

# Sulfur Removal from Coal Materials

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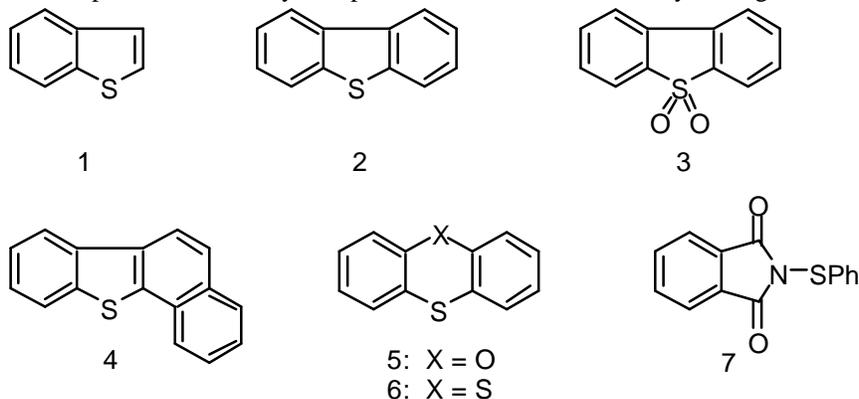
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**Abstract:** The objective of this work was to explore the use of phosphorus-containing reagents under relatively mild conditions to probe the structure of coal and to remove sulfur and oxygen from coal by taking advantage of the thermodynamically favored P=S and P=O bonds. None of the existing methods of desulfurization and deoxygenation of coal is completely satisfactory, especially for organically bound sulfur and oxygen.

We initiated this study a few years ago by derivatizing solid residues of different coals with a variety of phosphorus reagents, followed by washing with organic solvents and examining them with  $^{31}\text{P}$  MAS NMR spectroscopy. In an examination of coal desulfurization and deoxygenation, special attention was paid to Illinois No. 6 coal treated with *n*-Bu<sub>3</sub>P. In addition to residual *n*-Bu<sub>3</sub>P and *n*-Bu<sub>3</sub>PS remaining in the solid coal, evidence for two additional species, namely, *n*-Bu<sub>3</sub>PH<sup>+</sup> and [(coal)-C-O]<sub>3</sub>PO was adduced. Their chemical shifts are  $34 \pm 2$  and  $2.5 \pm 0.5$  ppm, respectively. The latter resonance was observed regardless of the coal treated and the phosphorus reagent employed.

In a recent patent from our laboratory, data on the desulfurization of Illinois No. 6 coal with tributylphosphine under mild conditions was presented. Here we report details of this work, the desulfurization of other types of coals and coal-related materials (i.e. coal-derived pyrite, FeS<sub>2</sub> and FeS) by the same method, and also the desulfurization of Illinois No. 6 coal utilizing alkali metals (Na and Li) in liquid ammonia or in hydrocarbon solvents. In the reaction of this coal with Bu<sub>3</sub>P at 250 °C, 93.6% of sulfur removal was realized. The presence of alkali metals in the Bu<sub>3</sub>P improved the desulfurization. Alkali metal/*liq.* NH<sub>3</sub> systems gave rise to moderate desulfurization efficiently albeit with *ca.* 32% weight loss. Our procedure with Bu<sub>3</sub>P also revealed high efficiencies for desulfurizing low-sulfur (0.62 - 2.32%) coals (sulfur removal: 52.2% to 93.4%) and coal-related materials, i.e., coal-derived pyrite, FeS<sub>2</sub> and FeS.

We then set out to determine if metallic sodium is capable of removing sulfur from organosulfur compounds particularly thiophenes under mild conditions. Indeed, dibenzothiophene is desulfurized under relatively mild conditions by metallic sodium in tetradecane at 150 °C in 24 hours to give biphenyl in 99% yield after methanol/H<sub>2</sub>O work up according to GC analysis. Moreover, benzothiophene and other cyclic species such as **1-7** as well as cyclic organosulfur compounds are



desulfurized quantitatively by lithium or sodium upon heating in a hydrocarbon solvent. This method is quite general and efficient for a variety of dialkyl and alkyl-aryl organosulfur compounds. Except for diphenyl sulfide, reactions of organosulfur compounds containing one or more phenylthio groups with sodium generally underwent quantitative conversions, giving thiophenol as the major product at 100 °C or 150 °C. Although diphenyl sulfide showed the lowest reactivity in this reaction, quantitative conversion to biphenyl was observed at 254 °C. At this temperature conversions of the remaining substrates to hydrocarbon products were very good, except for 1,3-bis(phenylthio)propane which gave thiophenol as the major product. Interestingly in this respect, PhSCH<sub>2</sub>SPh is more readily converted to PhCH<sub>2</sub>Ph, Ph-Ph

and (presumably) CH<sub>4</sub> under similar conditions while (PhS)<sub>3</sub>CH requires 15 h at 254 °C for quantitative reduction to Ph-Ph and (presumably) CH<sub>4</sub>.

Although alkyl sulfides R<sub>2</sub>S did not desulfurize at 110 °C or 164 °C, at 254 °C, however, the corresponding alkanes were formed in high yields along with only small amounts of the corresponding alkylmercaptans. The reactions of cyclohexene sulfide and propylene sulfide in refluxing toluene gave essentially quantitative yields of cyclohexene and propylene, respectively. Benzyl methyl sulfide and disulfide were efficiently desulfurized to toluene, ethylbenzene, and/or bibenzyl. Raising the reaction temperature improved the desulfurization of benzyl phenyl sulfide because at lower temperature Bz-S bond cleavage by sodium was the predominant process.

Greater than 95% sulfur removal was observed when dialkyl mono or polysulfides were treated with Na in liquid ammonia. Polycyclic aromatic sulfur heterocycles were only moderately desulfurized under these conditions while phenylthio derivatives gave thiophenol as the major product and dithiophenols as the minor products.

#### Publications:

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