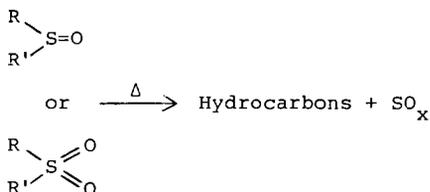
We believe that a similar mechanism is involved in the oxidation of benzyl phenyl sulfide under Ames process conditions.

Oxydesulfurization of the organic sulfides in coal has been formulated as a two-step process (8): 1. Selective oxidation of the sulfur to sulfoxides and sulfones with the latter as the favorable product; and 2. Thermal decomposition of the oxidation products, usually under basic conditions.

Step 1.



Step 2.



In this formulation, the reaction is initiated by oxidation of the sulfur and, in fact, is made possible by this oxidation which results in polarization and weakening of the carbon to sulfur bonds (8).

We find no evidence to support this hypothesis; oxidation of the sulfur was detected only in thiophenol and in the benzyl sulfides. In the first case, oxidation of mercaptans to disulfides is a facile reaction known to occur under conditions such as the Ames process. No further oxidation of the disulfide was detected. In the latter case, we submit that carbon-sulfur bond cleavage is initiated by oxidative attack at the benzyl position instead of at sulfur. This postulate is supported by our recent discovery that, under Ames process conditions, fluorene was oxidized rapidly and quantitatively to fluorenone while dibenzothiophene was removed unchanged from the same reaction mixture.

Oxidation of benzylic carbon hydrogen bonds in preference to sulfur would have a substantial impact on the development of processes for the oxydesulfurization of coal. We intend to investigate this phenomenon and explore methods for reducing or reversing the ratio of benzylic to sulfur oxidation.

#### ACKNOWLEDGEMENTS

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