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ORGANIC DESULFURIZATION OF ILLINOIS NO. 6 COAL

Leon M. Stock and Kuntal Chatterjee

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439RECEIVED
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INTRODUCTION

Advances in the organic desulfurization of coals 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 summarizes our work on the utilization of selective chemical reagents for the desulfurization of Illinois No. 6 bituminous coal.

THE SULFUR COMPOUNDS

The Argonne National Laboratory Premium sample of Illinois No. 6 bituminous coal contains 78% C (maf) with 2.0%S in organic compounds and 2.8%S in pyrite (1). Further, the pristine sample is free of elemental sulfur (2).

The organic sulfur compounds in this coal have been investigated in several laboratories, but the recent X-ray spectroscopic studies are particularly insightful (3,4). The XANES study at Exxon suggests that the coal contains 33% aliphatic, 26% aromatic, and 41% thiophenic organosulfur compounds (3), and the XPS work suggests that 69% of the sulfur atoms are bonded to sp^2 carbon atoms (3). The Kentucky group also used XANES spectroscopy and found that the sulfur in this coal was distributed in about the same way with 63% of the sulfur bonded to sp^2 carbon atoms (4). Both research teams indicate that this pristine coal is free of elemental sulfur and of oxidized organic sulfur compounds, such as, sulfoxides or sulfones (3,4).

Other studies of Illinois No. 6 coals have also concluded that they are relatively rich in aliphatic, sulfidic organic compounds (5,6,7). However, it is pertinent that the mass spectroscopic work on this coal has not provided evidence for aliphatic sulfur compounds (8,9,10).

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DESULFURIZATION

HYDRIDE REDUCTION.-- First, we selectively removed the pyrite by treating the sample with lithium aluminum hydride in tetrahydrofuran at 67°C for 24 hours (11,12,13). The product, which was recovered after acid hydrolysis, had less than 0.1% iron, and there were no pyrite reflections in the powder diffraction X-ray spectrum (13). Furthermore, pyrite is absent in the XANES spectrum of this material (3,4). Thus, all of the pyrite, even though some very small particles are present (14), can be removed by this chemical method. The material balance for sulfur is very good. This observation implies that, within experimental error, little organic sulfur is present in polysulfides because compounds of this class are reduced by lithium aluminum hydride (15).

SINGLE ELECTRON TRANSFER DESULFURIZATION.-- Next, the pyrite-free coal was treated with a single electron transfer reagent (SET) to selectively react with the aromatic sulfur compounds and heterocycles (13). We used potassium naphthalene(-1) in tetrahydrofuran at 67°C for 24 hours in most experiments. This procedure reduced the organic sulfur content by 33 to 50% in a series of experiments under different reactions conditions.

Scope of SET Desulfurization.-- The scope of single electron transfer reactions of organic sulfur compounds are reasonably well defined. To illustrate, dibenzothiophene can be completely converted to biphenyl. An intermediate, 2-phenylbenzenethiol, can be detected in the reaction mixture at short reaction times showing that the reaction occurs sequentially. The reaction proceeds smoothly in the presence of coal, but dihydro- and hexahydrobiphenyl are also obtained. The formation of these products reflects the presence of the hydrogen atom donor groups in coal. Aromatic thiols such as 1- and 2-naphthalenethiol are converted to sulfur-free products under the experimental conditions. In the presence of coal, the hydrogenation of naphthalenethiol takes place and dihydro- and tetrahydronaphthalenethiol are formed. Di-1-naphthyl sulfide undergoes carbon-sulfur bond cleavage to give naphthalene and, at short reaction times, 1-naphthalenethiol.

Di-1-octyl sulfide is converted to 1-octanethiol and an array of products in which the octyl groups are adducted to naphthalene. As expected,

1-nonanethiol and 1-decanethiol are recovered unchanged from the reaction mixture. Thus, aliphatic thiols are unreactive in single electron-transfer reactions.

These observations confirm that sp^2 carbon-sulfur bonds experience reasonably rapid cleavage. Aryl radicals are intermediates in the reactions of diaryl sulfides and heterocyclic compounds. The aromatic thiolates that are produced in these reactions experience further desulfurization, but the reactions are slower than the first carbon-sulfur bond cleavage reactions of the heterocyclic compounds and diaryl sulfides. Aryl alkyl sulfides experience facile carbon-sulfur bond cleavage to form alkanethiols. Dialkyl sulfides decompose to form thiols, but the sp^3 carbon-sulfur bonds in their anions firmly resist cleavage and the alkanethiolates survive the reaction.

X-ray Analysis.-- The correctness of this interpretation is supported by the XANES spectrum of original coal, the pyrite-free coal and the product (16). As shown in Figure 1, the single electron transfer agent reduces the signal intensity at 2470.5ev. This signal is, of course, attributable to sulfur atoms bonded to sp^2 carbon atoms in aryl sulfides and heterocyclic sulfur compounds (3,4).

BASE DESULFURIZATION.-- The next experiments centered on the use of Lochmann's base, a very reactive mixture of n-butyllithium and potassium t-butoxide, BASE, in heptane at 98°C for six hours (17). The application of this reaction to Illinois No. 6 coal resulted in 25 to 40% desulfurization.

Scope of BASE Desulfurization.-- The chemistry of base-catalyzed desulfurization has been less completely investigated. Dibenzothiophene and benzyl phenyl sulfide are recovered unchanged from the reaction after 6 hours of reflux at 98°C, but dodecyl sulfide goes cleavage to form dodecene and dodecanethiol. Saturated thiols such 1-decane- and 1-nonanethiol do not react, but naphthalenethiol undergoes quantitative desulfurization to yield naphthalene as the principal product. Activated sulfides such as dibenzyl sulfide undergo quantitative desulfurization to yield stilbenes and soluble inorganic sulfides via thio-Wittig reactions (18). These results suggest that BASE reacts preferentially with aromatic thiols and other sulfidic sulfur compounds such as aliphatic and benzylic sulfides. Generally, thiolates are

formed in these cleavage reactions, they do not undergo desulfurization. However, if the reactions yield water-soluble or volatile thiols, then desulfurization may appear to have occurred.

X-ray Analysis.-- This interpretation is also supported by the XANES results (16). The spectroscopic information displayed in Figure 2 shows that the signal at 2469.6ev that is assigned to sulfur bonded to sp^3 carbon is selectively removed by treatment with Lochmann's base.

SINGLE ELECTRON TRANSFER AND BASE.-- A sample of the pyrite-free Illinois No. 6 coal was treated with SET and BASE and, in a separate experiment, with BASE and SET (16,19). The results are shown in the equations.

The reagents act essentially independently to remove different types of organosulfur compounds in reducing the organic sulfur content of this sample of the Illinois coal to 0.7 to 0.8%, respectively.

ACID HYDROLYSIS. -- Several lines of evidence, for example, the facility with which hydrogen sulfide evolved during thermal reactions (20) and the appearance of signals that could be assigned to inorganic sulfides in the XANES spectrum suggested that the desulfurization procedure might have been even more successful than indicated by analytical data shown for sulfur in the chart. Accordingly, the residue from the reaction was treated with hydrochloric acid. The sulfur content decreased to below 0.25%.

This observation suggests that inorganic sulfides and acid labile compounds such as allylic sulfides are retained in the coal sample.

CONCLUSIONS

First, lithium aluminum hydride cleanly removes pyrite from the Illinois No. 6 coal to leave the original organosulfur compounds.

Second, the SET reagent selectively removes sulfur from heterocyclic sulfur compounds and aromatic sulfides. Lochmann's base does not remove the sulfur from the heterocycles, but does react with sulfidic sulfur compounds such as alkyl aromatic sulfides that are susceptible to base catalyzed elimination reactions.

Third, the organic sulfur compounds that remain after the dual SET and BASE treatment are dominantly aliphatic substances including alkyl and allylic thiols.

Fourth, the sulfur compounds that remain are susceptible to thermal decomposition and acid hydrolysis.

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Figure 1.-- The third derivative of the XANES spectrum of the pyrite-free coal (top) and the product of the SET reaction (bottom). The feature at 2470.5eV, which results from thiophenic and aromatic sulfur, is greatly reduced. Reproduced with the permission of the American Chemical Society.

Figure 2.--. The third derivative of the XANES spectrum of the pyrite-free coal (top) and the product of the BASE reaction (bottom). The feature at 2469.6eV which results from sulfidic sulfur is greatly reduced. Reproduced with the permission of the American Chemical Society.

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