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FUNCTIONAL GROUP ANALYSIS IN COAL AND ON COAL SURFACES BY NMR SPECTROSCOPY

Fossil Energy Quarterly Report

July 1, 1989 - September 30, 1989

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ABSTRACT

The reaction of $\text{Cl}\overline{\text{POCH}_2\text{CH}_2\text{O}}$ (2) with moisture in pyridine extracts of Argonne standard coal samples has been found to give results comparable with the ASTM D3302 moisture analyses of these samples. Differences in the two sets of results are discussed. Some exceptionally large solvent effects on ^{31}P chemical shifts of model compounds derivatized with 2 and 8 have been discovered. Initial experiments aimed at labile hydrogen functional group analysis of solid coal samples with 2 and $\text{Me}_2\overline{\text{NPOCH}_2\text{CH}_2\text{O}}$ (15) are described.

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OBJECTIVE

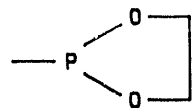
The purpose of this research is to develop a convenient, reliable and rapid NMR method for the determination of a labile-hydrogen functional group composition of coal and coal-derived materials. For this purpose, these functional groups, including water molecules, are derivatized with reagents containing NMR-active nuclei such as ^{31}P or ^{113}Sn . Knowledge of the heteroatom composition of coals is necessary for the development of increasingly sophisticated coal processing technologies.

INTRODUCTION

Because of the important roles of heteroatoms such as oxygen, sulfur, and nitrogen in coal processing, knowledge of the forms in which these heteroatoms appear in coal is required¹. For example, oxidation of coal during weathering can have a serious economic impact on coal recovery by surface-based coal cleaning processes², and also on its caloric content³. The phenolic and carboxylic acid groups created in weathering have been shown to have an adverse effect on froth flotation owing to the influence these groups have on the wettability and electrokinetic properties of coal⁴.

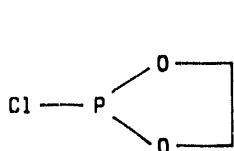
Although Fourier transform phosphorus-31 nuclear magnetic resonance (NMR) spectroscopy has become routine for the qualitative detection of various species in both liquid and solid materials⁵, quantitative applications are still in the developmental stage. The phosphorus-31 nucleus is highly sensitive to its chemical environment, displaying a chemical shift range of over 600 ppm. The peaks are generally very narrow (approximately a few tenths of a ppm for solutions), thus allowing differentiation among compounds having nearly the same chemical environments.

Over the past two years, we have focused our attention on selecting an optimum number of phosphorus reagents from compounds 2 - 12, in Figure 1.

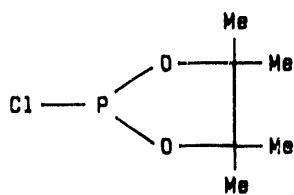


a phospholanyl framework

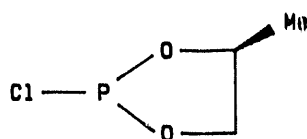
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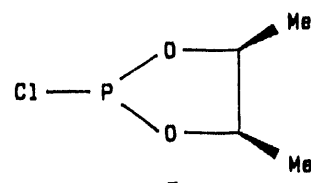
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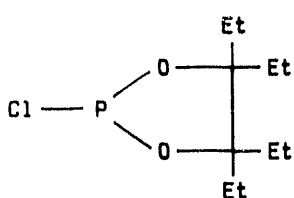
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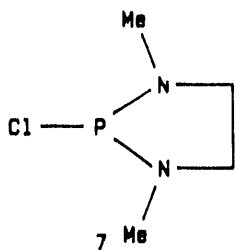
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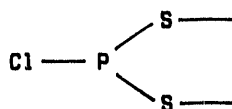
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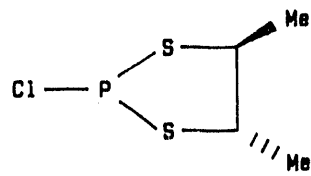
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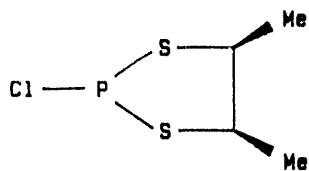
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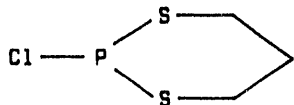
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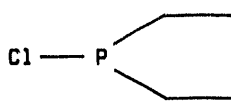
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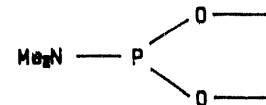
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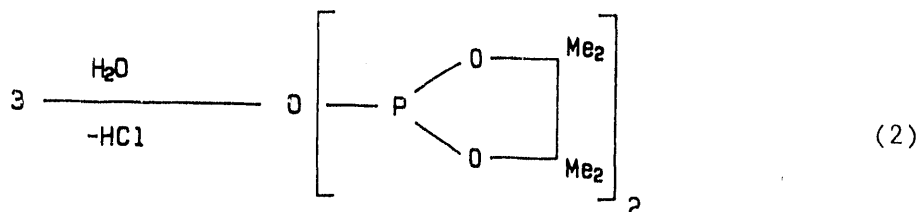
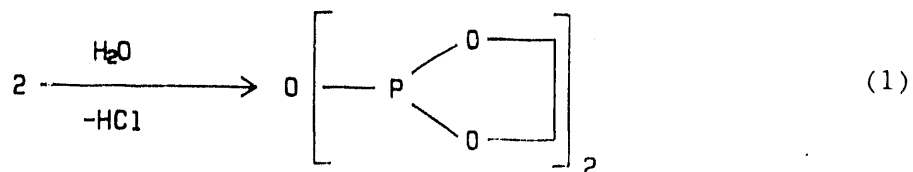
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Figure 1. Structures of Phosphorus-Containing Reagents.

The selection of 2, 3, and 8 was based on the ease with which these reagents react with the labile hydrogens in phenols, carboxylic acids, alcohols, amines, and thiols and their ability to present well-resolved ^{31}P NMR spectra for the various model compounds studied^{6,7}.

This groundwork enabled us to begin and complete Phase I and Milestone 1 of our FWP for FY 1989, namely the quantitative analysis of model compound mixtures using reagents 2, 3, and 8. Promising preliminary results for Phase II, namely the qualitative and quantitative analysis of coal condensates and extracts have already been obtained⁸.

Recently, we serendipitously discovered that reagents such as 2 and 3, when in excess, react with water in pyridine to give the products shown below⁶. Among the published methods for determining moisture contents of



coals are the ASTM thermogravimetric procedure⁹; microwave absorption¹⁰, transmission¹¹ and capacitance measurements¹²; gamma-ray backscattering^{12,13}, IR spectroscopy¹⁴, thermalization of fast neutrons¹⁵, and a recently reported gas chromatographic-mass spectral technique involving $^{16}\text{O}/^{18}\text{O}$ exchange¹⁶. NMR techniques appear to have been restricted to some early ^1H resonance measurements¹⁷. To our knowledge, no reports have appeared in which heteronuclear NMR spectroscopy has been applied to the determination of moisture in pyridine extracts of coal.

ACCOMPLISHMENTS

In the last quarterly report, we described some encouraging results of ^{31}P NMR moisture determinations of non-standardized coal samples using reagent 2. Since then, we have extended the method to two Argonne Premium Coal samples of two meshes each (Table I). The ampoules containing these samples were broken under N_2 and immediately extracted with pyridine as described earlier⁷.

Table I. Moisture Analyses of Argonne Premium Coal Samples.

Coal Sample	Mesh Size	Lit. ^a	ASTM D3302	Average	^{31}P NMR (2) ^b	Average
North Dakota Beulah-Zap Lignite Type	-100	32.24	31.38, 31.60	31.39	26.25, 29.77	28.01
North Dakota Beulah-Zap Lignite Type	-20	32.24	32.75, 32.87	32.81	25.19, 24.67	24.93
Pocahontas No. 3	-100	0.65	0.23, 0.24	0.24	0.62, 0.52	0.57
Pocahontas No. 3	-20	0.65	0.66, 0.69	0.68	0.59, 0.65	0.62

a) K. S. Vorres, Users Handbook for the Argonne Premium Coal Sample Program.

b) Using PPh_3 in C_6D_6 as an external standard.

As yet, we are unable to explain the disparity in the ASTM gravimetric results between the two meshes of the Pocahontas No. 3, especially in view of the consistency in the ^{31}P NMR results. It appears that the disparate and low ^{31}P NMR results for the North Dakota samples are a result of a minor limitation in our method. We have determined from standard solutions of moisture in pure pyridine, that when the concentration of water is too high, unwanted side reactions occur giving calculated water concentrations that are unacceptably low (Table II). Thus far, the following conditions appear to be optimal¹⁷:

1. $P(O-n Bu)_3$ instead of PPh_3 should be used as an internal standard in order to minimize the sweep width.
2. Reagent 2 should be added under ice cooling of the sample.
3. The nmr spectrum should be run after the sample has been in the ice bath for 2 to 5 minutes.
4. The moisture content of the pyridine solution should not exceed 4 mg/mL.
5. A large excess of reagent 2 is required.

Table II. ^{31}P NMR Analyses of Standard Pyridine/ H_2O Samples Using 2.

Experiment	Amount of Water Present (mmol)	Amount of Water Calculated (mmol)	Deviation (rel. %)	Deviation Within the Same Sample (rel. %) ^a
Sample 1	0.808	0.722	-10.64	+0.19
	0.808	0.726	-10.15	+0.74
	0.808	0.714	-11.63	-0.93
Sample 2	0.439	0.413	-5.92	-0.56
	0.439	0.412	-6.15	-0.80
	0.439	0.421	-4.10	+1.36

^a Multiple integrations on same sample.

During the next quarter, the Argonne Premium Coal Samples will be re-run using these nmr requirements.

In establishing the above-mentioned nmr conditions, we accidentally discovered an interesting and potentially useful phenomenon. Several model compounds display astoundingly large ^{31}P nmr chemical shift differences when measured in CDCl_3 versus pyridine. Compounds derivatized with **2** register differences ranging up to 9 ppm while those derivatized with **8** register shift differences ranging up to 16 ppm.

From the data in Tables III and IV, the shifts for both reagents are largest for amine derivatives but trends are presently not apparent. The origin of this unusually large solvent dependence of chemical shift is presently obscure. Once understood, however, it could be used to help identify primary and secondary amines, whose presence in coal extracts is controversial.

During this quarter, the derivatization of solid coal (Illinois No. 6) and model compounds (polyallyl alcohol (PAAL) and polyacrylic acid (PAAC)) with **2** was initiated, yielding some intriguing results. The solids were reacted with solutions of **2** in pentane and THF, with neat **2** and with gaseous **2**. Under all conditions, the ^{31}P absorptions of the three solid materials was in the upfield region (2 to 10 ppm, Table V) indicative of tetravalent phosphorus. We believe this is may be due to Arbuzov-type rearrangements of the derivatized functional groups occasioned by the presence of liberated HCl:

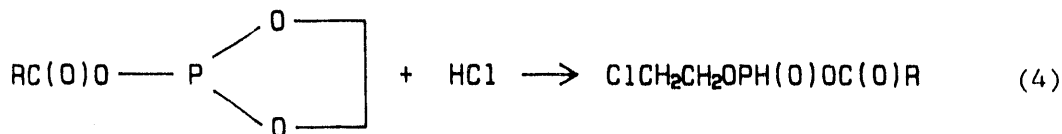
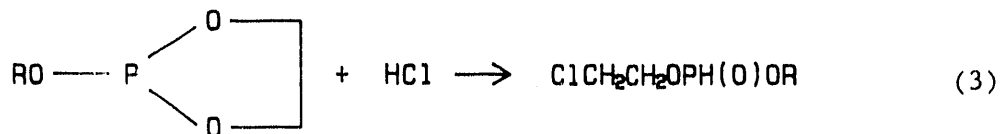


Table III. Chemical Shifts of Selected Model Compounds Derivatized with
2-Chloro-1,3,2-dioxaphospholane (2)^a.

Model Compound	Chemical Shift (ppm)		
	In CDCl ₃ ^b	In Pyridine	Difference ^c
<u>Phenols</u>			
2,3,6-trimethylphenol	131.54	132.32	+0.78
2,6-dimethylphenol	131.30	132.00	+0.70
guaiacol	130.82	131.22	+0.40
phenol	128.59	129.39	+0.80
β -naphthol	128.62		
8-quinolinol	128.77	129.22	+0.45
p-cresol	128.53	129.38	+0.85
3,5-dimethylphenol	128.64	129.58	+0.94
<u>Alcohols</u>			
methanol	133.3	132.64	-0.66
benzyl alcohol	134.4	133.72	-0.68
isoamyl alcohol	134.1	134.96	+0.86
<i>l</i> -menthol	135.9	136.31	+0.41
t-butanol	134.8	135.03	+0.23
cyclohexanol	134.6	134.93	+0.33
t-amyl alcohol		134.82	
<u>Acids</u>			
terephthalic acid	129.54	129.03	-0.51
benzoic acid	128.24	128.88	+0.64
<i>d</i> -mandelic acid	128.47		
2,4,6-trimethoxybenzoic acid	127.71	128.58	+0.87
L-methylcinnamic acid	127.99		

(continued)

Table III. Chemical Shifts of Selected Model Compounds Derivatized with 2-Chloro-1,3,2-dioxaphospholane (2)^a.

Model Compound	Chemical Shift (ppm)		
	In CDCl ₃ ^b	In Pyridine	Difference ^c
<u>Amines</u>			
2,6-dimethylaniline	137.9	133.77	-4.13
o-toluidine	134.9	131.81	-3.09
di-isopropyl amine	144.3	135.57	-8.73
N-ethylaniline	136.3		
pyrazole	120.1		
<u>Thiols</u>			
2-propanethiol	201.7	201.71	+0.01
thiophenol	194.7		
o-thiocresol	194.34		
3,4-dimethylthiophenol	194.97		

a) Blank spaces indicate data not yet collected.

b) See Reference 6.

c) Positive prefix indicates a shift to lower field, negative prefix for a shift to higher field.

Table IV. Chemical Shifts of Selected Model Compounds Derivatized with 2-Chloro-1,3,2-dithiaphospholane (8)^a.

Model Compound	Chemical Shift (ppm)		
	In CDCl ₃ ^b	In Pyridine	Difference ^c
<u>Phenols</u>			
2,3,6-trimethylphenol	160.72	162.15	+1.43
2,6-dimethylphenol	160.98	162.49	+1.51
guaiacol	160.45	161.44	+0.99
phenol	152.51	154.41	+2.20
β -naphthol	154.32	156.24	+1.92
8-quinolinol	167.38	170.02	+2.64
p-cresol	152.11	153.85	+1.74
3,5-dimethylphenol	153.33	155.43	+2.10
<u>Alcohols</u>			
methanol	145.98	145.96	-0.02
benzyl alcohol	145.11	145.52	+0.41
isoamyl alcohol	143.41	143.80	+0.39
l-menthol	151.78	152.32	+0.54
t-butanol	145.66	147.21	+1.55
cyclohexanol	147.17		
t-amyl alcohol		147.13	
<u>Acids</u>			
terephthalic acid	insoluble	157.57	
	product	158.66	
benzoic acid	154.55		
d-mandelic acid			
2,4,6-trimethoxybenzoic acid	159.83	153.05	-6.78
L-methylcinnamic acid	153.19		

(continued)

Table IV. Chemical Shifts of Selected Model Compounds Derivatized with 2-Chloro-1,3,2-dithiaphospholane (8)^a.

Model Compound	Chemical Shift (ppm)		
	In CDCl ₃ ^b	In Pyridine	Difference ^c
<u>Amines</u>			
2,6-dimethylaniline	103.88	87.72	-16.16
<i>o</i> -toluidine	100.61	85.07	-15.54
di-isopropyl amine	92.63	94.02	+1.39
N-ethylaniline	99.97	99.18	-0.79
pyrazole	91.43	91.93	+0.50
<u>Thiols</u>			
2-propanethiol	102.16	104.16	+2.00
thiophenol	113.43		
<i>o</i> -thiocresol	112.31		
3,4-dimethylthiophenol	112.94		

a) Blank spaces indicate data not yet collected.

b) See Reference 7.

c) Positive prefix indicates a shift to lower field, negative prefix for a shift to higher field.

Table V. Solid State ^{31}P NMR Data for Reactions of 2.

Solid Sample	^{31}P Chemical Shifts (ppm)			
	2 in Pentane	2 in THF	2 (neat)	2 in Gas Phase
Polyallyl Alcohol (PAAL)	10.0 ($J_{\text{P-H}}=700 \text{ Hz}$)	10.0 ($J_{\text{P-H}}=700 \text{ Hz}$)	9.6	9.8
	2.1 ($J_{\text{P-H}}=700 \text{ Hz}$)	2.1 ($J_{\text{P-H}}=700 \text{ Hz}$)	2.0	2.1
Polyacrylic Acid (PAAC)	8.3	8.3	8.0	8.3
Illinois Coal #6	5.46	5.46	5.46	5.50

These results require further investigation with monomeric solid model compounds since it is not clear why PAAL shows two resonances. Moreover, the origin of the peak in the Illinois No. 6 sample should be clarified. To circumvent the HCl problem, we derivatized the three solids with reagent 13 in hopes that the liberated Me_2NH would be unreactive. With derivatized PAAL and PAAC, this seems to be the case, since only one peak in the trivalent ^{31}P region (~ 130 ppm) is seen in each case (Table VI).

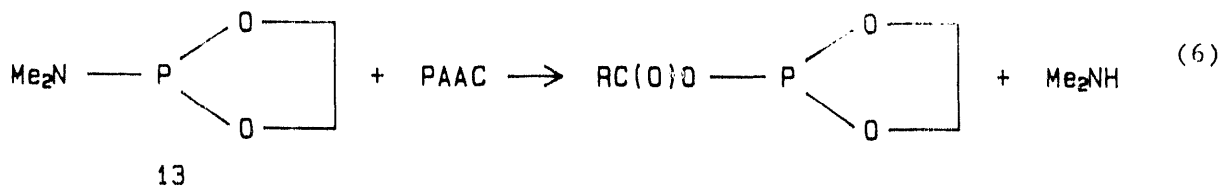
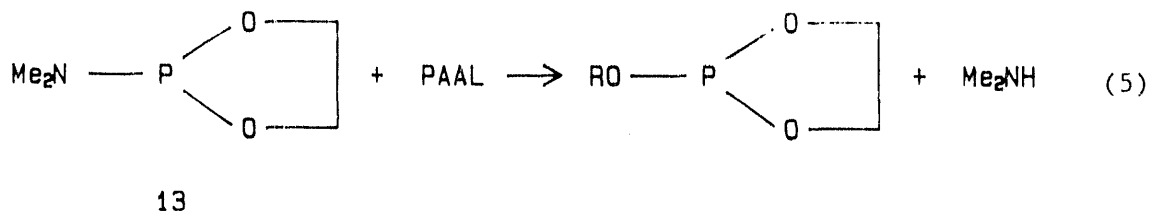


Table VI. Solid State ^{31}P NMR Data for Reactions of 13.

Solid Sample	^{31}P Chemical Shifts (ppm)			
	13 in Pentane	13 in THF	13 (neat)	13 in Gas Phase
Polyallyl Alcohol (PAAL)	132	132	131	132
Polyacrylic Acid (PAAC)	131	131	130	130
Illinois Coal #6	130	132	132	132
	56	33	25	23
	37	25	17	17
	23	2	9	10
	3		3	3

In addition to a similar peak in the 130-132 ppm region in the Illinois #6 sample, however, additional peaks are observed in the upfield tetra-coordinate phosphorus region. Hydrolysis by moisture in the coal may be responsible for this observation and further experiments are being designed to test this hypothesis.

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