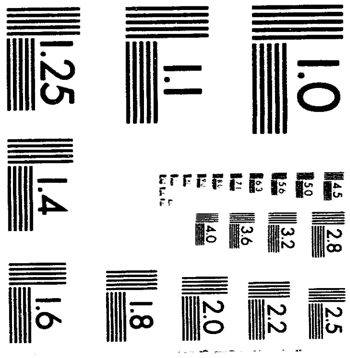
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HETERONUCLEAR PROBES OF COAL STRUCTURE AND REACTIVITY

October-December 1993
FG22-92PC92531

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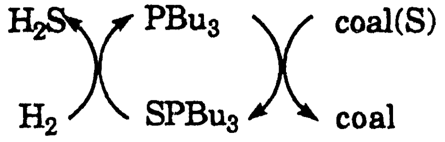
Quarterly Report
Due January 31, 1994

The highlights of the previous report were:

1. Vacuum impregnation of Ill. No. 6 with PBu_3 raised the sulfur removal from 92% to 99%.
2. Pre-drying the coal does not alter this result.
3. Whereas partial sulfur removal by PBu_3 from dibenzothiophene is catalyzed by Ill. No. 6, graphite is not a catalyst.
4. Whereas $FeCl_3$ catalyzes quantitative sulfur removal by PBu_3 from dibenzothiophene, zerovalent iron solubilized as $Fe(PBu_3)_x$ in PBu_3 is not.
5. An initial attempt to perform HDS on Ill. No. 6 catalyzed by PBu_3 failed:



6. The ^{31}P NMR peak at 32 ppm tentatively assigned to $HPBu_3^+$ was placed in doubt owing to its persistence in the presence of our superbase $P(MeNCH_2CH_2)_3N$.
7. Optimum HPLC parameters were established for SOH and ASOH oils (CONSOL coal resids).

A. On the Nature of the Catalysis of Desulfurization

1. Donna Hill coal. Reactions 1-3 summarize our rather surprising results. The first two reactions were carried out with prior vacuum impregnation of the PBu_3.

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Interestingly, the impregnation procedure in the case of reaction 1 gives no improvement of sulfur removal.

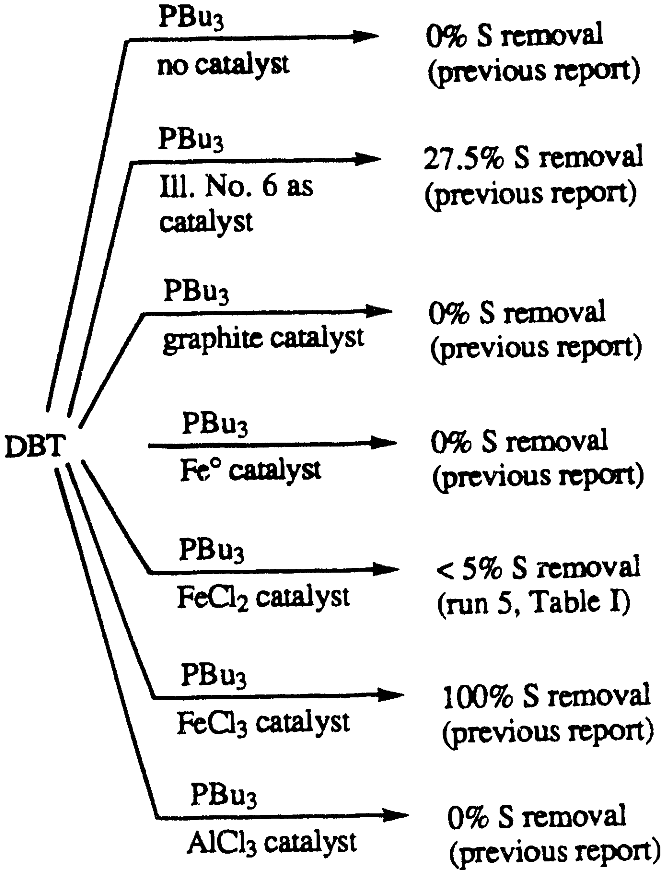
$$\text{Donna Hill} \xrightarrow[\text{no catalyst}]{PBu_3} \text{57.0\% S removal (run 1, Table I)} \tag{1}$$

$$\text{Donna Hill} \xrightarrow[AlCl_3\text{ catalyst}]{PBu_3} \text{70.0\% S removal (run 2, Table I)} \tag{2}$$

$$\text{Donna Hill} \xrightarrow[Ni_2B\text{ catalyst}]{PBu_3} \text{67.6\% S removal (run 3, Table II)} \tag{3}$$

2. Illinois No. 6. Using Ni_2B as a catalyst, only 40.12% sulfur was removed as $SPBu_3$ (run 4, Table I). This is puzzling in view of reaction 3 and the fact that we can remove 92% of the sulfur from Illinois No. 6 coal under the same conditions with no catalyst. It may be that in the present case Ni_2B is partially converted to NiS. Why this would be less of a problem with the Donna Hill sample is not clear.

3. Dibenzothiophene (DBT). Reactions 4-10 summarize our results to date. We now know that both Fe° and Fe^{2+} are not catalytic, whereas Fe^{3+} is. We thought this suggested that the metal could be acting as a hard Lewis acid (rather than a covalent complex-forming species). However, $AlCl_3$ is not catalytic suggesting that an Fe(III) species is specifically required. This conclusion is supported by the fact that we were able to see the ^{31}P NMR signal of $SPBu_3$ despite the paramagnetism of Fe^{3+}, perhaps suggesting the formation of a strongly ligated DBT-Fe(III) covalent complex, whereas in the attempt to use $FeCl_3$ as a catalyst to desulfurize Ill. No. 6 (previous report) the ^{31}P NMR signal for the $SPBu_3$ in the extract was too broad to measure. Thus any complexation with thiophenes would have to occur in the solid coal (which was filtered off) and DBT-free $FeCl_3$ would be present in the liquid extract to cause paramagnetic broadening of the $SPBu_3$ peak.



B. On the Significance of the ~32 ppm ^{31}P NMR Peak in PBu_3-Treated Coals.

1. Ill. No. 6 Pretreatment with NaOH. This coal when treated with 3N NaOH before the reaction with PBu_3 gives up only 15.22% of its sulfur (run 6, Table I). This contrasts the 92% S removal without such pretreatment (previous report). It is also the case that the ^{31}P NMR peak at 32 ppm in the solid coal is now of very low intensity compared with no such pretreatment. This seems to be consistent with the assignment of this peak to $HPBu_3^+$ and more importantly, an implied role for the acidic species in the coal (i.e., phenols and carboxylic acids) in desulfurization. It is interesting that a prominent peak assigned to $OPBu_3$ also appears in the coal showing that coal de-oxygenation also occurs.

2. Methylated Ill. No. 6. The objective here was to substantiate the above conclusion by converting all acidic protons to innocent methyl groups. The literature procedure involves treatment of the coal with $Bu_4N^+OH^-$ (to neutralize the protons as H_2O) and then to methylate the RO^- ions by MeI. As expected, the sulfur removal upon subsequent treatment with PBu_3 was low (11.4%, run 7, Table I) but surprisingly the 32 ppm peak in the solid remained. We tentatively attribute the latter result to incomplete deprotonation by aqueous $Bu_4N^+OH^-$ in the first step. We have substantiated this tentative conclusion by treating an Ill. No. 6 sample (pre-reacted with PBu_3) with our superbase $P(MeNCH_2CH_2)_3N$. We indeed observed formation of $HP(MeNCH_2CH_2)_3N^+$ in the ^{31}P NMR spectrum, demonstrating that protons were indeed still available.

3. Donna Hill Pretreated with PhOH. We had hoped to realize enhanced sulfur removal from this coal by vacuum impregnating it with PhOH before the PBu_3 reaction. This does not seem to work (run 8, Table I) since the same amount of sulfur is removed as without the phenol pretreatment. This could indicate two possibilities: (1) acidic protons do not play a role in desulfurizing this coal with PBu_3, (2) the impregnation material would have to be more acidic (e.g., $PhCO_2H$). It is also interesting that the solid coal residue contains no peak at 32 ppm, suggesting the possibility that the phenol was rapidly extracted by the PBu_3 and so became too dilute to aid in the desulfurization.

4. Illinois No. 6 Treated with PBu_3 and $P(MeNCH_2CH_2)_3N$. Illinois No. 6 samples treated with PBu_3 and then with our superbase $P(MeNCH_2CH_2)_3N$ reveal a peak at -11 ppm characteristic of the robust $HP(MeNCH_2CH_2)_3N^+$ cation. It appears that the peak at 32 ppm decreases in intensity, suggesting that this peak could be due to $HPBu_3^+$.

C. The ^{31}P NMR Peak at ~3 ppm.

1. Donna Hill Coal. This peak is always seen in coals, with a wide variety of phosphorus reactants, including P_4. We have speculated that it arises from a [(coal)C-O]$_3$P=O species. How this massive redox reaction occurs is puzzling, although there are examples of reactions of organophosphorus compounds breaking their C-P bonds in the presence of O_2 and radical sources. The latter, of course are indeed present in coals. The source of the oxygen in coal is not clear. It seems unlikely to be O_2 and we thought it might come from OH bonds. The fact that we see this 3 ppm peak in Donna Hill reacted with PBu_3 but do not detect the 32 ppm resonance suggests that [(coal)C-O]$_3$P=O species forms from an oxygen source other than OH (unless it is a very non-acidic OH such as alcohols) or that it arises from ether linkages. It is not likely that the [(coal)C-O]$_3$P=O species forms faster than protonation occurs, since the latter reactions are always very rapid. Curiously, a peak at 30 ppm does show up in Donna Hill pretreated with anhydrous $AlCl_3$ before reacting it with PBu_3. Could this be Cl_3AlPBu_3? This would be consistent with the peak at 32.73 ppm seen in the PBu_3 extract (run 2, Table I).

2. Illinois No. 6 Coal. To add further mystery to the situation, the 3 ppm peak is missing in methylated Ill. No. 6 after the PBu_3 reaction. This would suggest that this peak does arise from OH oxygen. Clearly more work needs to be done on this problem. Washing an Illinois No. 6 sample (prereacted with PBu_3) with H_2O/THF appears to decrease the intensities of all the peaks, suggesting hydrolysis of the [(coal)C-O]$_3$P=O species as well as the $HPBu_3^+$ cation.

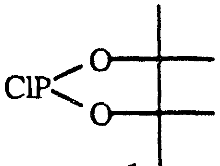
D. Solid State ^{119}Sn NMR Spectroscopy of Derivatized Illinois No. 6 Coal

1. $Bu_3SnOSnBu_3$ as the Derivatizing Agent. We have confirmed our result that the reaction of OH groups in Illinois No. 6 with $(Bu_3Sn)_2O$ gives two ^{119}Sn NMR bands in the solid derivatized sample centered at 110 ppm. These peaks are in the four-coordinate region of Sn (presumably Bu_3SnO-coal) and are contradictory to the observation in a Moessbauer study of an absorption in the five-coordinate region which was rationalized on the basis of the coordination of a nearby oxygen in the coal (e.g., Bu_3SnO-coal (HO-coal)). An attempt to force five-coordination was made by impregnating the derivatized sample with PhOH and $PhCO_2H$. Again, only the peaks in the tetracoordinate region were seen, but in the case of $PhCO_2H$ treatment, one of the bands decreased and the other resonance became sharper and shifted slightly upfield, perhaps because of exchange of the coal oxygen-tin bond for an oxygen in $PhCO_2H$.

2. $ClSn(CH_2CH_2CH_2)_3N$ as the Derivatizing Agent. Interestingly, the solid state ^{119}Sn NMR spectrum of the title reagent shows three (possibly more) peaks 0.3 kHz apart. This splitting may arise from ^{119}Sn-^{35}Cl J coupling which has also been seen in $ClSnI_3$. The corresponding spectrum of an Ill. No. 6 sample derivatized with the title reagent is essentially the same, suggesting that no reaction occurred.

E. ^{31}P NMR Spectrum of a Consol Coal Resid.

The polar fraction of a Consol coal resid was analyzed with reagent **1**.



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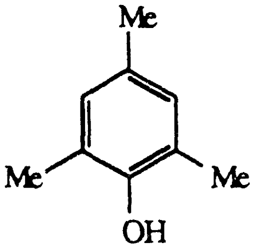
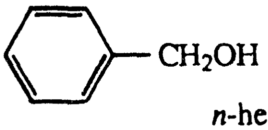
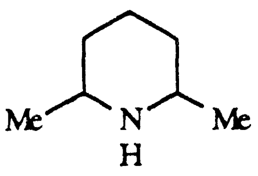
Preliminary results reveal resonances consistent with the presence of the compounds below:





$HO(CH_2)_3OH$

n-hexanol



F. High Performance Liquid Chromatography.

HPLC analysis of coal liquefaction oils obtained from Consol, Inc., was continued.

1. **Effect of Acidic Mobile Phase on Resolution.** Glacial acetic acid (1%) added to both eluting solvents (H_2O and THF) resulted in no improvement of resolution of the three samples examined.

2. **Installation of a Longer Column.** The 100 mm reverse-phase column was replaced with a 200 mm column for better resolution. The new optimized conditions for the ASOH oil are:

a. solvents: H_2O and MeCN

b. gradient-elution time-table:

min:	0	59	60	70	75	90
% MeCN:	10	75	95	95	10	10

c. flow rate: 1 mL/min

d. sample: 20 µL

e. wavelength: 215 nm

f. T: 25 °C

3. **Fractionation of Polar Fraction of ASOH Oil.** A Foxy 200 Isco fraction collector was assembled and connected to the HPLC instrument. The polar fraction of the ASOH oil was isolated by the SPE procedure and concentrated (10:1 by wt) by evaporation of the solvent (THF). A 20 µL sample of the concentrate was injected and fractionated. The fraction collector was programmed using time windows corresponding to the peaks in the chromatogram. The 13 subfractions will be analyzed by ^{3}P NMR using reagent 1.

G. Future Work

1. Since paramagnetism precluded analyzing for sulfur (as $SPBu_3$ in the extract) in the Ill. No. 6 treated with PBu_3 in the presence of $FeCl_3$, a sulfur analysis of the extract should be done.
2. To efficiently methylate Ill. No. 6, a vacuum impregnation with $P(MeNCH_2CH_2)_3N/Et_2O$ should be carried out followed by vacuum impregnation of Me_3OBF_4/Et_2O (or MeI) followed by vacuum drying and PBu_3 treatment. This should give us more certainty on the role of protons in desulfurization.
3. Oxidized DBT (i.e., the sulfoxide and the sulfone) should be treated with PBu_3 to determine if $OPBu_3$ and DBT are formed. This would tell us if weathered coals could be desulfurized with PBu_3.
4. React Ill. No. 6 with PBu_3 in the presence of Ni_2B and H_2 to determine if catalytic HDS can be effected.
5. Verify the ^{31}P NMR analysis of the ASOH oil using a ^{119}Sn reagent.
6. React Ill. No. 6 with $Me_2NSn(CH_2CH_2CH_2)_3N$ and obtain the solid state ^{119}Sn NMR spectrum to determine if this reagent is more reactive than the chloro analogue.
7. Carry out HPLC analyses of model phenols.

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Table I. Reactions with PBu_3.

Run No.	Reactants	PBu_3 Reaction Conditions	^{31}P Chemical Shifts[a] (ppm)	% Sulfur Removal (relative)
1	Donna Hill	250 °C, reflux, 2 d	48.56, 47.28	57.03
2	Donna Hill anhyd. $AlCl_3$	250 °C, reflux, 2 d prior vac. impreg.	63.39, 56.96, 48.27, 32.73	70.02
3	Donna Hill anhyd. Ni_2B	250 °C, reflux, 2 d	48.40, 44.76	67.57
4	Ill. No. 6, anhyd. Ni_2B	250 °C, refl, 36 h	48.48, 44.73	40.12
5	DBT, anhyd. $FeCl_2$	250 °C, reflux, 20 h	48.56, 32.59	< 5%
6	Ill. No. 6 pretreated	250 °C, reflux, 2 d	48.43, 44.21	15.22
7	Ill. No. 6, MeI via vac. impreg.	250 °C, reflux, 2 d	48.47, 44.02	11.39
8	Donna Hill, vac. impreg. with $PhOH/Et_2O$	250 °C, reflux, 2 d prior vac. impreg.	48.61, 46.92	57.01

[a] Peaks due to internal standard Ph_3PMeI and excess PBu_3 seen in all cases.

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