A Novel Approach to Catalytic Desulfurization of Coal

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Technical Report

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Toward the Solution of an Analytical Problem

A nagging and persistent problem with reaction 1 (which we 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 $\text{SPBu}_3/\text{PBu}_3$ product mixture. Further complicating the ^{31}P NMR experiments are paramagnetic mineral materials extracted from the coal.

We sought first 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. We then tried passing the mixture through a bed of KHSO_4 to achieve reaction 2 wherein the HPBu_3^+ was expected to remain

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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.

At the time we were doing these experiments, we were setting up a new gas chromatograph for another project. Thus we sought to quantitatively separate a $\text{SPBu}_3/\text{PBU}_3$ mixture using the column we had. This was unsuccessful, but in consultation with the manufacturers we tried a column which they suggested and this appears to work very well with excellent peak resolution.

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 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 2. In other words, PBU_3 is not expected to remove sulfur

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 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 as original sulfur and how much has become incorporated as SPBU_3 . The latter presumably can be removed by washing with an organic solvent.

With the solution to our analytical problem in hand, we plan during the present quarter to investigate a range of coal samples and also DBT by our extraction process.

Sulfur Removal from Dibenzothiophene (DBT)

Using ^{31}P NMR peak integration methods (which we do not yet regard as definitive) we analyzed the sulfur removal from DBT under several conditions. Reaction 3 removes less than 10% of the sulfur but with 1,4-cyclohexadiene

present as a hydrogen donor, 39% sulfur removal is realized. Interestingly, when *p*-chlorophenol is used in place of phenol, 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 *p*-chlorophenol because we had evidence from research carried out under the previous grant that phenolics in coal aided sulfur removal by P Bu_3 .

Thus far, other acidic catalysts/promoters (e.g., FeCl_3) do not work nearly as well in reaction 3 (even with hydrogen donors) as does *p*-chlorophenol.

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

Cytex Corporation of Niagara Falls, Ontario in Canada called me to inquire about the issued patent referred to above. Cytex manufactures PBu_3 (and other phosphines) in large quantities and 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.