A Novel Approach to Catalytic Desulfurization of Coal

DOE Grant No.: DE-FG22-95PC95208 -01

Semi-Annual Report

Due: May 31, 1996

Prof. John G. Verkade, PI

Gilman Hall

Iowa State University

Abstract. Efforts toward quantitation of the sulfur removed from coal in the reaction below by column chromatography of the products followed by weighing

$$\text{Coal(S)} + \text{excess } PBu_3 \xrightarrow{\text{heat}} \text{Coal} + SPBu_3/PBu_3$$

the $SPBu_3$ and vacuum distillation of the $SPBu_3/PBu_3$ mixture followed by gas chromatographic analysis are described. The first method failed, but the latter is more successful. It has been discovered that para-chloro phenol catalyzes the removal of sulfur from dibenzothiophene by PBu_3 under mild conditions.

Project objectives.

A. Optimize the coal desulfurization reaction with respect to time, temperature,

$$\text{Coal(S)} + \text{excess } PR_3 \longrightarrow \text{Coal} + S{=}PR_3/PBu_3 \qquad (1)$$

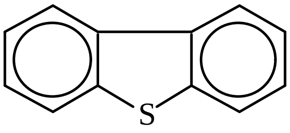
coal type and the R groups (including R = H), and also on extraction, impregnation and sonication conditions.

B. Optimize the conditions for the HDS reaction

$$H_2 + SPR_3 \rightleftharpoons H_2S + PR_3 \qquad (2)$$

(which allows the PR_3 to function as an HDS catalyst for coal) with respect to R group, temperature, pressure, H_2 gas flow rate and inert solvent presence.

C. Determine the product(s) and the pathway of the novel redox reaction that



DBT

$$+ PR_3 \xrightarrow[\text{(no solvent)}]{\text{reflux}} S{=}PR_3 + ? \qquad (3)$$

appears to *quantitatively* remove sulfur from dibenzothiophene (DBT) when R = Bu when $FeCl_3$ is used as a catalyst.

D. Impregnate sulfur-laden coals with Fe^{3+} to ascertain if the PR_3 desulfurization rate increases.

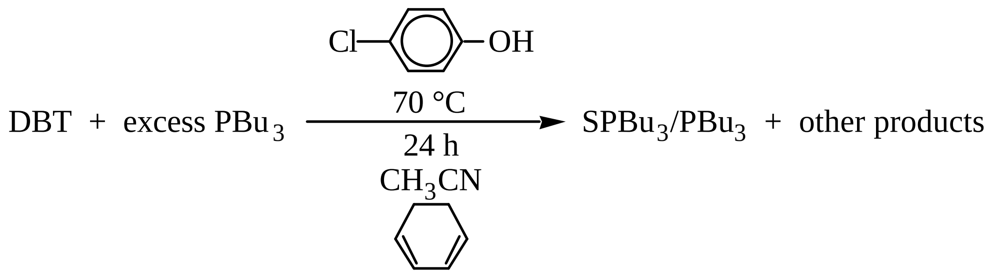
E. Determine the nature of the presently unextractable phosphorus compounds formed in solid coals by PR_3.

F. Explore the efficacy of PR_3/Fe^{3+} in removing sulfur from petroleum feedstocks, heavy ends (whether solid or liquid), coal tar and discarded tire rubber.

G. Explore the possibility of using water-soluble PR_3 compounds and Fe^{3+} to remove sulfur from petroleum feedstocks and heavy ends in order to remove the SPR_3 (and Fe^{3+} catalyst) by water extraction (for subsequent HDS of the SPR_3).

H. Explore the possibility of using solid-supported PR_3 compounds (plus Fe^{3+} catalyst) to remove sulfur from petroleum feedstocks and heavy ends in order to keep the oil and the SPR_3 (formed in the reaction) in easily separable phases.

Summary of Progress. An analytical method has been developed for speciating and quantitating the $SPBu_3$ and PBu_3 obtained in reaction 1 in Objective A. The analytical problem is a non-trivial one because part of the coal dissolves in the $SPBu_3/PBu_3$ reagent mixture and part of this mixture is embedded in the coal residue. It has been discovered that the removal of 62% of the sulfur from dibenzothiophene (DBT) in reaction 3 in Objective C is catalyzed under very mild conditions by para-chloro phenol (reaction 4). This result aids in the



(4)

understanding of the pathway whereby PBu_3 removes organically bound sulfur from coal.

Results. A nagging and persistent problem with reaction 1 (which was discovered during the course of our research under the previous UCR grant) has been the determination of how much sulfur is actually removed from the coal. ^{31}P NMR analysis by integration of the $SPBu_3$ and PBu_3 peaks indicated that up to 90% of the sulfur was removed in some reactions. Elemental analysis of the coal residues gave variable and often conflicting results owing to the fact that some of PBu_3 and $SPBu_3$ remains in the coal matrix, and also, a small amount of the coal is dissolved in the $SPBu_3/PBu_3$ product mixture. Further complicating the ^{31}P NMR integrations are the paramagnetic mineral materials extracted from the coal that broaden the peaks and interfere with quantitation of the peak areas.

At first, efforts were made to quantitatively separate the product $SPBu_3$ from the reaction by the obvious method of column chromatography. This failed, however, because $SPBu_3$ and PBu_3 do not elute separately very well owing to the large excess of PBu_3 used in the reaction. Attempts were then made to pass the mixture through a bed of $KHSO_4$ to achieve reaction 5 wherein the $HPBu_3^+$ was

$$SPBu_3 + PBu_3 + KHSO_4 \longrightarrow SPBu_3 + \underline{HPBu_3^{+}K^{+}SO_4^{2-}} \qquad (5)$$

expected to remain on the column. While the desired separation does occur to a large extent, the eluate is not pure $SPBu_3$, and further separation and purification must be carried out on a silica gel column. This procedure is not very satisfactory at best, since there are too many opportunities for loss and incomplete separation.

A problem with this approach, however, is that we cannot inject the products of reaction 1 directly onto the column; not even a carefully centrifuged reaction mixture. Metal compounds (primarily iron species) are dissolved in the product mixture and such materials would damage the column. We therefore treated the centrifuged reaction mixture with aqueous base to precipitate the metal salts as their hydroxides and separated the aqueous and organic phases. The organic phase was to be subjected to GC and the centrifuged aqueous phase to elemental analysis for sulfur and phosphorus. We felt that it was likely that there would be negligible sulfur and phosphorus in the aqueous phase since $SPBu_3$ and PBu_3 are not very soluble in water. If these methods corroborated our ^{31}P NMR results, we would use this approach wherever appropriate, since it is more convenient. This methodology turns out to be unworkable for a variety of reasons, including retention of metal species in the organic phase as complexes ligated by PBu_3.

We then developed another technique which now appears to work quite well. After the coal sample is refluxed in PBu_3, we vacuum distilled the $SPBu_3$, PBu_3 and other volatile organics into a separate vessel, leaving the non-volatile metal salts and coal residue behind. In carrying out this procedure with an Illinois No. 6 coal-derived pyrite sample we were able to remove 52% of its sulfur content as indicated by our gas chromatographic analysis. This is *very* encouraging since the calculated amount removable by our method is 50% according to reaction 6. In other words, PBu_3 is not expected to remove sulfur

$$\underset{\text{iron pyrite}}{FeS_2} + PBu_3 \longrightarrow FeS + SPBu_3 \qquad (6)$$

from the FeS product of this reaction and this was demonstrated in an identical reaction with FeS.

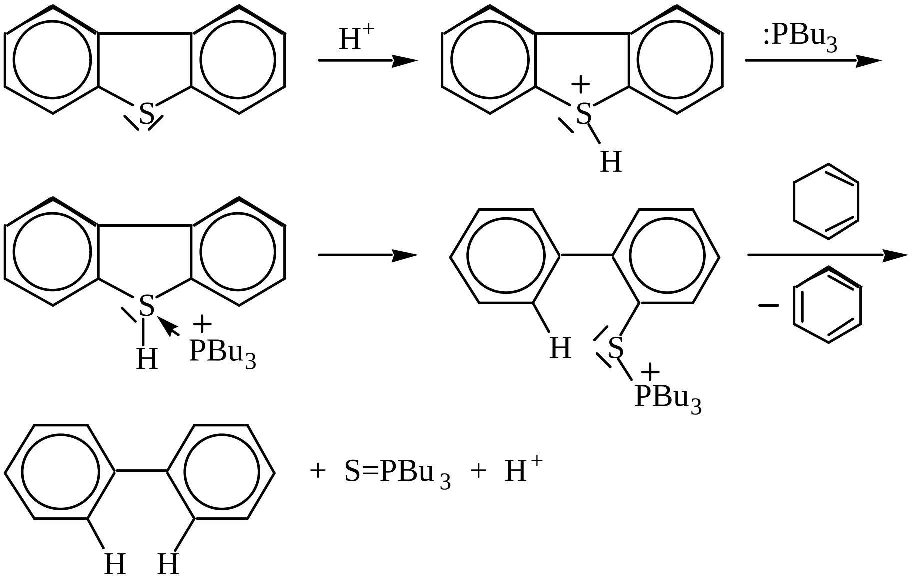
The above apparent solution to our analytical problem has an additional advantage in that virtually all the coal (except its small amount of unextracted sulfur content) will be left after the vacuum distillation. Thus elemental analyses for residual sulfur content will be more informative in telling us how much sulfur that remains is as original sulfur and how much has become incorporated as $SPBu_3$.

Using ^{31}P NMR peak integration methods (which we do not yet regard as definitive) we analyzed the sulfur removal from DBT. Thus reaction 7 results

$$\text{DBT} + \text{excess } PBu_3 \xrightarrow[\substack{28\text{ h} \\ CH_3CN}]{70\ ^\circ C} SPBu_3/PBu_3 + \text{other products} \qquad (7)$$

in less than 10% of the sulfur being removed when phenol is used as a catalyst, but with 1,4-cyclohexadiene present as a hydrogen donor, 39% sulfur removal is realized. Interestingly, when para-chloro phenol is used in place of phenol (reaction 4) 62% sulfur appears to be removed after 24 hours. We find this result remarkable since DBT has never given up so much sulfur so easily under any conditions found in the literature. We did these reactions with phenol and para-chloro phenol present because we had evidence from research carried out under the previous grant that phenolics in coal aided sulfur removal by PBu_3. These results suggest that nucleophilic attack of PBu_3 on sulfur in DBT is facilitated by sulfur protonation as shown in Scheme 1. Here the proton acts as a catalyst since it is regenerated. Why para-chloro phenol is more effective in reaction 7 than phenol itself is not clear. Thus an acid stronger than para-chloro phenol (e.g. HO_2CCF_3) does not work in this reaction.

Scheme 1



Expectation for achieving project objectives. Although we can now distill pure $SPBu_3/PBu_3$ from the mixture produced by reaction 1 for quantitation of the sulfur removed, we must address the problem of properly analyzing the coal residue for sulfur. Here the problem is that the residue still contains a small amount of a mixture of $SPBu_3/PBu_3$ trapped in the matrix, plus some unremoved sulfur left in the coal. An elemental analysis will be helpful here since it will represent the sum of the $SPBu_3$ and PBu_3 trapped in the residue. Perhaps the problem of $PSBu_3$/PBu_3 entrapment can be avoided by preswelling the coal with pyridine and then vacuum distilling out a mixture of pyridine/$SPBu_3$/PBu_3, leaving the coal residue unadulterated.

The 62% desulfurization of DBT was measured by ^{31}P NMR integration, a method of dubious value unless it can be verified by another analytical technique. Since DBT is too nonvolatile to go through a GC column for quantitation of the mixture produced by reaction 4, the vacuum distillate will be passed through the GC for quantitation of sulfur removed as $SPBu_3$. The residue of the distillation and the distillate will be weighed for mass balance purposes.

Experimental details.

Coal/PBu_3 reactions. In a typical reaction, about one g of Ill. No. 6 (or coal-derived pyrite, or FeS) was mixed with *ca.* 5 mL of PBu_3. After heating at 250 °C for 48 h under an atmosphere of N_2, the mixture was allowed to cool to room temperature. The reaction vessel was then cooled to liquid N_2 temperature and evacuated to 0.03 mm. The closed system was then subjected to vacuum distillation at 130-140 °C until no more liquid distilled. The distillate was then analyzed by gas chromatography using a Hewlett Packard 6890 GC system after dissolving *ca.* 40 mg of distillate in about 10 mL of $CHCl_3$ using a volumetric flask. The GC oven temperature was 200 °C and the carrier gas was helium.

DBT/PBu_3 reactions. In a typical run about 0.1 g of DBT was dissolved in *ca.* 5 mL of CH_3CN. To this was added 0.1 equivalent of phenol (or para-chloro phenol or

HO_2CCF_3) 2 equivalents of cyclohexadiene and 2 equivalents of PBu_3. The reaction mixture was then heated under nitrogen for 24-28 h at 70 °C. The solvent was removed in vacuo and the residue was dissolved in C_6D_6 or CD_3CN for ^{31}P NMR spectroscopic analysis. The percent sulfur removed was estimated by measuring the ratio of ^{31}P NMR peaks of $SPBu_3$ and PBu_3.

Patent/Publication Activities. The patents below have been issued:

Verkade, J. G.; Mohan, T.; Angelici, R. J. "Catalytic Hydrodesulfurization of Coal", US Patent 5,437,696, August 1, 1995.

Verkade, J. G.; Mohan, T. "Mild Desulfurization of Sulfur-Bearing Materials", US Patent 5,509,945, April 23, 1996.

The publications below have appeared:

Erdmann, K.; Mohan, T. and Verkade, J. G. "^{31}P Solid State NMR Study of Coals Treated with Phosphorus Reagents", *Energy and Fuels* **1995**, *9*, 354.

Erdmann, K.; Mohan, T.; Verkade, J. G. "HPLC and ^{31}P NMR Analysis of Phenols in Coal Liquefaction Oils", *Energy and Fuels* **1996**, *10*, 378.

Commercial Activity. Cytec Corporation of Niagara Falls, Ontario in Canada called me to inquire about the issued patents referred to above. Cytec manufactures PBu_3 (and other phosphines) in large quantities. They are interested in the potential market for their products and in the research we are doing to bring our process closer to commercialization. They have kindly offered to supply us with free research samples of PBu_3 and other PR_3 compounds we could try.