

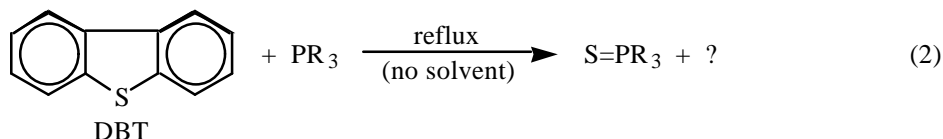
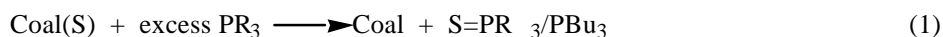
# A NOVEL APPROACH TO CATALYTIC DESULFURIZATION OF COAL

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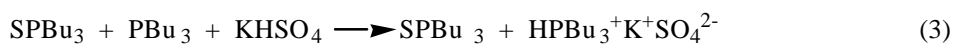
## Abstract

A nagging and persistent problem with reactions 1 and 2 (which were discovered during the course of our research under the



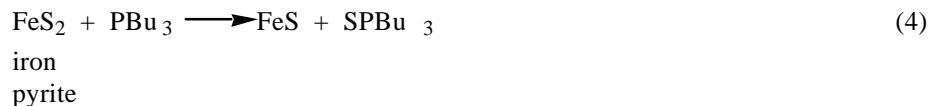
previous UCR grant) has been the determination of how much sulfur is actually removed from coal and dibenzothiophene. <sup>31</sup>P NMR analysis by integration of the SPBu<sub>3</sub> and PBu<sub>3</sub> peaks indicated that up to 90% of the sulfur was removed in some reactions. Elemental analysis of the coal residues gave variable and often conflicting results owing to the fact that some of PBu<sub>3</sub> and SPBu<sub>3</sub> remains in the coal matrix, and also, a small amount of the coal is dissolved in the SPBu<sub>3</sub>/PBu<sub>3</sub> product mixture. Further complicating the <sup>31</sup>P NMR integrations are the paramagnetic mineral materials extracted from the coal that broaden the peaks and interfere with quantitation of the peak areas.

Efforts to quantitatively separate the product SPBu<sub>3</sub> from the reaction by column chromatography failed because SPBu<sub>3</sub> and PBu<sub>3</sub> do not elute separately very well owing to the large excess of PBu<sub>3</sub> used in the reaction. Passing the mixture through a bed of KHSO<sub>4</sub> to achieve reaction 3 (wherein the HPBu<sub>3</sub><sup>+</sup> was expected to remain on the column) did not result in satisfactory

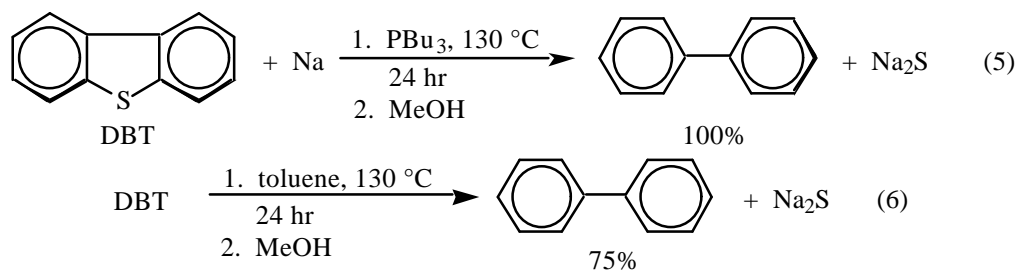


separation.

A different technique was developed which worked quite well. After the coal sample is refluxed in PBu<sub>3</sub>, the SPBu<sub>3</sub>, PBu<sub>3</sub> and other volatile organics are vacuum distilled into a separate vessel, leaving the non-volatile metal salts and other coal residues behind. In carrying out this procedure with an Illinois No. 6 coal-derived pyrite sample 52% of its sulfur was removed as indicated by gas chromatographic analysis. This was encouragingly close to the calculated amount removable by our method (50%) according to reaction 4.



The removal of sulfur from organic sulfur-containing compounds, dibenzothiophene (DBT) in most cases, has been investigated by reacting DBT with an active metal (Na or Li) in a solvent such as toluene, tetradecane, liquid ammonia or PBu<sub>3</sub> at atmospheric pressure followed by the addition of methanol to react excess metal. GC analysis of the organic volatiles was then carried out. Examples of some of these reactions are shown below. Using lithium and a reaction



temperature of 250° (because of the higher melting point of lithium) DBT underwent complete conversion to biphenyl in 24 hours using either tetradecane or  $\text{P Bu}_3$  as a solvent. The possible role of  $\text{P Bu}_3$  in reaction 5 will be discussed. Using liquid ammonia as a solvent, DBT loses 100% of its sulfur to the dissolved sodium in only 6 hours at the astonishingly low temperature of -38 °C. The results of recent experiments on the desulfurization of Illinois No. 6 in the presence of  $\text{P Bu}_3$  using our newly developed GC analytical technique will also be presented.