

**THE CHEMICAL BASIS FOR REMOVAL OF ORGANIC SULFUR  
FROM COAL via JPL CHLORINOLYSIS**

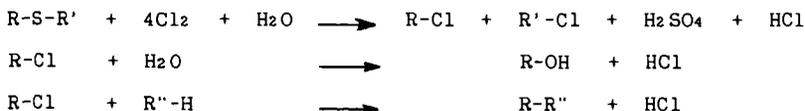
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**INTRODUCTION**

Because of the environmental problems attributable to Acid Rain, sulfur removal has been one of the most important areas of coal utilization research. Although a number of physical and chemical desulfurization processes which effectively remove inorganic sulfur have been developed, only a small portion of the organic sulfur can be removed under these conditions (1). This is not surprising in view of the well established chemical stability of C-S bonds in thiophenes, arylsulfides, and thiophenols which comprise much of the organic sulfur component in coal.

While it seems obvious that investigation of the chemistry of coal desulfurization is necessary to develop more efficient and economical processes, this important research area has received little attention. For example, Chlorinolysis was investigated by the Jet Propulsion Laboratory more than ten years ago and reported to remove up to 60% of the organic sulfur (2). Yet the chemical pathway by which organic sulfur is removed is still unknown and is most often expressed with appropriate ambiguity in **Scheme 1** (3):

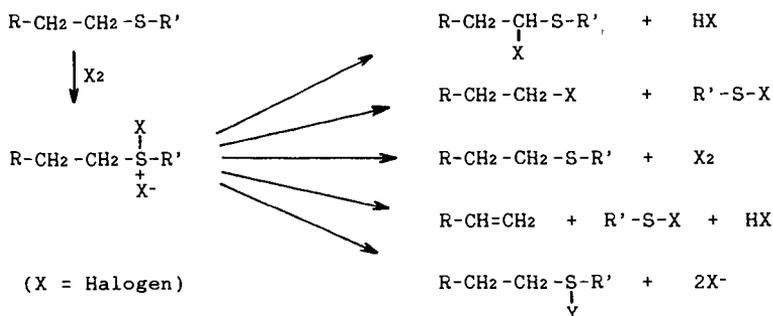


**Scheme 1**

However, the reactions of halogens with divalent sulfur compounds such as thiols, sulfides, and thiophenes have been studied extensively and are known to afford a complex product slate which is dependent on the specific halogen, the presence of nucleophiles, solvent, and temperature (4). In every case the reaction appears to proceed via initial formation of an intermediate halosulfonium salt. Established transformations from this species are shown in **Scheme 2**.

We have investigated the behavior of various organic sulfur functional groups under JPL Chlorinolysis conditions ( $\text{Cl}_2/\text{CH}_2\text{CCl}_3/\text{H}_2\text{O}$ ) in order to elucidate the major desulfurization pathways. We have also looked at undesirable chlorination side reactions and have briefly examined conditions which minimize the ratio of chlorination to desulfurization.

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Scheme 2

## EXPERIMENTAL

### General

Solvents and commercially available model organic sulfur compounds were used as received after checking their purity by gas chromatography. Di-*n*-butyltrisulfide was prepared by the reaction of *n*-butylthiol and thionyl chloride (4); and  $\alpha$ -chlorosulfoxides were prepared by Tsuchihashi's method from the corresponding sulfoxide and sulfuryl chloride in the presence of pyridine (5). Gas chromatograms were run on a Varian 3700 using a 30 meter OV-101 fused silica capillary column; and yields were determined on the basis of internal standards. Products were identified by comparison of retention times and spectroscopic data with those of authentic samples. Sulfate analysis were performed by Ames Laboratory Analytical Services, ALAS. In order to minimize side reactions caused by excess chlorine, the reactions were carried out using the apparatus shown in Figure 1.

### Chlorinolysis Procedure

The organic sulfur compound (6 mMol), dissolved in 60 mL of methylchloroform, was placed in the reaction flask with 30 mL of distilled water; and the vessel was immersed in a constant temperature bath. The reaction mixture was stirred and a gentle stream of nitrogen was bubbled through the mixture. Liquid chlorine (6mMol) was slowly vaporized into the nitrogen stream, and stirring and nitrogen bubbling were continued for a predetermined reaction time. After separating the layers, the aqueous layer was extracted with methylene chloride, and the combined organic extracts were analyzed by GC. Water was removed from the aqueous layer, and the residue was dissolved in methanol before treating it with diazomethane in ether. The resulting mixture was analyzed for methyl sulfonates by GC.

## RESULTS & DISCUSSION

Our initial experiments were designed to identify discrete intermediates in the desulfurization pathway. Consequently, reactions were carried out at low temperatures using an apparatus (Figure 1) capable of precise control of chlorine addition. The results from these experiments are shown in Table 1.

Table 1. JPL Chlorinolysis of Coal Model Organic Sulfur Compounds.

Starting Material	Cl <sub>2</sub> (Equiv)	Temp (°C)	Time (Hr)	Products (%)	
Ph-S-Ph	1.0	0	0.5	Ph-S-Ph (92)	Ph-S(=O)-Ph (5)
	3.0	25	2.0	O (Tr)	O (93)
Dibenzothiophene	1.0	0	0.5	Sulfoxide (90)	Sulfone (7)
	3.0	25	2.0	(Tr)	(96)
Ph-S-H	2.0	0	0.5	Ph-S-Cl (70)	Ph-SO <sub>3</sub> H (13)
	3.0	25	2.0	O (0)	(93)
Bu-S-Bu	1.0	0	0.5	Bu-S-Bu (41) <sup>a</sup>	Bu-S-CH-Pr (20)
	3.0	25	2.0	O (0) <sup>b</sup>	O Cl (0)
Dimethylthiophene	1.0	0	0.5	No products detected by GC	
	2.0	25	2.0	No products detected by GC	

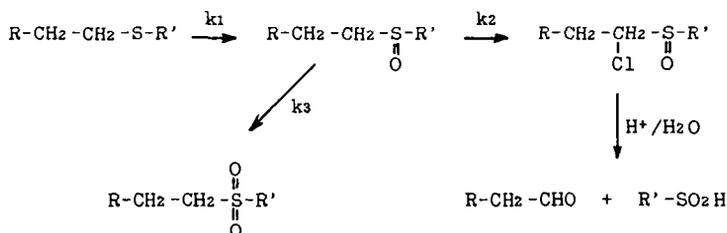
<sup>a</sup> 30% Starting Material remaining.

<sup>b</sup> No Starting Material detected.

As previously reported (5), the reaction of chlorine with phenyl sulfide and dibenzothiophene proceeds via consecutive oxidation at sulfur. Under mild conditions (0°C, 30 min., 1 equiv Cl<sub>2</sub>) the sulfoxides were obtained in very high yields (>90%) compared to compared to reactions carried out under ambient conditions (6). Extensive amounts of sulfones are produced under the latter conditions. Similarly, benzenethiol was converted to the corresponding sulfinyl chloride in substantial yield (70%) under mild conditions and quantitatively to benzenesulfonic acid under slightly more severe conditions.

In the case of *n*-butylsulfide, the reaction mixture was complex and highly dependent on reaction conditions, suggesting the involvement of consecutive multi-step reaction pathways. This reaction was examined more closely by cooling the reaction mixture to 0°C and slowly (2 min.) adding chlorine in 0.5 equivalent aliquots at 5 minute intervals. Samples of the reaction mixture were withdrawn for analysis just prior to the introduction of each aliquot of chlorine, and the results are plotted in Figure 2. Only trace amounts of *n*-butylsulfone were detected in the reaction mixture. In a separate experiment, when an equimolar mixture of *n*-butylsulfide, -sulfoxide, and -sulfone was reacted with excess chlorine, only the sulfone (80%) was recovered.

In fact,  $\alpha$ -chlorination of alkylsulfoxides is a well established reaction (7); and it is also known that under acidic conditions,  $\alpha$ -chlorosulfoxides are readily hydrolyzed, proceeding via carbon-sulfur bond scission to afford the corresponding aldehyde and sulfinic acid (8). In conjunction with this information, our experiments provide clear evidence for the intermediacy of the  $\alpha$ -chlorosulfoxide as shown in reaction Scheme 3.



( $k_1 > k_2 \gg k_3$ )

### Scheme 3

In order to determine whether  $\alpha$ -chlorosulfoxides can be hydrolyzed under JPL Chlorinolysis conditions,  $\alpha$ -chlorosulfoxides were prepared and subjected to standard reaction conditions with excess chlorine at ambient temperature for two hours. The results are shown in Table 2; in both cases, the labile C-S bond was cleaved under these mild conditions. These observations provide additional support for Scheme 3 as a desulfurization pathway.

Table 2. JPL Chlorinolysis of  $\alpha$ -Chlorosulfoxides.

Starting Material	Product (%)
$  \begin{array}{c}  \text{Bu-S-CH-C}_3\text{H}_7 \\  \parallel \quad   \\  \text{O} \quad \text{Cl}  \end{array}  $	Bu-SO <sub>3</sub> H (76)
$  \begin{array}{c}  \text{Ph-S-CH}_2\text{-Cl} \\  \parallel \\  \text{O}  \end{array}  $	Ph-SO <sub>3</sub> H (94)

A final set of experiments were performed to provide additional information about the fate of sulfur functionalities under JPL Chlorinolysis conditions. The sulfate ion concentration was determined in the reaction mixtures of a series of coal model organic sulfur compounds. The results, given in Table 3, clearly reveal significant limitations concerning the type of C-S bonds that can be cleaved. Specifically, C-S bonds undoubtedly survive intact in aryl thiol, diaryl sulfide, and dibenzothiophene systems even though the sulfur itself is oxidized. On the other hand, dialkyl sulfides, thiophenes, and perhaps alkyl thiols appear to be susceptible to significant desulfurization.

It is particularly interesting that polysulfides, including elemental sulfur, are desulfurized almost quantitatively. While the concentration of polysulfides has not been established for a wide range of coals, it appears to be significant in some coals. For example, polysulfides were found to comprise 20% of the sulfur in a pyridine extract of Western Kentucky No. 9 coal (9). The wide range

of sulfur removal reported by JPL (1) may reflect not only differences in rank but also differences in the concentration of labile organic sulfur functional groups such as polysulfides.

**Table 3. Yields of SO<sub>4</sub> from JPL Chlorinolysis Reaction Mixtures.<sup>a</sup>**

Starting Material	SO <sub>4</sub> (%) <sup>b</sup>
Diphenyl Sulfide	0
Dibenzothiophene	0
Thianaphthene	0
Thiophenol	0
2,5-Dimethylthiophene	12
Dibutyl Sulfide	38
Dibutyl Trisulfide	94
Sulfur	98

<sup>a</sup> Excess Cl<sub>2</sub>, 50°C, 1 hour.

<sup>b</sup> Based on sulfur.

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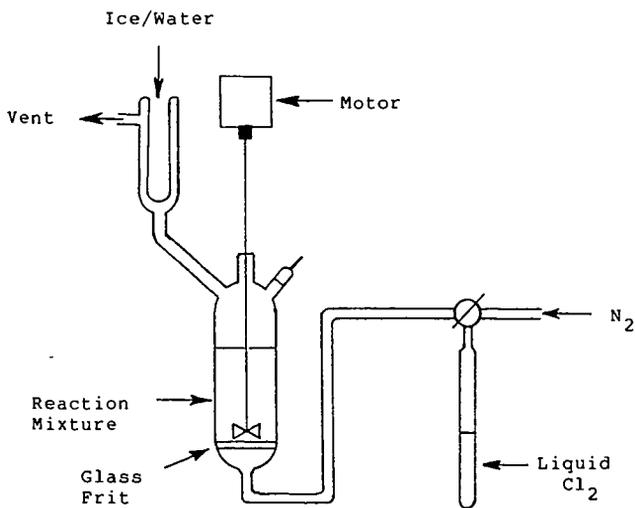


Figure 1. Chlorination Apparatus

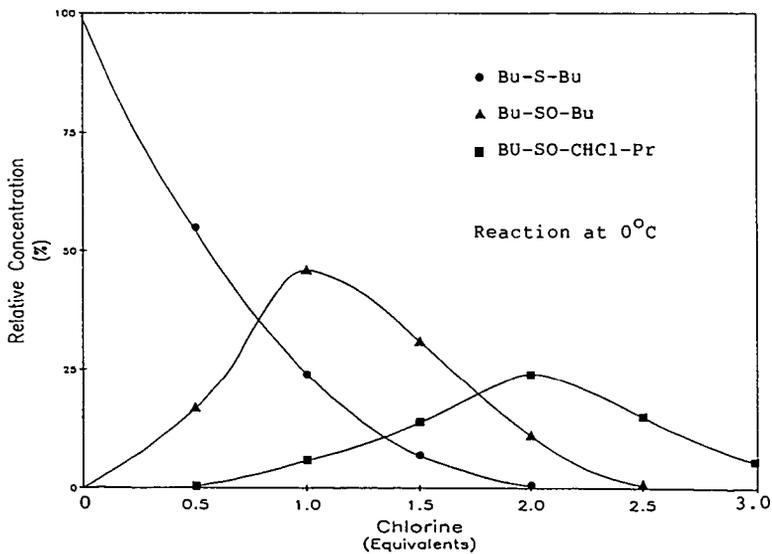


Figure 2. Chlorinolysis of Di-*n*-butyl Sulfide