O

DOE/PC/92531--T3 1 D-2

HETERONUCLEAR PROBES OF COAL STRUCTURE AND REACTIVITY

John G. Verkade

92531

Gilman Hall

Iowa State University

NOV 2 1993

Quarterly Report

Due October 31, 1993

July - September 1993

The highlights of the previous report were:

1. A ^{31}P peak at 32 ppm in the residue of Ill. No. 6 treated with PBu_3 was tentatively assigned to HPBu_3^+ .
2. PBu_3 was shown to partially de-oxygenate as well as desulfurize Ill. No. 6.
3. The peak at 3 ppm in Ill. No. 6 treated with a wide variety of phosphorus reagents is most likely due to an $(-\text{O})_3\text{P}=\text{O}$ species, suggesting the occurrence of a powerful oxidation reaction in the case of P_4 or PBu_3 , for example.
4. Although PBu_3 effectively removes sulfur from Ill. No. 6, elemental P_4 does not.
5. Three coal resids from Consol, Inc., were successfully separated into polar and non-polar fractions.

Results

A. Desulfurization of Illinois No. 6

1. **Vacuum impregnation.** The most exciting finding in this quarter is the quantitative removal of sulfur from Illinois No. 6 coal using PBu_3 . In previous quarterly reports we described the removal of 92% sulfur by refluxing a suspension of Illinois No. 6 in PBu_3 for two days. The secret for quantitative removal (98.7%, run 1 in Table I) is to place the coal sample under vacuum, then adding the PBu_3 while the sample is still under vacuum and finally raising the pressure of the system to atmospheric with an inert gas before refluxing for two

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

days. This procedure permits better penetration by the PBU_3 into the pores which have been emptied of trapped gases and possibly water.

2. Vacuum treatment without vacuum impregnation. The possibility that prior evacuation (drying) of the coal sample was responsible for the quantitative sulfur removal rather than the subsequent impregnation of PBU_3 under vacuum was also tested. After evacuation, the sample was brought to atmospheric pressure before refluxing in PBU_3 . The percentage of sulfur removal was the usual 92% (run 2 in Table I). Thus vacuum drying does not seem to be responsible.

3. Prolonged vacuum treatment at 60 °C. It appears that prolonged vacuum treatment (two days) at an elevated temperature (60 °C) in order to dry the coal also does not improve the sulfur removal after vacuum impregnation and refluxing (run 3 in Table I).

4. Chemical drying. Similarly it appears that drying the coal with 2,2-dimethoxy propane prior to refluxing with PBU_3 (without vacuum impregnation)

also does not improve sulfur removal (run 4 in Table I).

B. On the Nature of the Catalysis of the Desulfurization

1. Graphite. In earlier reports we showed that Illinois No. 6 itself catalyzed the removal of sulfur from dibenzothiophene by PBU_3 . Using graphite as a high surface area carbonaceous substitute for the Illinois No. 6 failed in a similar experiment (run 5 in Table I).

2. Spanish coal. In a previous quarterly report we concluded that only 50% of the 2.71% sulfur contained in a Donna Hill coal was removed by PBU_3 reflux (without vacuum impregnation). A similar experiment with Spanish Coal (which contains 9.31% sulfur) provided only a 17% sulfur removal (run 6 in Table

I). The question that remains: why do these coals fail to give up more of their sulfur?

3. Zerovalent iron? In an earlier report we showed that FeCl_3 catalyzed the quantitative sulfur removal from dibenzothiophene (DBT) by refluxing PBU_3 . Since it is conceivable that the redox reaction below could occur,

we purposely created a reduced Fe/PBU_3 solution as follows:

An attempt to use such a solution as a catalyst to remove sulfur from DBT failed.

4. Trivalent or divalent iron? Since trivalent iron catalyzes the quantitative removal of sulfur from DBT, it is possible that this catalyst is partially reduced as the reaction proceeds. In a partial test of this hypothesis, we observed a refluxing solution of anhydrous FeCl_3 in PBU_3 and discovered that the originally violet solution slowly turns bright orange.

C. Attempted Hydrodesulfurization of Illinois No. 6

1. Hydrogenation of PBU_3 /coal. In an experiment collaboratively concocted with Prof. R. J. Angelici on our faculty, we tried to use PBU_3 as a homogeneous catalyst for hydrodesulfurizing Illinois No. 6 (run 7, Table I):

This attempt failed to produce any detectable H_2S at atmospheric pressure. The enthalpies are disfavored, but not by a great deal (10-20 kcal/mol, depending on whose numbers are used). The reaction is also not entropically driven.

D. Solid State ^{31}P NMR Results on Treated Coals

1. **Illinois No. 6 with prior PBU_3 impregnation.** The observed peaks are the same (run 3, Table I) as those for a similar sample not impregnated under vacuum with PBU_3 .

2. **Illinois No. 6 dried with 2,2-dimethoxypropane, then PBU_3 .** The observed peaks (run 4, Table I) are the same as for samples not treated with 2,2-dimethoxypropane. However, a much lower relative intensity of the peak at 50 ppm is observed, suggesting that somewhat better SPBU_3 extraction occurs.

3. **Spanish coal + PBU_3 .** The spectrum (run 6, Table I) is similar to that of an analogously treated Illinois No. 6 sample except that there is an additional minor peak at 38 ppm.

4. **Illinois No. 6 + H_2/PBU_3 .** In this residue the observed peaks (run 7, Table I) are the same as those for the analogous experiment without H_2 .

5. **The peak at 32 ppm.** In earlier reports we speculated that it could be due to HPBU_3^+ . We treated a solid Illinois No. 6 sample with $\text{P}(\text{MeNCH}_2\text{CH}_2)_3\text{N}$, our patented non-ionic superbases (run 8, Table I). Because this peak was unaltered by this treatment, it is highly unlikely that it is due to HPBU_3^+ .

6. **The peak at 3 ppm.** In earlier reports we speculated that this ubiquitous peak could be ascribed to $(\text{ArO})_3\text{PO}$ where the Ar group is part of the coal matrix. If this is true, hydrolysis should wash the peak out as H_3PO_4 or leave the H_3PO_4 in the matrix with a chemical shift of 0 ppm. Treatment of an Illinois No. 6 sample with an $\text{H}_2\text{O}/\text{THF}$ mixture at room temperature for 5 hours failed to remove the peak, however (run 9, Table I).

7. **Illinois No. 6 + P_4 /toluene.** In a previous report we observed that sulfur removal by P_4 followed by NaOH washing to remove the P_xS_y as thiophosphates was unsuccessful. The solid residue displays only the mysterious peak at 3 ppm.

E. HPLC of Coal Resids

Further studies were carried out to optimize separation of the phenolic fractions (isolated by solid phase extraction) of three coal resids supplied by CONSOL. The following chromatographic parameters were varied:

1. **Strength of organic modifier in H₂O.** Three different organic solvents (MeOH, MeCN and THF) were evaluated.
2. **Mobile phase composition.** A variety of isocratic as well as gradient elution programs were tried.
3. **Flow rate.** One, 1.5 and 2.0 mL/min flow rates were evaluated.
4. **Sample amount.** Ten and 20 μ L volumes were used.
5. **Detection wavelength.** Wavelengths of 215, 254 and 274 nm were evaluated.

Preliminary results indicate that the best conditions are as follows:

1. **SOH and ASOH oils.**

organic modifier: MeCN

gradient mobile phase:

min	0	45	47	60	65	75
%MeCN	5	50	95	95	5	5

flow rate: 1.5 mL/min

sample: 20 μ L

wavelength: 215 nm

2. **Recycle distillate V-1074**

organic modifier: MeCN

gradient mobile phase:

min	0	5	10	20	35	40	40
%MeCN	5	10	80	95	95	5	5

flow rate: 1.5 mL/min

sample: 20 μ L

wavelength: 215 nm

F. Future Work

1. **Vacuum impregnation.** Since Donna Hill and Spanish coal both contain iron (7.75% and 1.26%, respectively) which compares favorably with that in Illinois No. 6 (0.30%), vacuum impregnation of the Donna Hill and Spanish coal may improve sulfur removal by PBu_3 .

2. **The iron catalyst.** Since zerovalent iron in PBu_3 does not work and FeCl_3 does, it remains to test FeCl_2 , since it may be that:

We will also try the $\text{FeCl}_3/\text{PBu}_3$ solution at different times in its transformation from violet to orange to determine where maximum catalysis occurs. It may also be possible to learn something about the number of species present by following the UV/visible spectral changes for isosbestic points.

3. **The solid state peak at 3 ppm.** It may be that H_2O treatment is insufficient to hydrolyze what may be $(\text{ArO})_3\text{P}=\text{O}$. Thus we will attempt a base hydrolysis followed by acidification to see if H_3PO_4 can be observed in the coal matrix.

4. **Catalytic HDS.** We will repeat the Illinois No. 6/ H_2 / PBu_3 reaction in a pressure bomb at temperatures approaching 300 °C in hopes that the enthalpies (and rates) will be in our favor under more vigorous conditions. If necessary, we will add a hydrogenation catalyst such as Pd/C .

5. **HPLC of coal resids.** These studies will continue. We have recently ordered an RP-HPLC column twice as long as that currently being used in hopes of improving the chromatographic resolution.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Table I. Reactions with Bu₃P

Run No.	Reactants	Reaction Conditions	³¹ P chemical shifts, ppm	% sulfur removal
			solution (solid)	(relative)
1	Ill. #6, without vac.	250 °C, reflucl for 2 d with prior vac. impregnation	48.50, 45.23 ^a	98.69
2	Ill. #6, dried under vac.	250 °C, reflux, 2 d without prior vac. impregnation	48.44, 44.88 ^a	92.17
3	Ill. #6, dried under vac. at 60 °C for 2 d	250 °C, reflux, 2 d with prior vac. impregnation	48.51, 44.32 ^a (50, 32, 3, -33)	98.69
4	Ill. #6 dried with 2,2-dimethoxypropane	250 °C, 2 d reflux without prior vac. impregnation	48.47, 44.51 (50, 31, 3, -33)	91.96
5	dibenzothiophene	250 °C, reflux, 17 h, graphite	44.24	none
6	Spanish coal	250 °C, reflux 2 d	48.51, 44.66 ^a (51, 33, 3, -33 (38))	16.97 ^b
7	Ill. #6	250 °C, reflux for 2 d with prior vac. impregnation under a constant flow of H ₂	(50, 32, 3, -33)	^c
8	Ill. #6	H ₂ O/THF, room temp., 5 h	(52, 32, 3, -33)	
9	Ill. #6	P(MeNCH ₂ CH ₂) ₃ N/C ₆ H ₆ /CH ₃ CN	(54, 33, 3)	

^aPeaks due to the internal standard, Ph₃PMeI, and the excess Bu₃P are also seen. The peaks at 44 and 48 ppm are assigned to OPBu₃ and SPBu₃, respectively. ^bThe total sulfur content of this coal was reported to be 9.31%. ^cThe H₂ flow carried some vapors of Bu₃P. Hence no attempt was made to quantitate the ³¹P NMR of the extract.

DATE

FILMED

3 / 7 / 94

END