A Novel Approach to Catalytic Desulfurization of Coal

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Abstract

The desulfurization of Illinois No. 6 coal (4.83% S) was investigated with Bu_3P and with alkali metals (Na, Li) in Bu_3P , hydrocarbon solvents and liquid ammonia. In the reaction of this coal with Bu_3P at 250°C , elemental analysis of the residue revealed that apparently 92.3% sulfur removal was realized. The addition of alkali metals to the Bu_3P did not improve the desulfurization but rendered coal components more soluble in the extract. Alkali metal/liquid ammonia systems gave rise to moderate desulfurization efficiency albeit with *ca.* 32% weight loss of the coal. Our procedure with Bu_3P also revealed high efficiencies for apparent sulfur removal (37.3% to 91.9%) from low-sulfur (0.62% to 2.32%) coals. Coal-related materials, such as coal-derived pyrite, FeS_2 and FeS also lost sulfur on treatment with Bu_3P . ^{31}P MAS NMR experiments indicate that the incorporated phosphorus compound is primarily $\text{Bu}_3\text{P}=\text{O}$ ($\delta^{31}\text{P}$ 31.5-32.55 ppm) while small amounts of $\text{Bu}_3\text{P}=\text{S}$ were detected ($\delta^{31}\text{P}$ 48-56 ppm) in some cases.

Project Objectives

- A. Optimize the coal desulfurization reaction with respect to time, temperature, coal type, and
- $$\text{Coal (S)} + \text{excess PR}_3 \longrightarrow \text{Coal} + \text{S}=\text{PR}_3/\text{PBu}_3 \quad (1)$$

The R groups (including $\text{R} = \text{H}$), and also on extraction, impregnation and sonication conditions.

- B. Optimize the conditions for the HDS reaction

(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 appears to

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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.

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 our laboratory,⁹ data on the desulfurization of Illinois No. 6 coal with tributylphosphine under mild conditions were presented. Here we report details of that work, the desulfurization of other coals and coal-related materials by the same method, and also the desulfurization of Illinois No. 6 coal utilizing alkali metals (Na and Li) in liquid ammonia and in hydrocarbon solvents.

Results

In this document we report data meeting Objectives A, D, and E.

Effect of particle size, liquid NH₃ pretreatment and sonication

Moderate desulfurization (ca. 61% sulfur removal) was observed in the reactions of 20 or 80 mesh Illinois No. 6 coal with tributylphosphine, while greater desulfurization (76.2%) was realized with 100 mesh Illinois No.6 coal (Table 1). The particle size of the coal was not observed to affect desulfurization efficiency in a consistent manner. Coal pretreatment with liquid ammonia at -78 °C for 3 h to induce swelling or the addition of Celite to improve dispersion and filtration of the coal residue actually reduced desulfurization efficiency. Sonication instead of heating was also disappointing (Table 1). The desulfurization reaction in this work occurs as shown in eqn 1 in

which the sulfur present in coal is predominantly converted to tributylphosphine sulfide. Earlier we observed in CPMAS ³¹P NMR studies that the phosphorus species incorporated into the coal residue from this reaction can include Bu₃P, Bu₃P=S, Bu₃P=O, Bu₃PH⁺ and a phosphate ester that can be written as (Coal-O)₃P=O.¹⁰ After the desulfurized coal residue was washed with ethyl ether and/or methylene chloride eight times for all entries in Table 1, only Bu₃P=O could be detected in the filtrate by GC analysis. The >100% mass recovery and the relatively high phosphorus content of the residue in entry 7 suggest that any loss of starting mass by sulfur removal and coal solubility is overcompensated by phosphorus incorporation.

The mass balance problem

Before proceeding to a discussion of our additional results, we address the we used to calculate the sulfur removal percentages in Table 1 and in subsequent tables. Arriving at a mass balance in these reactions has thus far not been successful. Reaction 1 as written is greatly oversimplified inasmuch as Bu₃P 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.

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

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 the mass changes that

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

have occurred. It may be noted that in most cases, the values for %S removal calculated with equation 2 exceed those arrived at with equation 3 by 1-23%, thus we are apparently erring on the conservative side.

Effect of methanol pretreatment

Methanol has been reported to extract 86% of the sulfur (90% of the organic sulfur) from Illinois IBC-108 coal at 500 °C under pressure.¹¹ Under the much milder conditions used here, methanol treatment did not enhance the desulfurization of Illinois No. 6 coal with Bu₃P (Table 2). Not unexpectedly, methanol by itself did not extract a detectable amount of sulfur from Illinois No. 6 coal at 65 °C. Pretreatment of coal with methanol in a variety of ways prior to its reaction with Bu₃P at 250 °C only decreased the desulfurization efficiency of Bu₃P used by itself. It is plausible that the greater polarity and smaller bulk of methanol molecules compared with those of Bu₃P allowed methanol molecules to hydrogen bond within the coal pores, thus blocking penetration of the larger Bu₃P molecules

Effect of alkali metal presence

It is reasonable to expect better desulfurization efficiency if the Bu₃P=S generated in reaction 1 could be removed as it was formed, in order to inhibit accumulation of this compound in the coal pores, thereby reducing further access of Bu₃P to the coal matrix. Recently, we found that alkali metals (i.e., sodium and lithium) efficiently desulfurize polycyclic aromatic sulfur compounds and a variety of phenylthio and alkylthio compounds.¹² Phosphine sulfides were also easily desulfurized as illustrated in eqn 4.¹² Addition of sodium to the Bu₃P under the same conditions as

those used for Bu₃P by itself in the treatment of 100 mesh Illinois No. 6 coal (Table 1) resulted in decreased desulfurization by a few percent to 74.7%, albeit with less incorporation of phosphorus (Table 3). However, the mass recovery was also substantially less. The addition of lithium appears to interfere with sulfur removal from Illinois No. 6 coal for reasons that are presently obscure. GC analysis of the extract after workup of the reaction mixture indicated that a small amount of Bu₃P=S was still present in the washings of the residue. These observations demonstrate that although sodium or lithium can desulfurize the Bu₃P=S generated from coal during the reaction, few if any of the miniscule beads of molten metal that formed were apparently not small enough to penetrate the coal pores for reaction with the Bu₃P=S that had become trapped in the pores.

Proposed process for sulfur removal from coal

Should the economics ever favor coal desulfurization with R₃P, two potential methods for reducing Bu₃P=S back to Bu₃P for recycling are indicated in Scheme 1. Here the extracts containing Bu₃P=S could be filtered into a separate reactor containing the alkali metal. The Bu₃P regenerated in the second reactor could then be distilled or pumped back to the desulfurization reactor. A third route is suggested in Scheme 2. The data in Table 3 (entries 3 and 4) reveal that

Scheme 1

Scheme 2

the use of sodium or lithium as a reducing agent is feasible. Thus by using Bu_3P as the solvent, $Bu_3P=S$ is completely converted to Bu_3P by sodium (eqn 4). The distillate (containing mostly Bu_3P and $Bu_3P=S$) from the reaction of Illinois No. 6 coal with Bu_3P at 250 °C was also completely desulfurized under the conditions of eqn 5 according to GC analysis (entry 4, Table 3).

Although Na and Li remove sulfur from a variety of organosulfur compounds (including thiophenes) in hydrocarbon solvents at temperatures above the melting points of the metals,¹² these metals displayed only poor to moderate efficiencies for desulfurizing coal in refluxing hydrocarbon solvents, such as tetradecane, mesitylene and toluene (Table 4).

Effect of coal/ PR_3 ratio

By using half the amount of Illinois No. 6 coal (0.500 g instead of the 1.000 g used in Table 1, entry 2), up to 92.3% apparent sulfur removal was realized using Bu_3P by itself (Table 5). A temperature of 250 °C (the boiling point of Bu_3P) and a time of 48 h appears to be optimal for Illinois No. 6 coal. The higher desulfurization efficiencies may be attributed to the greater dilution of the $Bu_3P=S$ generated by Bu_3P during the reaction. Here the addition of Celite again only reduced desulfurization efficiency (entries 4 and 6 in Table 5).

Other coals, and coal materials

The conditions in entry 4 of Table 5 were then applied to the desulfurization of a series of low-sulfur coals (Table 6). Where two mesh sizes of coals were employed, the desulfurization efficiencies were similar except in the cases of entries 1a, b and 4a, b. Interestingly, 70-90% desulfurization was achieved in most cases, with the Illinois No. 6, Pittsburgh No. 8 and Blind Canyon coal samples releasing approximately 90% of their sulfur.

Coal-derived pyrite, pyrite and FeS were also subjected to the same desulfurization conditions (Table 7). According to the atomic S/Fe ratios obtained from elemental analyses of the reaction residues in entries 3 (0.89) and 4 (0.90) it would appear that the FeS generated from

FeS₂ was partially desulfurized. By assuming that the phosphorus content is present as Bu₃P, however, the amount of the available sulfur removed was 52.65 and 51.05%, respectively, which is close to the 50% value expected since FeS is very stable.¹³ By making the same corrections for the phosphorus contents of the coal-derived pyrites in entries 1 and 2, the quantities of the available sulfur removed were 47.13 and 55.13%, respectively. The latter somewhat high value may be due to the reaction in eqn 6 which stems from the presence of acidic biphenol.

The HPBu₃⁺ cation, which readily forms in phenols, may also be involved in hydrogen transfer to the sulfidic sulfur. The sulfur removal from FeS in Table 7 is 11% (entry 5). The percent sulfur removed from the demineralized coal sample in Table 7 is only 31% (entry 7).

Nature of our sulfur removal process

Because virtually all of the inorganic sulfur in Illinois No. 6 is pyritic and since FeS does not appear to be appreciably desulfurized under our conditions, only about half of the ~ 3% inorganic sulfur in Illinois No. 6 is removed by Bu₃P. This would indicate that virtually all of the approximately 2% organic sulfur in this coal is removed (entry 4, Table 5). Since almost all of the organic sulfur in Illinois No. 6 is thiophenic sulfur, all of this type of sulfur is apparently removed under our conditions. It could be suggested that thiophenic compounds merely dissolve out of the coal into the extract and are not chemically attacked by the Bu₃P. Although this conjecture receives support from our earlier observations that Bu₃P does not react with dibenzo[*b,d*]thiophene or benzo[*b*]thiophene to any detectable extent at 250 °C for several days,¹³ neither of these compounds was detected in the ¹³C NMR spectra of the extracts. Earlier, we showed that HPBu₃⁺ (observed by ³¹P NMR spectroscopy in Illinois No. 6 treated with Bu₃P) can be formed from phenolic (or carboxylic acid) protons present in the coals. We also showed that desulfurization of this coal with Bu₃P was negligible when the acidic protons were replaced with alkyl groups or Na⁺ ions, thus concluding that labile protons in coal facilitate desulfurization. It is interesting that the elemental analyses of the residues were consistent with incorporation of biphenol to the solid matrix (Table 7) when biphenol was added. Such incorporation could occur as a result of the reaction of biphenol with Bu₃P to form Bu₃PH⁺ and biphenolate anion. A variety of acids do not facilitate this reaction for thiophenes by themselves, however.¹⁴ Thus for some as yet unknown reason, labile hydrogens carry out this function only in the coal matrix, and seem to do so only when minerals are present, as is shown by the lack of desulfurization of the demineralized coal samples in entry 7 Table 7 wherein only 31.3% of (organic) sulfur removal was obtained and a 95.6% mass recovery was realized.

The effect of liquid ammonia

Birch reduction has been used to reduce a variety of functional groups in organic synthesis.¹⁵ Potassium (or sodium) in liquid ammonia has been used for the multistage alkylation of coals as an aid in studying coal structures.¹⁶ The reactions of Illinois No. 6 coal with Na or Li in liquid ammonia gave comparable desulfurization efficiencies (56-57% sulfur removal) with a *ca.* 32% weight loss of the coal sample (Table 8). It is known that treatment of coal with alkali metal in liquid NH₃ renders the coal more vulnerable to extraction by organic solvents.¹⁵ In our study (Table 8, entries 3 and 5), the water-soluble species in the reaction residues would include Na₂S or Li₂S which had to be extracted from the residue to render a meaningful sulfur analysis.

Conclusion and future work

The reaction of coal with Bu_3P at 250°C under atmospheric pressure appears to be a generally efficient route to desulfurizing coals. The problem of mass balance is still a nagging one, however, because part of the coal is extracted into the Bu_3P and part of the Bu_3P remains in the coal matrix as Bu_3P , $\text{Bu}_3\text{P}=\text{S}$, $\text{Bu}_3\text{P}=\text{O}$ and Bu_3PH^- phenolates, according to ^{31}P CP MAS NMR spectroscopy. This severely obfuscates the meaning of the S elemental analyses in terms of actual sulfur removal.

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 the design is radically different. The problem with the Soxhlet apparatus is that there is considerable hang-up of an extractant by adsorption on all of the surfaces above the liquid, including the extraction chamber and up into 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 (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 extract mass gain. 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 this 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 extract-dissolved and coal-trapped $\text{Bu}_3\text{P}=\text{S}$.

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.

Experimental Section

Gas chromatographic analyses were carried out on Hewlett-Packard 6980 GC system with a 25 m 200 μ diameter HP fused silica capillary coated with HP-1 cross-linked methyl silicone (0.33 μm). Elemental analyses of sulfur in coal residues and extracts were conducted by Desert Analytics Laboratory, Tucson, Arizona, USA. Bu_3P was purified by reacting it with CS_2 to form the $\text{Bu}_3\text{P}\cdot\text{CS}_2$ adduct and then distilling the CS_2 from this crystalline adduct under reduced pressure to decompose it to pure Bu_3P . Coal samples were purchased from Argonne National Laboratory, Argonne, Illinois, USA. Demineralized Illinois No. 6 was prepared by reacting the coal with LiAlH_4 in refluxing THF followed by washing with diluted HCl, H_2O , and MeOH.¹⁷

A. Reactions of coal with Bu_3P and/or alkali metals: Under argon, coal (1.000 g or 0.500 g), Bu_3P (7 mL) or hydrocarbon solvent (3-5 mL), and other substances as indicated in the tables (i.e., Celite, Na or Li, etc.) were added to a 50-mL two-necked Schlenk bottle fitted with a condenser connected at the top to an argon line. The mixture was vigorously stirred at the temperatures and times shown in the tables. After cooling the reaction mixture to room temperature, 5 mL of ethyl ether was added followed by filtration. Where Na or Li was used, the first work-up step included quenching unreacted metal with 5 mL of methanol at 0 °C under argon. The solid was copiously washed with diethyl ether until no $\text{Bu}_3\text{P}=\text{S}$ was detected by GC analysis and then it was further washed with water or other solvent as indicated in the tables. The residue was then dried in vacuo for elemental analysis.

B. Reactions of coal with $\text{Bu}_3\text{P}/(\text{MeOH})$: Coal was treated with methanol in the manner indicated in Table 2 and the reactions were carried out under argon. The work-up of the reactions was the same as that in A.

C. Reactions of coal-related materials with Bu_3P : Under argon, 1.000 g of coal-related material (as indicated in Table 7) and 7 mL of Bu_3P were added to the reactor (1.0 mmol of biphenol was added as indicated) and the reaction was carried out at 250 °C for 48 h. The work-up procedure was the same as that in A.

D. Reactions of coal with $\text{M}/\text{liq NH}_3$: Under argon, 30 mL of liquid ammonia was added to a 150 mL two-necked Schlenk bottle charged with 1.000 g of coal, Na or Li (30 mmol) was added in portions. The reaction mixture was vigorously stirred at -78 °C under a slow argon flow for 3 h and then ammonia was evaporated by slowly warming the reaction mixture to room temperature. The unreacted metal was then quenched with 5 mL of methanol at 0 °C under argon. The mixture was filtered and washed with diethyl ether and further washed as indicated in the tables. The solid was then dried in vacuo for elemental analysis.

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Table 1 Desulfurization of Illinois No. 6 Coal with Bu_3P .

entry	size	temp/time	% mass	% S	% P	% S
	(mesh)	(°C/h)	recovery	(residue)	(residue)	removal
1	20	250/48	88.5	1.85	2.56	61.7
2	80	250/48	84.9	1.30	2.22	73.1 ^a
3	100	250/48	76.9	1.15	3.83	76.2
4 ^c	20	250/48	85.1	2.36	2.33	51.1
5 ^d	80	250/48	90.2	1.15	0.81	64.3
6 ^e	100	25-30/48	78.6	3.39	0.58	29.8
7 ^f	100	>RT/0.41	106.8	3.28	4.62	32.1

^aReaction conditions: the coal samples (1.000 g, 4.83% S), Bu_3P (7 mL), 0.1 MPa. ^bAfter the reaction was complete, the reaction mixture was centrifuged and a small weighed amount of the supernatant was removed and oxidized in air to constant weight to allow all the Bu_3P oxidize to $\text{Bu}_3\text{P}=\text{O}$. This oxidized sample was then submitted for sulfur elemental analysis. In this case, the calculated percent S removal based on the 0.74% sulfur content found in the oxidized supernatant is 75.4%. ^cThe coal sample was stirred in 30 mL of liq. NH_3 at -78°C for 6 h and followed by evaporating the NH_3 before it was reacted with Bu_3P . ^dCelite (0.500 g) was added as a filter aid. ^eSonicated at 1.0 AMPS in a water bath. ^fSonicated by a probe (300 w, 5 x 5 min).

Table 2. Effect of Methanol Pretreatment of Illinois No. 6 Coal on its Desulfurization with Bu_3P .^a

entry	pretreatment method ^b	Bu_3P (mL)	temp/time (°C/h)	% mass recovery	% S (residue)	% P (residue)	% S removal
1	A	-	65/24	~100	4.94	0	0
2	B	1	65/24	81.7	4.52	0.40	6.4
3	B	2	65/48	86.0	3.60	1.72	25.5
4	C	7	250/48	111.7	1.89	3.74	60.9
5	D	7	250/48	87.6	3.79	2.21	21.5
6	E	7	250/48	100.8	2.05	3.34	57.6
7 ^c	C	7	250/48	100.0	1.79	3.70	62.9

^aThe coal samples (1.000 g, 20 mesh) contained 4.83 % S. ^bA: The coal was treated with methanol (8 mL) at reflux. B: The coal was swollen in methanol (8 mL) at room temperature for 24 h and then Bu_3P was added and the reaction mixture was refluxed. C: The coal was swollen in methanol (8 mL) at room temperature for 24 h, the methanol was evaporated on a rotary evaporator and then the Bu_3P was added. D: A mixture of Bu_3P and the coal preswollen in 8 mL of methanol at room temperature for 24 h was stirred at room temperature for 5 min followed by evaporating the methanol under vacuum. E: The mixture of coal, Bu_3P and methanol (8 mL) was stirred at room temperature for 24 h and then the methanol was evaporated.

^cHere a 0.500 g coal sample was used.

Table 3. Alkali Metal Regeneration of Bu_3P from $\text{Bu}_3\text{P}=\text{S}$ during Coal Desulfurization.^a

entry	substrate	M	temp/tim	washing	% mass	% S	% P	% S
		e						
		(mmol)	(°C/h)	solvent	recovery	(residue)	(residue)	remova
								!
1	coal	Na (10)	250/48	$\text{Et}_2\text{O}/$	65.3	1.22	1.38	74.7
				MeOH/H_2				
				O				
2	coal	Li (10)	250/48	$\text{Et}_2\text{O}/\text{H}_2\text{O}$	69.6	1.93	1.03	60.0
3	$\text{Bu}_3\text{P}=\text{S}^b$	Na (5)	200/24		-	-	-	100 ^c
4	distillate ^d	Na (5)	200/24		-	-	-	100 ^e

^aReaction conditions: Illinois No.6 coal (1.000 g, 100 mesh, 4.83 % S); solvent, Bu_3P (7 mL).

^b $\text{Bu}_3\text{P}=\text{S}$, 1.0 mmol. ^cGC analysis. ^dThe distillate (5.33 g) was obtained by distilling under reduced pressure a reaction mixture of Illinois No. 6 coal (1.000 g, 100 mesh, 4.83 % S) heated with 7 mL of Bu_3P at 250 °C for 48 h. ^eNo $\text{Bu}_3\text{P}=\text{S}$ was detected in the reaction mixture by GC analysis after the reaction was complete.

Table 4. Desulfurization of Illinois No. 6 Coal with Na or Li.^a

entry	M	reaction solvent	temp (°C)	washing solvent ^b	% mass recovery	% S (residue)	% S removal
1	-	tetradecane	254	Et ₂ O	83.4	4.20	13.0
2	Na	tetradecane	254	Et ₂ O/H ₂ O	92.1	3.30	31.7
3	Li	tetradecane	254	Et ₂ O/H ₂ O	75.0	4.72	2.3
4	Na	mesitylene	164	Et ₂ O/H ₂ O	73.2	3.35	30.6
5	Na	toluene	110	Et ₂ O/H ₂ O	78.1	3.57	26.1

^aReaction conditions: coal sample (1.000 g, 100 mesh, 4.83 % S); metal (10 mmol); solvent, 3-5 mL; 0.1 MPa; 24 h. ^bAfter the reaction was quenched with methanol, the reaction residue was washed with the solvents indicated.

Table 5. Desulfurization of Illinois No. 6 Coal with Bu₃P under Various Conditions.^a

entry	temp/time	% mass	% S	% P	%S	% S	$\delta^{31}\text{P}^d$
	(°C/h)	recovery	(residue)	(residue)	removal	removal ^c	(residue)
1	200/48	86.9	2.49	1.63	48.4	62.8	33.3, 54.2 ^e
2	250/24	86.0	1.64	1.86	66.0	81.3	31.5
3	300/24	82.0	0.66	3.46	86.3	96.5	31.7
4	250/48	83.5	0.37	3.87	92.3	~100	31.8
5	250/72	81.8	1.60	2.36	66.9	83.1	31.6, 53.0 ^d
6 ^b	250/48	93.0	0.36	4.02	88.8	93.6	32.5

^aThe coal, sample (0.500 g, 100 mesh contained 4.83 % S. ^bCelite (0.250 g) was added. ^cResults obtained from the sulfur elemental analyses of the oxidized extracts. (See entry 2 in Table 1.) ^dCPMAS NMR. ^eThis peak is small and broad.

Table 6. Desulfurization of Other Types of Coals with Bu₃P.*

entry	seam (% S)	size (mesh)	% S (residue)	% P (residue)	% mass recovery	% S removal	³¹ P MAS NMR of residue (ppm)
1a	Illinois No. 6 (4.83)	20	2.45	2.18	72.0	49.3	32
1b	Illinois No. 6 (4.83)	100	0.37	3.87	83.6	92.3	32
2a	Upper Freeport (2.32)	20	0.39	1.76	74.8	83.2	32, 48.1 ^b
2b	Upper Freeport (2.32)	100	0.43	1.50	80.8	81.5	32, 50.4 ^b
3a	Pittsburgh No. 8 (2.19)	20	0.22	1.83	90.2	90.0	32, 56.7 ^b
3b	Pittsburgh No. 8 (2.19)	100	0.32	1.70	78.8	85.4	31, 56 ^b
4a	Beulap-Zap (0.80)	20	0.36	4.47	62.6	55.0	
4b	Beulap-Zap (0.80)	100	0.22	3.13	64.0	72.5	
5	Pocahontas No. 3 (0.66)	100	0.15	1.10	81.6	77.3	
6a	Wyodak-Anderson (0.63)	20	0.20	3.24	66.0	68.2	
6b	Wyodak-Anderson (0.63)	100	0.20	4.05	68.0	68.2	

Table 6 continued

entry	seam (% S)	size (mesh)	% S (residue)	% P (residue)	% mass recovery	% S removal	³¹ P MAS NMR of residue (ppm)
7a	Blind Canyon (0.62)	20	<0.05	1.92	81.6	>91.9	32, 51 ^b
7b	Blind Canyon (0.62)	100	<0.05	1.42	81.2	>91.9	32, 56 ^b
8a	Lewiston-Stockton (0.71)	20	0.14	1.03	89.2	80.3	
8b	Lewiston-Stockton (0.71)	100	0.19	1.24	76.4	73.2	
9	Hanna No. 80 (1.10)	100-200	0.69	2.58	68.2	37.3	
10	West Kentucky No. 9 (2.74)	100-200	1.67	2.07	78.4	39.0	

*Reaction conditions: coal sample, 0.500 g; Bu₃P, 7 mL; 250 °C; 48 h; 0.1 MPa. ^bThe ³¹P MAS NMR peak is small and broad and the singlet around 31 ppm is the major peak.

Table 7. Desulfurization of Coal-related Materials with Bu_3P .^a

entry	substrate	% S	%C	%H	%N	% P	% mass	% S
	(%S)	(residue)	residue			(residue)	recovery	removal
1	coal-derived pyrite (41.00)	26.13	9.89	1.20	0.15	0.76	66.4	36.3
2	coal-derived pyrite (41.00) ^b	21.94	13.96	1.76	0.10	0.94	71.9	46.5
3	FeS_2 (52.73)	33.65	0.61	0.09		0.16	62.9	36.2
4	FeS_2 (52.73) ^b	31.34	5.75	0.84		1.92	44.9	40.6
5	FeS (36.47)	32.46	3.70	0.33		1.51	89.1	11.0
6	FeS (36.47) ^b	32.01	3.86	0.57		0.94	89.8	12.2
7	demineralized Illinois No. 6 ^c	1.03				2.01	95.6	31.3

^aSubstrate, 1.000 g; Bu_3P , 7 mL; 250 °C; 48 h; 0.1 MPa. ^bBiphenol (0.186g, 1.0 mmol) was added. ^c0.500 g.

Table 8. Desulfurization of Illinois No. 6 Coal with M/liq NH_3 .^a

entry	M	washing solvent	weight of residue (g)	% S (residue)	% N (residue)	% S removal
1	-	Et_2O	0.856	3.73	1.32	22.8
2	Na	Et_2O	1.096	2.72	1.50	43.7
3	Na	$\text{Et}_2\text{O}/\text{H}_2\text{O}$	0.682	2.05	1.40	57.6
4	Li	Et_2O	1.011	2.64	1.01	45.3
5	Li	$\text{Et}_2\text{O}/\text{H}_2\text{O}$	0.685	2.08	2.27	56.9

^aThe coal samples (1.000 g, 20 mesh) contained 4.83 % S and 1.16 % N.

A Novel Approach to Catalytic Desulfurization of Coal

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Abstract. The nonionic superbases $P(\text{MeNCH}_2\text{CH}_2)_3\text{N}$ (A) efficiently desulfurizes trisulfides to disulfides and monosulfides, disulfides to monosulfides, and propylene sulfide to propene. $\text{S}=\text{P}(\text{MeNCH}_2\text{CH}_2)_3\text{N}$ (B) was formed as the sulfur acceptor. $\text{P}(\text{NMe}_2)_3$ was a much poorer desulfurizing agent than A under the same reaction conditions. Thiocyanates and triphenylphosphine sulfide were also desulfurized with A, but N-(phenylthio)phthalimide formed $[\text{A}-\text{SP}]^+$ phthalimide in quantitative yield.

Project Objectives

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

the R groups (including $\text{R} = \text{H}$), and also on extraction, impregnation and sonication conditions.

- B. Optimize the conditions for the HDS reaction

(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 appears to

quantitatively remove sulfur from dibenzothiophene (DBT) when $\text{R} = \text{Bu}$ 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 $\text{PR}_3/\text{Fe}^{3+}$ 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.

Results

In this document we report that the highly basic phosphine A, which was developed

in our laboratories and is now commercially available, is an unusually powerful desulfurizing reagent for a variety of organosulfur compounds, but not for benzothiophene, dibenzothiophene or coal.

The Use of A as a Desulfurizing Agent. The desulfurization of organosulfur compounds with trivalent organophosphorus reagents has been studied for more than four decades. For example, one or more of the reagents triphenyl phosphine,¹⁻⁵ trisdimethylaminophosphine,^{4,6-8} trisdiethylaminophosphine,^{4,7-10} triethylphosphite,¹ trimopholinophosphine^{4,7} and tributylphosphine^{11,12} have been employed to convert trisulfides to the corresponding disulfides or monosulfides, β -keto sulfides to ketones, and sulfenimides to amines in moderate yields. Trialkyl phosphines can be used to remove sulfur from thioethers,¹³ thiols¹⁴ and organometallic dithiocarboxylates;¹⁵ trisdiethylaminophosphine effects reaction 1; triphenylphosphite effects reaction 2;¹⁶ and very recently thiol groups have been reductively eliminated photochemically from L-cysteine derivatives in the presence of triethylphosphite and triethylboron.¹⁷

In the course of our ongoing investigations on new synthetic applications of the exceedingly strong nonionic base and catalyst A first reported from our laboratories¹⁸⁻²⁰ and now sold commercially by Srem Chemicals, we found that B could be formed from A in the presence

of sulfur.²¹ Recently, we found that B could be desulfurized with excess sodium in refluxing toluene or in tetradecane at 160 °C. These results suggested a potential application of A in desulfurizing organosulfur compounds in a cyclic process since A can be recycled as shown in eqn. 3. Here we report desulfurizations with A under mild conditions.

Using 1.0 equiv of A, trisulfides were desulfurized primarily to disulfides with monosulfides as minor products at room temperature and the formation of B as the only other product (entries 1-3, Table 1). With more than 2.0 equiv of A, benzyl trisulfide was desulfurized to benzyl monosulfide via benzyl disulfide (entry 4, Table 1). Disulfides such as propyl, butyl, methyl benzyl and benzyl disulfides were efficiently desulfurized to monosulfides at room temperature or at 40 °C (entries 6, 10, 13 and 14, Table 1). Increasing the steric hindrance of the disulfide obviously decreased the desulfurization rate (entries 7 and 12, Table 1). Although (Me₂N)₃P was effective for desulfurizing trisulfides to disulfides and some activated monosulfides to sulfur-free compounds,^{4,6} it showed much poorer desulfurizing efficiency than A under the same reaction conditions (entries 5, 8, 9 and 11, Table 1). Using excess (Me₂N)₃P, benzyl trisulfide was desulfurized to benzyl disulfide (39.6%) and benzyl monosulfide (42.9%) in THF at room temperature within 25.5 h, but under the same conditions it was quantitatively desulfurized to dibenzyl monosulfide by A within 3 h (entries 4 and 5, Table 1). For disulfides,

(Me₂N)₃P led to poor desulfurization efficiencies (entries 8, 9 and 11, Table 1). Phenyl disulfide could not be efficiently desulfurized at room temperature by A and raising the temperature led to the formation of C (entry 15, Table 1). The ³¹P NMR spectrum of the reaction mixture of phenyl disulfide with A in tetradecane at 160 °C revealed a major peak at 45.1 ppm in addition to a small peak at 76.3 ppm (assigned to B). Acidifying the same reaction mixture with 1N HCl led

to the formation of phenylthiol which was detected by GC/MS analysis. Interestingly, propylene sulfide in the presence of A lost sulfur to give propene in high yield at room temperature (entry 16, Table 1).

Thiocyanatēs were desulfurized to their corresponding cyanides (entries 1, 2, Table 2). In the reaction of ethyl thiocyanate with A at room temperature, D ($\delta^{31}\text{P} = 50.7$ ppm) and B were formed in roughly equivalent amounts according to ³¹P NMR integration, but raising the temperature decomposed D to ethyl cyanide and B presumably via nucleophilic attack of cyanide anion at the Et-S bond. A and N-(phenylthio)phthalimide reacted cleanly at room temperature forming E quantitatively.²² Analogues of E wherein the cation is ArSP(NMe₂)₃⁺ (Ar = Ph or *p*-MeC₆H₄) have been suggested (on the basis of transient ³¹P chemical shifts at ~60 ppm) as intermediates in the desulfurization of the corresponding thioaryl phthalimides:²³

Even triphenylphosphine sulfide was desulfurized in moderate yield by A (60%, entry 4, Table 2) indicating that A is the stronger desulfurizing reagent. However, benzothiophene, dibenzothiophene and Illinois No. 6 coal were not desulfurized by A under conditions employed herein nor at elevated temperatures.

Conclusions

Compound A is a more powerful desulfurizing agent than its acyclic counterpart $\text{P}(\text{NMe}_2)_3$ and it is also more potent than PPh_3 in this respect. This observation is attributable to partial donation of electron density from the axial nitrogen to the phosphorus in a transannular interaction that can enrich the electron density on phosphorus, which in turn allows A to act as a stronger nucleophile for sulfur. However, the nucleophilicity of A is not sufficiently strong to remove sulfur from benzothiophene or dibenzothiophene. We had thought that the compact cage-like nature of A might allow this molecule to penetrate the pores of a coal such as Illinois No. 6. If A could remove sulfur from coal by a catalytic mechanism (for which we have some evidence using P^Bu_3) then A might function more effectively in this regard than P^Bu_3 . However, this is unfortunately not what we observed and in the next report we will describe the results of our return to the main objectives of this project.

It should be noted that the PI received an unsolicited invitation from the organizers of the Symposium on Microscopic Studies of Coal and Carbon to give a paper²⁴ at the 216th ACS National meeting held in Boston in August of 1998.

Experimental Section. Under argon, 1.0 mmol of substrate was added to a solution of A in the solvent and the reaction was carried out under the conditions stated in Tables 1 and 2. The reaction mixtures were subjected to GC, GC/MS or ^{31}P NMR analyses.

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22. Compound E, a yellow crystalline solid, was obtained by evaporating the solvent from the reaction mixture. ^1H NMR (CDCl_3): δ 7.83, 7.67, 7.62, 7.43, 7.34 and 7.23 (1:1:2:3:1:1 H, m each, 9CH aromatic protons), 2.98 and 2.94 (6H, t each, 3CH₂), 2.76 (6H, t, 3CH₂), 2.73 (9H, d, 3CH₃). ^{13}C NMR (CD_3CN): δ 174.9 (C=O), 135.8, 135.7, 131.4, 131.2, 131.1, 130.8, 130.7, 130.7, 129.6, 127.3, 51.78, 50.54(d), 37.65(d). ^{31}P NMR: δ 44.3 ppm. Anal. Calcd. for $\text{C}_{14}\text{H}_9\text{NO}_2\text{SP}$ (255.3): C, 65.87; H, 3.55; N, 5.49. Found: C, 65.42; H, 3.40; N, 5.30.
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Table 1. Desulfurization of alkyl sulfides with sodium.

substrate		solvent	temp/time	product ^a
			(°C/h)	yield (%)
$(n\text{-C}_6\text{H}_{13})_2\text{S}$	1	tetradecane	254/8	$n\text{-C}_6\text{H}_{14}$ (90.0), $n\text{-C}_6\text{H}_{13}\text{SH}$ (5.0)
$(n\text{-C}_8\text{H}_{17})_2\text{S}$	2	tetradecane	254/8	$n\text{-C}_8\text{H}_{18}$ (97.5), $n\text{-C}_8\text{H}_{17}\text{SH}$ (< 2.0)
$(n\text{-C}_{12}\text{H}_{25})_2\text{S}$	3	tetradecane	254/23.5	$n\text{-C}_{12}\text{H}_{26}$ (> 99.0)
$(\text{C}_6\text{H}_{10})\text{S}^b$	4	toluene	110/7	cyclohexene (> 99.0), cyclohexane (< 0.1)
$(\text{C}_3\text{H}_6)\text{S}^c$	5	toluene	110/4	$\text{CH}_3\text{CH}=\text{CH}_2$ (> 99.0) ^d
PhCH_2SMe	6	mesitylene	164/4	PhMe (89.0), PhEt (10.9)
PhCH_2SMe	6	tetradecane	254/4	PhMe (72.1), PhEt (27.4)
PhCH_2SSMe	7	mesitylene	164/4	PhMe (16.6), PhEt (3.4), $(\text{PhCH}_2)_2$ (50.9) ^e
PhCH_2SSMe	7	tetradecane	254/4	PhMe (44.3), PhEt (5.8), $(\text{PhCH}_2)_2$ (48.4) ^e
PhCH_2SPh	8	toluene	110/5.5 ^f	PhMe (24.0), PhSH (22.0), $(\text{PhCH}_2)_2$ (0.7) ^g
PhCH_2SPh	8	tetradecane	254/5.5	PhMe (95.0), PhSH (1.0), Ph_2CH_2 (1.1), $(\text{PhCH}_2)_2$ (0.6) ^g
$\text{C}_{10}\text{H}_{12}\text{S}_2^h$	9	tetradecane	140/5.5	PhMe (21.6), Ph-Bu (< 1.0), $(\text{PhCH}_2)_2$ (75.0) ⁱ
$\text{C}_{10}\text{H}_{12}\text{S}_2^h$	9	tetradecane	254/5.5	PhMe (49.2), Ph-Bu (< 0.5), $(\text{PhCH}_2)_2$ (50.0) ⁱ

^aGC analysis, 100% conversion. ^b $(\text{C}_6\text{H}_{10})\text{S}$ = cyclohexene sulfide. ^c $(\text{C}_3\text{H}_6)\text{S}$ = propylene sulfide, 3.2 mmol.

^dConversion > 99.0%. ^eMethane is presumably produced. ^f25.5% conversion. ^g PhH

was detected but not quantitated owing to its volatility. ^h $\text{C}_{10}\text{H}_{12}\text{S}_2$ = 2-phenyl-1,3-dithiane.

ⁱPropane is presumably produced.

Table 2. Desulfurization of alkylthio compounds with sodium.

substrate		temp/time ^a	conversion	product
		(°C/h)	(%)	yield (%)
S(CH ₂ CH ₂ OH) ₂	10	254/4	100	CH ₃ CH ₂ OH (95.5)
S(CH ₂ CH ₂ CH ₂ OH) ₂	11	254/5	100	CH ₃ CH ₂ CH ₂ OH (90.0)
thiomorpholine	12	254/7.5	100	Et ₂ NH (> 95.0)
1,4-thioxane	13	254/8	100	Et ₂ O (> 95.0)
thiochroma-4-one	14	164/5.5 ^b	100	PhCOC ₂ H ₅ (> 99.0)
PhCH ₂ SH	15	254/13.5	85.2	PhMe (64.5), (PhCH ₂) ₂ (20.5)
Ph ₃ CSH	16	254/18	100	Ph ₃ CH (69.9), (Ph ₃ C) ₂ (27.3)
PhCH ₂ SCN	17	140/5	100	PhMe (6.4), (PhCH ₂) ₂ (90.0)
PhCH ₂ SCN	17	254/5	100	PhMe (21.1), (PhCH ₂) ₂ (76.5)
PhSO ₂ CH=CHPh	18	110/6 ^c	100	PhCH=CH ₂ (95.0), PhSH (< 1.0) ^d
PhSO ₂ CH=CHPh	18	254/6	100	PhCH=CH ₂ (95.0), PhSH (11.5) ^d

^aUnless otherwise stated the solvent is tetradecane. ^bMesitylene. ^cToluene. ^dThe PhSO₂ moiety is presumably transformed to other unidentified compounds plus PhH which was detected but not quantitated owing to its volatility.