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

Fossil Energy Quarterly Report

October 1, 1989 - December 31, 1989

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ABSTRACT

An accurate knowledge of the oxygen-bearing labile hydrogen functional groups (e.g., carboxylic acids, phenols and alcohols) in coal is required for today's increasingly sophisticated coal cleaning and beneficiation processes. Phospholanes (compounds having the general structure $\overline{\text{POCH}_2\text{CH}_2\text{O}}$ (1)) are a class of compounds being investigated as reagents for the tagging of labile hydrogen functional groups in coal materials with the NMR-active ^{31}P nucleus. Of twelve such reagents investigated so far, 2 (2-chloro-1,3-dioxaphospholane, $\text{Cl}\overline{\text{POCH}_2\text{CH}_2\text{O}}$) and 8 (2-chloro-1,3-dithiaphospholane, $\text{Cl}\overline{\text{PSCH}_2\text{CH}_2\text{S}}$) have been found to be useful in identifying and quantitating, by ^{31}P NMR spectroscopy, labile hydrogen functional groups in an Illinois No. 6 coal condensate. Reagent 2 has also been used to quantitate moisture in pyridine extracts of Argonne Premium Coal Samples. Preliminary ^{119}Sn NMR spectroscopic results on model compounds with the new reagent $\text{CF}_3\text{C}(\text{O})\text{NHSnMe}_3$ (N-trimethylstannyltrifluoroacetamide, 14) suggest that labile hydrogen functional groups in coal materials may be more precisely identified with 14 than with phospholanes.

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OBJECTIVE

The purpose of this research is to develop a convenient, reliable and rapid NMR method for the determination of labile-hydrogen functional groups which are components 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 ^{119}Sn . Knowledge of the heteroatom composition of coals is necessary for the development of increasingly sophisticated coal processing technologies.

INTRODUCTION

The presence in coal of heteroatoms such as oxygen, sulfur, and nitrogen is important in determining the processing methodology to be utilized. Because of this, a knowledge of the forms in which these heteroatoms occur in coal is required¹. Thus, for example, oxidation of coal during weathering has a potentially serious economic impact on coal recovery by surface-based coal cleaning processes², and also on its caloric content³. Moreover, the phenolic and carboxylic acid functionalities created during weathering have an adverse effect on froth flotation owing to the influence these groups have on the wettability and electrokinetic properties of coal⁴.

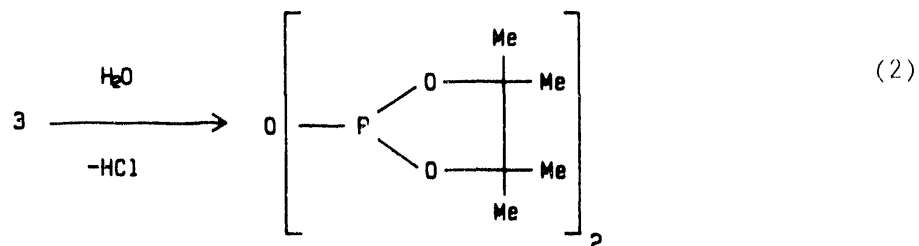
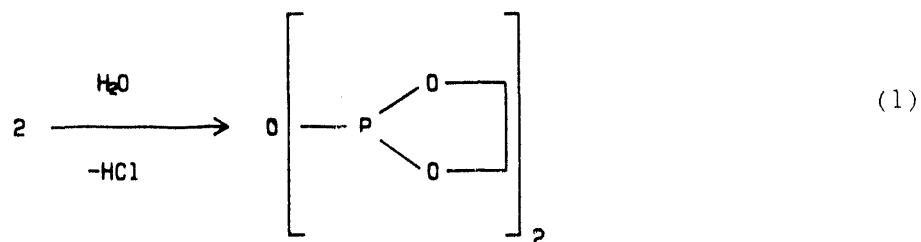
Fourier transform phosphorus-31 nuclear magnetic resonance (NMR) spectroscopy has long been routine for the qualitative detection of various species in both liquid and solid materials⁵. Quantitative applications, however, are still in the embryonic stage of development. The same is true of ^{119}Sn NMR spectroscopy. The ^{31}P and ^{119}Sn nuclei are highly sensitive to their chemical environments, displaying wide chemical shift ranges. The NMR absorptions are generally quite narrow in solution, thus allowing differentiation among compounds having nearly the same chemical environments. In the solid state, chemical shifts are generally broader by several orders of magnitude than in solution because of chemical shift anisotropy. We have observed, however, that solid model compounds and coals derivatized with phosphorus reagents, although still appearing to be solids

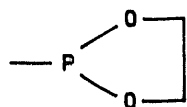
after derivatization, can display rather narrow isotropic shifts characteristic of liquids. This potentially advantageous phenomenon is apparently due to greater freedom of the derivatizing moieties.

Recently, we have directed our efforts to selecting an optimum number of phosphorus reagents from the class of compounds known as phospholanes (1 in Figure 1). The selection of 2, 3, and 8 from the twelve (2 - 12) we investigated^{6,7} was based on the ease (room temperature) with which these reagents react with the labile-hydrogens in phenols, carboxylic acids, alcohols, amines, and thiols and their ability to present well-resolved ³¹P NMR spectra for the various model compounds studied.

This groundwork enabled us to 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. Substantial portions of Phase II and Milestone 3, namely the qualitative and quantitative analysis of coal condensates and extracts, have also been accomplished^{8,9}. The ³¹P spectrum in Figure 2 of a mixture of phenols derivatized with reagent 8 reveals the excellent resolution of chemical shifts realized with this reagent.

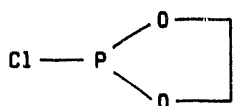
From our last quarterly report¹⁰, it will be recalled that we discovered serendipitously that reagents such as 2 and 3, when in excess, react with water in pyridine to give the products shown below⁶. Although other methods for determining moisture contents of coal exist (see last quarterly



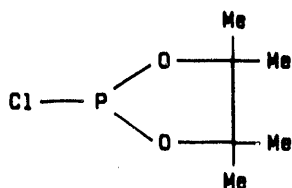


a phospholanyl framework

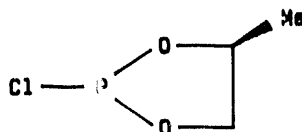
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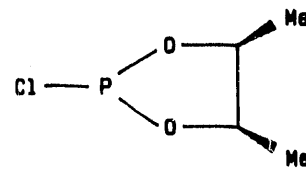
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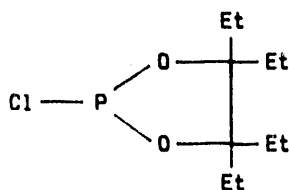
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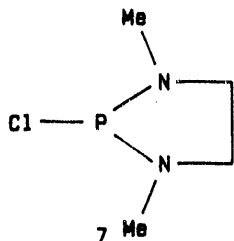
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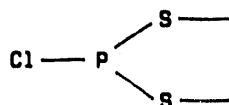
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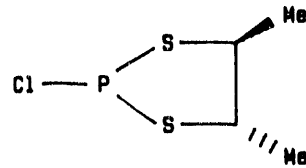
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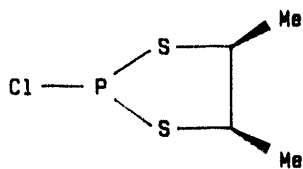
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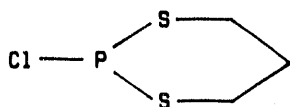
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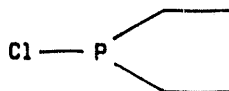
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Figure 1. Structures of Phosphorus-Containing Reagents.

report)¹⁰, NMR techniques appear to have been restricted to some early ¹H resonance measurements. 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. Since moisture in solid coal affects its beneficiation, cleaning and value as a fuel, it is necessary that we eventually gain a more precise knowledge not only of precise water contents but also how water is distributed in coal for example as surface moisture, physically absorbed water and chemisorbed water. Potentially, our NMR approach lends itself to differentiating among these types of moistures in solid coals.

ACCOMPLISHMENTS

We have confirmed our suspicion described in the last quarterly report¹⁰ that relatively high water concentrations in pyridine extracts of coal lead to an artificially low intensity of the ³¹P NMR peak associated with the desired product in reaction 1. Table I contains data acquired from further refinement of our optimal conditions¹¹. From these experiments, we conclude that the optimal water concentration in pyridine is actually in the range of 2 mg/mL rather than the 4 mg/mL that was reported earlier. The deleterious effect of higher water concentrations appears to be due to precipitation of pyridine hydrochloride (formed from HCl and pyridine) with which the desired product in reaction 1 is co-precipitated. At low water concentrations, less HCl is produced and the pyridine hydrochloride formed remains in the solution. Concentrations of water substantially below 2 mg/mL are undesirable since the larger number of NMR scans requires longer spectral acquisition times, during which further reaction of the product of reaction 1 with reagent 2 appears to occur (see last quarterly report)¹⁰. The use of the solid reference tris(2,3,6-trimethylphenyl) phosphite in place of the liquid tri-n-butyl phosphite did not alter the precision of these results.

During this quarter, further moisture determinations were carried out with a North Dakota Beulah-Zap coal (Argonne Premium Coal Sample, No. 8) since the values reported in the last quarterly report¹⁰ were extremely low compared with the ASTM D3302 method. In Table II, collected data for two mesh sizes and two pyridine extraction times for this coal are found. It is clear that the longer extraction time leads to higher moisture contents. This finding accords with that of previous workers¹² who reported that lignite-type coals require longer oven heating to drive off moisture than

Table 1. ^{31}P NMR Analysis of Standard Pyridine/ H_2O Samples Using 2.

Expt.	Amount of Water Present (mmol/mL)	Amount of Water Calculated (mmol/mL)	Deviation (rel. %)	Deviation From Calculated Avg. (rel. %) ^a
Sample 1	0.404	0.361	-10.64	+0.32
		0.357	-11.76	-0.93
		0.362	-10.40	+0.60
Sample 2	0.220	0.207	-5.92	+0.08
		0.206	-6.38	-0.40
		0.207	-5.69	+0.32
Sample 3	0.091	0.090	-1.75	-2.00
		0.093	+1.53	+1.27
		0.092	+0.98	+0.73
Sample 4	0.090	0.088	-1.34	-1.05
		0.090	± 0.00	+0.30
		0.090	+0.45	+0.75
Sample 5	0.070	0.069	-0.57	± 0.00
		0.071	+2.44	+2.90
		0.067	-3.59	-2.90
Sample 6	0.024	0.026	+4.51	-2.05
		0.027	+8.61	+1.79
		0.026	+6.97	+0.26

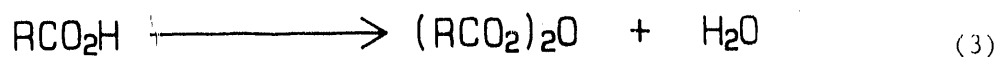
^a Multiple integrations on same sample.

higher-rank coals. The moisture contents for the four-hour extractions tend to be higher than the ASTM values. This could be due to greater effectiveness of the extraction/NMR method in releasing chemisorbed water or possibly to a contribution from decomposition of oxygen-containing functional groups in lignite coals which are reported to occur even below 100°C ¹². The latter seems unlikely since the ASTM and extraction methods require temperatures that are roughly in the same range (105° and 115° , respectively). Moreover, preliminary experiments with benzoic acid reveal that anhydride formation (reaction 3) under our extraction conditions does not appear to be a problem.

Table II. Moisture Determination of a North Dakota Beulah-Zap Coal (Argonne Premium Coal Sample).

	Moisture Content			
	Lit. ^a (%)	ASTM D3302 (%)	³¹ P NMR Spectroscopy (%)	Pyridine Extracting Time (%)
-100	32.24	31.39	26.25	2
			29.77	
		32.76	37.80	4
			36.75	
			37.37	
			33.00	
-20	32.24	32.75	25.19	2
			24.67	
		34.29	35.36	4
			34.43	
			38.46	
			39.55	

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



The release of chemisorbed water by our method (as is believed to be the case in azeotropic distillation of coals with xylene or toluene^{13a,14}) is more likely to be the cause of the high moisture contents in Table II. Further investigations are warranted in order to clarify these results and also to determine via solid state ³¹P NMR spectroscopy whether or not the pyridine-extracted coal residue is free of water. While a given coal extract in Table II gives reproducible results from the two or three NMR samples taken from it, separate four-hour extraction experiments do not. Because the coal samples used for extraction are relatively small (ca. 150 mg) sample inhomogeneity on this scale may be a problem and this question should be resolved.

As we expected, 14 reacts with labile hydrogen functional groups under mild conditions. Thus alcohols, phenols, and acids are nearly quantitatively converted to their corresponding tin derivatives at room temperature, according to the stoichiometry indicated in reaction 5. Since our analysis



of coal materials will take place in the presence of excess reagent, the conversions will undoubtedly be quantitative for all practical purposes, although this remains to be proven.

Preliminary studies with model compounds have informed us that the ^{119}Sn NMR shifts of derivatives such as MeC(O)OSnMe_3 , EtOSnMe_3 and PhOSnMe_3 have chemical shifts that lie within a range of only about 4 ppm in hexane, and moreover the shifts are quite concentration dependent (e.g., 15 ppm over a range of 0.1 to 1.3M for EtOSnMe_3). However, in pyridine, the solvent in which we plan to carry out our coal material analyses, this range widens to highly encouraging 17 ppm, with the welcome bonus that the chemical shifts are completely concentration independent. Presumably, the ^{119}Sn NMR shift sensitivity to concentration in hexane stems from the poor donor ability of this solvent coupled with the proclivity of tin to become five-coordinate. The latter is accomplished with the oxygen heteroatom lone pairs in neighboring solute molecules. This effect is expected to be concentration dependent. Pyridine, on the other hand, is a good donor solvent, efficiently complexing the tin atom in all the solute molecules over a wide range of concentrations (0.05 to 3M in the case of PhOSnMe_3 , for example). Before proceeding to pyridine solution nmr studies of coal condensates and pyridine extracts of coal derivatized with our new ^{119}Sn reagent, we will first record the ^{119}Sn NMR shifts of a series of model compounds derivatized with 14 in pyridine in order to establish a data base.

The greater spread of chemical shifts of ^{119}Sn in pyridine solutions than of ^{31}P should allow us to identify the organic substituents on a given labile hydrogen functional group even more precisely. This ^{119}Sn NMR

technique will then be extended to solid coal samples. A thorough knowledge of the oxygen functional group content and environment is crucial to efficient processing and beneficiation of coal.¹

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