

A NOVEL APPROACH TO CATALYTIC DESULFURIZATION OF COAL

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A Novel Approach to Catalytic Desulfurization of Coal

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Abstract. A gas chromatographic method has been developed for the quantitation of sulfur removed from coal as tributyl phosphine sulfide (SPBu₃). This method also works very well for speciating and quantitating the products of sulfur removal from organosulfur removal from organosulfur compounds such as dibenzothiophene. Remarkably mild conditions have been discovered for quantitative sulfur removal from dibenzothiophene and other organosulfur systems using relatively cheap elemental sodium.

Project objectives.

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



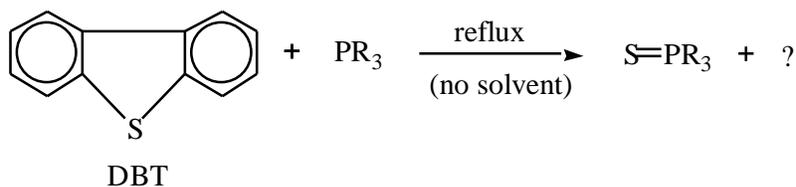
and the R groups (including R = H), and also on extraction, impregnation and sonication conditions.

- B. Optimize the conditions for the HDS reaction



(which allows the PR₃ to function as an HDS catalyst for coal) with respect to R group, temperature pressure, H₂ gas flow rate and inert solvent presence.

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



quantitatively remove sulfur from dibenzothiophene (DBT) when R = Bu and when FeCl₃ is used as a catalyst.

- D. Impregnate sulfur-laden coals with Fe³⁺ to ascertain if the PR₃ desulfurization rate increases.
- E. Determine the nature of the presently unextractable phosphorus compounds formed in solid coals by PR₃.
- F. Explore the efficacy of PR₃/Fe³⁺ 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 PR₃ compounds and Fe³⁺ to remove sulfur from petroleum feedstocks and heavy ends in order to remove the SPR₃ (and Fe³⁺ catalyst) by water extraction (for subsequent HDS of the SPR₃).
- H. Explore the possibility of using solid-supported PR₃ compounds (plus Fe³⁺ catalyst) to remove sulfur from petroleum feedstocks and heavy ends in order to keep the oil and the SPR₃ (formed in the reaction) in easily separable phases.

Background

For environmental reasons, many efforts aimed at efficient desulfurization of coals have been made over the past two decades. Sulfur present in coals can be removed by physical, chemical, or microbial methods.¹ The microbial process is slow but quite effective in removing all types of organic and inorganic sulfur simultaneously using a single type of bacterium. The simpler physical methods are currently more economical compared with processes that convert coal into liquid or gaseous fuels. Chemical processes developed in the past for the removal of both organically and inorganically bound sulfur from coal include the use of high temperature alkaline solutions,¹ molten caustic at ca. 380°C,^{1d} alkoxides in refluxing alcohol,^{1e} KOH in supercritical alcohols,^{1f} oxidation with hydrogen peroxide² and peroxyacetic acid,³ reductions involving hydrogenation,^{1b} carboxylation,⁴ zerovalent metal treatment,⁵ reactions with single-electron transfer agents,^{1c,6} and strong base.⁷ Although these methods remove sulfur from coals to varying extents, other routes that improve coal desulfurization continue to be sought. Over the past decade, many organometallic systems

have been investigated for their HDS properties and a substantial number of successful examples of C-S bond cleavage in benzothiophenes and dibenzothiophenes by such systems have been reported.⁸ In a recent patent from laboratory,⁹ data on the desulfurization of Illinois No. 6 coal with tributylphosphine under mild conditions were presented.

Here we report results bearing on Objective A and more specifically our further efforts to resolve the mass balance problem in reaction 1.

Results

We first describe the mass balance problem that continues to plague us. Arriving at a mass balance in these reactions has thus far not been successful. Reaction 1 as written is greatly oversimplified inasmuch as Bu_3P is incorporated into the residue as its oxide, sulfide and protonated cation. Moreover, coal components are undoubtedly solubilized judging from the very dark coloration of the extract. Separation of the extract components has also not been achieved thus far. We considered the use of equation 2 wherein M = mass, SM = starting material, Res = residue, and Rem = removal.

$$\%S_{Rem} = \left(\frac{M_{SM} \times \%S_{SM} - M_{Res} \times \%S_{Res}}{M_{SM} \times \%S_{SM}} \right) \times 100\% \quad (2)$$

Because M_{Res} does not simply represent the loss of coal components by reaction and/or solubilization, and because M_{Res} can sometimes exceed M_{SM} (see entry 7, Table 1), equation 2 is not warranted. We have thus opted at this time for equation 3, which disregards

$$\%S \text{ removal} = \left(\frac{\%S_{SM} - \%S_{RES}}{\%S_{SM}} \right) \times 100\% \quad (3)$$

the mass changes that have occurred. It may be noted that in most equation 3 by 1-23%, thus

To attack this problem, we have designed an apparatus that will allow us to perform accurate mass balances, as well as expose the coal sample to fresh Bu_3P throughout the extraction run. The design we have developed is similar to that of a Soxhlet apparatus, but its appearance and function is quite different. The problem with the Soxhlet apparatus is that there is considerable hang-up of an extractant by adsorption on all the surfaces above the liquid, including the extraction chamber and the inside of the reflux condenser. The Soxhlet cup also retains considerable Bu_3P by absorption into the fibrous cup material. It is

unfeasible to weigh the adsorbed and absorbed Bu_3P in the apparatus because its mass is small relative to that of the apparatus and the cup containing the extracted coal, respectively.

Our apparatus design in Figure 1 (which greatly minimizes glass surface) consists of a 50 mL flask fitted with a small water-cooled cold finger at the end of which is suspended an “envelope” created from filter paper. The envelope contains the weighed coal sample to be extracted. Several grams of Bu_3P is accurately weighed into the flask via a syringe and reflux is carried out at 250°C . The cold finger condenses the Bu_3P and allows the hot condensate to wash through the filter paper. The conditions are controlled such that the condensate is very nearly 250°C . At the end of the run, the flask is allowed to cool to room temperature. The hang-up of Bu_3P on the relatively small amount of glass surface is calculated to be small compared with the original mass of liquid whose total volume we calculate from its density. (Accumulation of a drop of Bu_3P at the end of the cold finger is prevented by connection of the cold finger end to the filter paper holding the sample). After a volumetric aliquot of extract is withdrawn and weighed in a syringe, we can calculate the new density of the extract and also calculate quite precisely how much mass the coal has lost by extraction, realizing that a corrected mass must be calculated for the amount of Bu_3P trapped in the coal residues, and an extract density correction must be made for the Bu_3P in the filter paper. The former can be done by phosphorus elemental analysis of the extracted coal sample, and the latter correction can be accomplished as follows. The filter paper containing the extracted sample is transferred to a clean apparatus of the same design and washed with refluxing ether. The filter paper envelope is then dried and weighed to gauge the coal mass loss which is then compared with that calculated from the mass gain of the extract. Sulfur elemental analyses on both the extract and the extracted residue can then be compared and used as checks on the accuracy of the sulfur elemental analysis. All of the manipulations must be carried out under nitrogen or argon to prevent oxidation of Bu_3P .

A potential complication of the calculated sulfur removal might be the sulfur that is trapped in the residue as $\text{Bu}_3\text{P}=\text{S}$ (which is detectable by CP MAS ^{31}P NMR spectroscopy). We believe this will now be a negligible problem because of constant exposure of the sample to pure hot condensed Bu_3P that will wash out the $\text{Bu}_3\text{P}=\text{S}$ much more completely. Thus in our sealed tube experiments described in the previous report, a mixture of extract (containing dissolved $\text{Bu}_3\text{P}=\text{S}$) and coal residue is present throughout the run which allows an equilibrium to be established between $\text{Bu}_3\text{P}=\text{S}$ dissolved in the extract and trapped in the coal.

By solving the mass balance problem, we will be more confident that there is fascinating, but puzzling, chemistry that goes on in the coal matrix that we are unable to duplicate outside of the matrix with thiophene compounds. That is, pure thiophenes in refluxing Bu_3P do not lose significant amounts of sulfur regardless of the presence of a variety of metal ions and/or HPBu_3^+ and/or a catalytic amount of coal.

Dr. Guangtao Zhang, a postdoctoral student in my group carried out a series of experiments with the apparatus shown in Figure 1. He found, however, that unfortunately the degree of sulfur extraction was variable and poor. The problem is that the temperature of the tributylphosphine passing through the coal inside the filter paper is actually considerably below 250°C owing to the fact that the reflux finger cools the refluxing tributylphosphine too greatly, even when no coolant is allowed to flow through the finger. Thus the envelope and its contents is unable to reach 250°C , the temperature at which the extraction efficiency is highest according to the results described in our previous reports.

It should be pointed out that it is also very difficult to control the level of the reflux line in the apparatus while still maintaining a liquid flow through the envelope at a sufficiently high temperature for extraction. There appears to be too much conduction of heat away from the filter paper/coal and too little flow of tributylphosphine through the coal.

Thus most of the liquid extractant contact seems to flow over the outside of the envelope. Most of the tributylphosphine seems to run over the outside of the envelope. We believe we can solve this problem by using tea bag cloth, which is more porous and will hopefully still retain the powdered coal if the mesh is not too fine. These experiments will be carried out by Dr. Xiadong Liu in the remaining period of this grant.

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