HETERONUCLEAR PROBES OF COAL STRUCTURE AND REACTIVITY

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Introduction

The main findings in the last quarterly report are:

1. Dibenzothiophene gives up about 27.5% of its sulfur to refluxing Bu_3P after 15 hours if a catalytic amount of Ill. No. 6 is present, and 100% is given up in the presence of FeCl_3 as a catalyst.
2. Coal-derived pyrites gave up 83% of its sulfur in refluxing Bu_3P .
3. Use of a heating mantle to reflux the Bu_3P causes better sulfur extraction than an oil bath.
4. Replacement of labile protons in Ill. No. 6 by Me groups results in poorer sulfur removal by Bu_3P .
5. The ubiquitous peak at 3 ppm in the solid residue of Ill. No. 6 treated with Bu_3P , Bu_3PO and Ph_3P suggests a common product, tentatively believed to be an $-\text{O}_3\text{PO}$ moiety.
6. The peak at 3 ppm does not appear to be due to the formation of H_3PO_4 in the coal from the extractants, since treatment of Ill. No. 6 with H_3PO_4 did not give rise to a 3 ppm peak.

Results

A. During this past quarter we further addressed the question of which species catalyzes removal of sulfur from coal by Bu_3P .

1. The reaction of anhydrous FeCl_3 with Bu_3P (run 1, Table I) produces in addition to a peak for unreacted Bu_3P (-30 ppm) a sharp peak at 32 ppm. In

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view of the paramagnetism of FeCl_3 , it would appear that the latter peak could represent a zerovalent $\text{Fe(PBu}_3)_x$ complex. The oxidation product could then be Cl_2PBu_3 or $\text{ClPBu}_3^+\text{Cl}^-$ (with its ^{31}P resonance possibly buried beneath the Bu_3P resonance) but this remains to be seen. It was tempting to assign the 36 ppm peak seen in solid Ill. No. 6 treated with Bu_3P at room temperature (run 1, Table II) to $\text{Fe(PBu}_3)_x$, but we currently believe this resonance may be associated with the HPBu_3^+ cation (see section B).

2. FeCl_3 was added to a reaction of Bu_3P and Ill. No. 6 (run 2, Table I) to determine if sulfur extraction was more efficient. Quantitation of the SPBu_3 in the extract was not possible, however, owing to the paramagnetism of the solution introduced by the addition of the iron. We plan to do a sulfur analysis of the extract.

B. Experimental evidence favoring HPBu_3^+ formation in solid coals treated with Bu_3P has been observed:

1. Dissolving PhOH and PhCO_2H in Bu_3P (runs 3 and 4, Table I) gives rise to ^{31}P NMR peaks with $^1J_{\text{PH}} \cong 450$ Hz at 37 ppm for $\text{HPBu}_3^+ \text{ } ^-\text{OPh}$ and 39 ppm for $\text{HPBu}_3^+ \text{ } ^-\text{O}_2\text{CPh}$.
2. Examination of our ^{31}P NMR spectra of Ill. No. 6 treated with Bu_3P at room temperature (run 1, Table II) reveals a peak at 36 ppm which is strongly coupled to nearby protons. This result is consistent with protonation of the Bu_3P since this reaction also occurs under mild conditions in solution.
3. Coals treated with Bu_3P at higher temperatures (Ill. No. 6, demineralized Ill. No. 6, Penn Seam-see last report and runs 2-7, Table II) display a solid state ^{31}P peak in this region ranging from 35 to 32 ppm which is strongly proton coupled.

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4. As expected, Ill. No. 6 in which all but 15% of the organic matter has been removed leaving 85% coal-derived pyrites does not show a peak in this region (run 8, Table II).
5. A Donna Hill coal sample does not reveal a peak in this region (run 9, Table II).
6. Ill. No. 6 samples treated with a variety of other phosphorus reagents (OPBu₃, 85% H₃PO₄, P₄, PPh₃, P(NMe₂)₃) do not display a ³¹P NMR peak in this region (see previous report).
7. Ill. No. 6 in which the labile hydrogen groups were methylated with MeI unexpectedly gave a relatively very intense peak at 32 ppm when treated with Bu₃P. Possible explanations are a) methylation was incomplete. b) H₂O in the coal protonates Bu₃P. Thus the coal is initially treated with Bu₄N⁺ -OH before the MeI reaction. c) Another phosphorus species resonates in this region. d) Our hypothesis of an HPBu₃⁺ species is incorrect.
8. Somewhat puzzling is the observation that pyridine washing of the coal does not remove the 32 ppm peak and in fact does not produce a detectable decrease in its relative intensity. It is curious that this peak is sometimes seen in extracts as a broad hump. We will try a stronger base to see if more complete removal of this peak from the solid can be effected.
9. Ill. No. 6 given a second treatment with fresh Bu₃P causes the 32 ppm peak to significantly intensify suggesting perhaps deeper penetration of the reagent to break up more deep-seated hydrogen bonding.

C. Additional aspects of the quantitation of sulfur removal from coal using Bu₃P were addressed.

1. The last report contained a quantitation by ³¹P NMR of a Bu₃P-treated demineralized Ill. No. 6 sample which was anomalously high. We conjectured that this might be associated with simultaneous oxygen removal

as OPBu₃, which we discovered resonates so close to SPBu₃ that their ³¹P NMR peaks overlap in Bu₃P as a solvent. In pyridine, however, these peaks are well separated (46.8 and 48.8 ppm, respectively) and so pyridine was added after the extraction in run 5 in Table I. Indeed the peaks are resolved in this mixed solvent mixture and the sulfur analysis (4.35%) by this technique revealed that 92.0% of the total sulfur content of the sample (4.73%, Desert Analytics) was removed as SPBu₃. Noteworthy is the observation that Bu₃P de-oxygenates as well as desulfurates coal.

2. Because of the relatively small concentration of the OPBu₃ in the extract, infrared spectroscopy in the ν P=O region was not helpful in detecting this compound.
 3. Whereas we can remove 92% of the sulfur in Ill. No. 6, only 50% of the sulfur is removed from a Donna Hill sample (run 6, Table I).
 4. Washing the solid Ill. No. 6 residue with pyridine decreases the solid state ³¹P NMR intensity to barely detectable for the SPBu₃ peak, but this is not the case for pentane washing. We have not yet quantitated the amount that pyridine washes out.
 5. Increasing the temperature and/or duration of treatment of Ill. No. 6 with Bu₃P increases the ratio of the 50 ppm peak in the solid residue relative to the 32 ppm peak, suggesting that, as expected, the desulfurization reaction is more difficult than the protonation of Bu₃P to HPBu₃⁺. Interestingly, the ratio of the 32 ppm peak relative to the 3 ppm peak remains about the same suggesting that (−O)₃P=O formation is also more facile than desulfurization.
- D.** Experiments aimed at determining the origin of the 3 ppm ³¹P NMR peak in solid coal samples treated with Bu₃P and OPBu₃ were carried out.

1. All phosphorus reagents we have used on Ill. No. 6 so far except H_3PO_4 (including SPBu_3 , OPPh_3 , SPPH_3 , $\text{OP}(\text{OBu})_3$, Ph_3P , and $\text{P}(\text{NMe}_2)_3$ (runs 11-17, Table II) reveal this peak in the solid residues.
2. Demineralized Ill. No. 6 treated with Bu_3P and OPBu_3 (runs 18 and 19, Table II) also exhibits this peak, although much less intensely in run 19.
3. Ill. No. 6 treated first with NaOH and then with OPCl_3 or SPCl_3 also displays this peak (runs 20 and 21, Table II). Because OPCl_3 absorbs at 3 ppm, run 20 is inconclusive. The peak at 5 ppm in the OPCl_3 experiment lies in the region for $\text{OPCl}_x(\text{OR})_{3-x}$ and the formation of several such compounds could explain its breadth. This peak may also have the same origin in the SPCl_3 experiment (run 21, Table II) since $\text{SPCl}_x(\text{OR})_{3-x}$ compounds resonate at lower field (25-23 ppm).
4. This peak also appears in an Ill. No. 6 sample reacted with P_4 (run 22, Table II).
5. This peak is relatively weak in the Penn Seam (NIST) coal (run 7, Table II) and the Donna Hill coal (run 9, Table II) perhaps because of a lower oxygen content (which still must be verified).
6. This peak appears in methylated Ill. No. 6 (run 23, Table II).
7. These results taken together with those in the last report suggest that the peak at 3 ppm is most likely due to an $(-\text{O})_3\text{P}=\text{O}$ species, i.e., an organophosphate yet to be identified. If this is so, it means that a strong oxidation reaction occurs which is capable of cleaving P-C and P=S groups and of converting P(0) and P(III) to P(V) even at room temperature. Interestingly, oxidation of the reagent can also occur, since OPBu_3 is detected. It also appears that these oxidation reactions do not require the presence of labile protons, although they may be helpful.

8. It is somewhat puzzling that coal-derived pyrites treated with Bu_3P (run 8, Table II) also displays this peak (although it is of decreased intensity) since all but 15% of the organic material has been removed.
9. This peak is not decreased in intensity by washing the coal (run 10, Table II) with pyridine.

E. On the role of labile hydrogens in desulfurization by Bu_3P .

1. As stated in point 4 of the Introduction, methylated Ill. No. 6 appears to result in less sulfur removal on treatment with Bu_3P than unmethylated samples. This conclusion appears to be substantiated by the experiment with the Donna Hill coal (run 6, Table I) wherein only 50% of the sulfur was removed and no peak at 32 ppm (HPBu_3^+) appeared in the solid (run 9, Table II).

F. Sulfur removal by other reagents.

1. $\text{P}(\text{NMe}_2)_3$ does not remove sulfur since no peak at 80 ppm for $\text{SP}(\text{NMe}_2)_3$ was found in run 7, Table I).
2. As expected, extracts of Ill. No. 6 treated with OPCl_3 and SPCl_3 (runs 8 and 9, Table I) produced only peaks for excess reagent.
3. A preliminary experiment using white phosphorus and Ill. No. 6 (run 10, Table I) revealed only unreacted P_4 at -470.0 ppm in the extract. This is not unexpected since the reaction products P_4S_x and P_4O_x are not expected to be soluble in toluene. The residue displayed peaks at 3 and -520 ppm (run 22, Table II). If the latter peak represents P_4 , it is shifted considerably upfield from the solution value.

G. Shakedown experiments with the HPLC.

1. We have obtained three coal resids from Consol, Inc. and separated them into non-polar and polar fractions using Sep-Pak Plus cartridges (following

the general procedure of Chao and Suatoni¹⁾ with satisfactory UV spectral verification.

2. We are now in the process of examining these fractions with the HPLC in the hope of separating phenols on a preparative scale for derivatization with ³¹P NMR reagents for speciation in conjunction with mass spectrometry.

G. Future Work

1. If Fe(PBu₃)_x is a catalyst for desulfurization, make a catalyst solution by heating Fe₃(CO)₉ with Bu₃P or by reducing FeCl₃ with NaNp or Na(Hg) in the presence of Bu₃P, and then add dibenzothiophene.
2. Try graphite as a desulfurization catalyst.
3. Repeat the dibenzothiophene/active carbon catalyst/Bu₃P experiment and then add FeCl₃ or Fe(PBu₃)_x to see if the extra ³¹P NMR peaks are sulfur intermediates which then can catalytically form SPBu₃.
4. See if FeS/Bu₃P/iron catalyst results in sulfur removal.
5. React a Bu₃P-treated coal with RSSR, ROOR and HO₂CCF₃ to see what happens, if anything, to the 3 and 32 ppm peak.
6. Impregnate Ill. No. 6 with some phenols and/or carboxylic acids to see if the 32 ppm peak grows on Bu₃P treatment.
7. Try refluxing Bu₃P treated coal in pyridine and/or a stronger base such as our superbases P(MeNCH₂CH₂)₃N to try to verify that the 32 ppm is due to HPBu₃⁺.
7. Treat a Bu₃P-treated coal with moisture or steam if necessary to see if H₃PO₄ is formed from the 3 ppm material in the coal.
8. Dry coal with 2,2-dimethoxypropane to see if moisture has an effect on desulfurization and on the formation of the peaks at 32 and 3 ppm.

9. Compare sulfur removal in a coal/Bu₃P/pyridine experiment with coal/Bu₃P/iron catalyst experiment, both with pyridine washing of the product.
10. Continue with HPLC examination of coal resids.

References

1. Chao, G. K.-J. and Suatoni, J. *J. Chromatog. Sci.* **1982**, 20, 436.

Table I. Solution ^{31}P NMR Data for Phosphorus Reagent Reactions.

run no.	reactants	reaction		^{31}P chemical shifts (δ ppm)
		conditions		
1	FeCl_3 , Bu_3P	250 °C, 17 h refl.		32, -30.01 ^a
2	Ill. No. 6, Bu_3P , FeCl_3	250 °C, 48 h refl.		48.78, 48.53
3	PhOH , Bu_3P	25 °C, 15 h		39.43 ($^1J_{\text{PH}} = 453 \text{ Hz}$), -30.01 ^a
4	PhCO_2H , Bu_3P	25 °C, 15 h		37.57 ($^1J_{\text{PH}} = 450 \text{ Hz}$), -30.01 ^a
5	Ill. No. 6, Bu_3P	250 °C, 48 h refl. ^b		48.65, 47.17
6	Donna Hill, Bu_3P	250 °C, 48 h refl. ^b		48.57, 45.87
7	Ill. No. 6, $\text{P}(\text{NMe}_2)_3$	50 °C, 15 h		120.01 ^c
8	Ill. No. 6, OPCl_3	room temp., 15 h		1.99 ^d
9	Ill. No. 6, SPCl_3	room temp., 15 h		25.82 ^e
10	Ill. No. 6, P_4	toluene, refl. 24 h		-470.0 ^f

^a Bu_3P . ^bPyridine added to extract after run was over. ^c $\text{P}(\text{NMe}_2)_3$. ^d OPCl_3 . ^e SPCl_3 . ^f P_4 .

Table II. Solid State ^{31}P NMR Data on Solid Coals Reacted with Phosphorus Reagents.

run	reaction		31P chemical shifts
No.	reactants	conditions	
1	Ill. No. 6, Bu3P	25 °C, 15 h	52a, 36, 3, -32.5b
2	Ill. No. 6, Bu3P, C6H5N ^m	110 °C, 15 h	52a, 34, 3, -32.5b
3	Ill. No. 6, excess Bu3P	250 °C, 15 h refl.	56, 50a, 48, 32, 3, -32.5b
4	Ill. No. 6, Bu3P	250 °C, 48 h refl.	50a, 32, 3, -5, -32.5b
5	Ill. No. 6, excess Bu3P	250 °C, 48 h refl.	49.5a, 32, 3, -32.5b
6	Ill. No. 6, Bu3P	250 °C, 72 h refl.	49a, 32, 3, -32.5b
7	Penn Seam (NIST), Bu3P	250 °C, 48 h refl.	51a, 34, 3, -32.5b
8	Ill. No. 6 derived pyrites Bu3P	250 °C, 7 h refl.	3
9	Donna Hill, Bu3P	250 °C, 48 h refl.	3
10	Ill. No. 6, Bu3P	250 °C, 48 h refl. ^c	60, 56, 53, 51, 33, 3, 0, -5
11	Ill. No. 6, SPBu3 ^d	room temp	102, 52-60, 47.7, ^e 3, -1
12	Ill. No. 6, OPPh3 ^d	room temp	28, 26.5, ^f 3
13	Ill. No. 6, SPBu3 ^d	room temp	52-69, 44, 3
14	Ill. No. 6, OP(OBu)3 ^d	room temp	2.5, -0.4 ^g
15	Ill. No. 6, Ph3P	90 °C, 15 h	7, 3, -6, ^h -9
16	Ill. No. 6, Ph3P	377 °C, 15 h refl.	44, 29, 3, -6 ^h
17	Ill. No. 6, P(NMe2)3	50 °C, 15 h ⁱ	3, -1, -5, -8, -10
18	demineralized Ill. No. 6,	250 °C, 15 h refl.	55, 50, ^a 46, 33, 3, -32.5b

	Bu ₃ P			
19	demineralized Ill. No. 6,	room temp	55, 52, 48, 47, 46, 3	
	Bu ₃ P			
20	Ill. No. 6, OPCL ₃ ^j	room temp	5, 3, -10 (or 21) ^k	
21	Ill. No. 6, SPCl ₃ ^j	room temp	29, ^l 5, 3, -10 (or 21) ^k	
22	Ill. No. 6, P ₄	toluene, refl. 24 h	3, -520	
23	Methylated Ill. No. 6, Bu ₃ P	250 °C, refl. 15 h	48, 45, 32, 3, -32.5 ^b	

^aSPBu₃. ^bBu₃P. ^cWashed twice with pyridine after treatment. ^d1:1 mixture. ^eSPBu₃. ^fOPPh₃. ^gOP(OBu)₃. ^hPh₃P. ⁱ7.5:1 mixture. ^jCoal was pretreated with NaOH. ^kWhich peak is the real and which is the sideband is still under investigation.

^lSPCl₃. ^mBu₃P:C₆H₅N = 1:2.

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