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FOSSIL ENERGY

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

FOSSIL ENERGY QUARTERLY REPORT
April 1, 1989 - June 30, 1989

J. G. Verkade

Ames Laboratory
Iowa State University
Ames, Iowa 50011-3020

Date Transmitted: June 1989

Prepared for:
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

Operated for the U. S. Department of Energy
under contract No. W-7405-ENG-82

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ABSTRACT

The compound $\mathrm{Cl\overline{POCH_2CH_2O}}$ (**2**) reacts clearly with moisture in pyridine extracts of coal to form $\mathrm{O(\overline{POCH_2CH_2O})_2}$. This reaction was used as a basis for the development of a rapid and convenient determination of the moisture content in coals by ^{31}NMR spectroscopy. The compound $\mathrm{Cl\overline{PSCH{=}CHS}}$ (**15**) was synthesized and evaluated as a reagent for analyzing labile hydrogen functional groups in coal. This reagent proved to be less suitable than **2**, however.

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OBJECTIVE

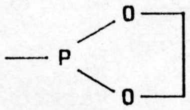
The purpose of this research is to develop a convenient, sensitive, reliable and rapid technique for the determination of the labile-hydrogen functional group composition of coal and coal-derived materials by the NMR spectroscopy of their derivatives made with reagents containing the NMR-active nuclei ^{31}P, ^{113}Sn, or ^{205}Tl. Knowledge of the heteroatom composition of coals is necessary to the development of increasingly sophisticated coal processing technologies.

INTRODUCTION

Oxygen, sulfur and nitrogen play a very important role in coal processing, consequently rendering it necessary to acquire a knowledge of the forms in which these heteroatoms appear in coal[1]. The oxidation of coal during weathering can have a significant deleterious economic impact on coal recovery by surface-based coal cleaning processes, such as recovery by froth flotation and oil agglomeration[2], and also on its caloric content in its utilization as a fuel[3]. The phenolic and carboxylic acid groups created in weathering appear to have an adverse effect on froth flotation owing to the influence these groups have on the wettability and electrokinetic properties of coal[4].

Fourier transform phosphorus-31 nuclear magnetic resonance (NMR) spectroscopy has in recent years become a routine method for the measurement of various species in both liquid and solid materials[5]. The technique is highly sensitive to the chemical environment of the ^{31}P nucleus, 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 in most cases differentiation between compounds having nearly the same chemical shifts.

In 1987 and 1988, we focused our attention on selecting an optimum number of phosphorus reagents from compounds 2 - 12, in Figure 1. The



a phospholanyl framework

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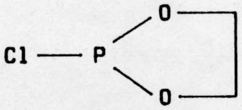

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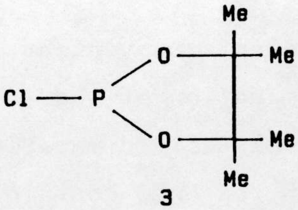

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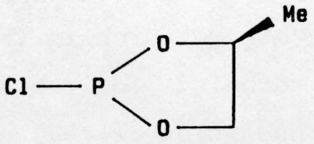

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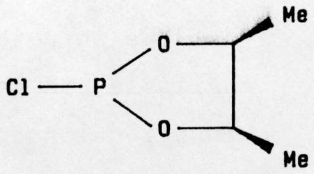

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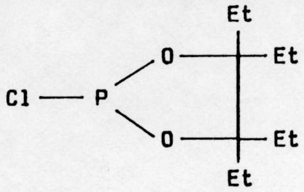

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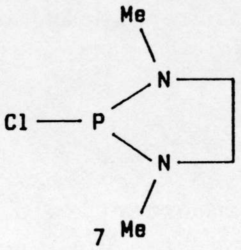

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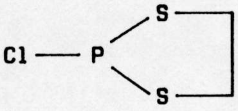

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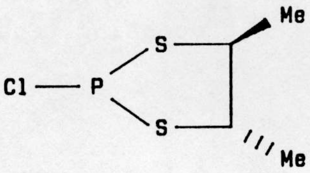

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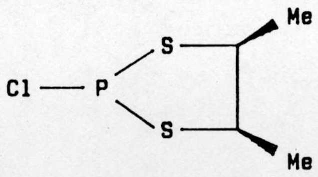

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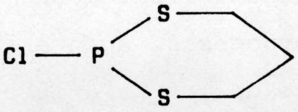

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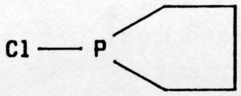

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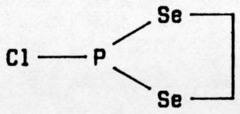

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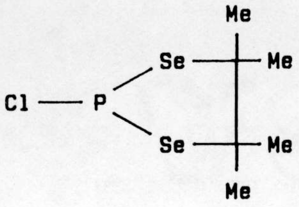

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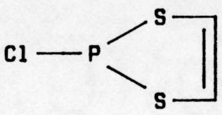

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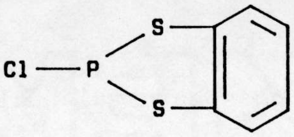

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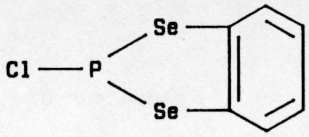

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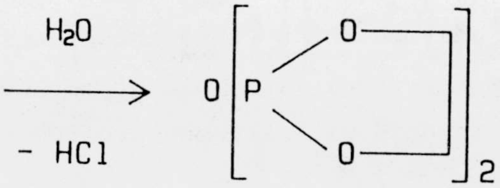
Figure 1. Structures of Phosphorus-Containing Reagents.

selection of **2**, **3**, and **8** was based on the abilities of these reagents to react cleanly with the labile-hydrogens in phenols, carboxylic acids, alcohols, amines, and thiols under mild conditions, and to present well-resolved ^{31}P NMR spectra for the various compounds derivatized in qualitative studies. Most of our results of these studies have been published[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**. Phase II, namely the qualitative and quantitative analysis of coal condensates and extracts, was begun by Dr. Lensink (our postdoctoral research associate) before he left in December of 1988.

During 1988, we serendipitously discovered that reagents such as 2 and 3 when in excess, react with water in pyridine to give the products shown below.[6] Among the published methods for determining moisture contents of

2



31-P = 121.85 ppm (1)

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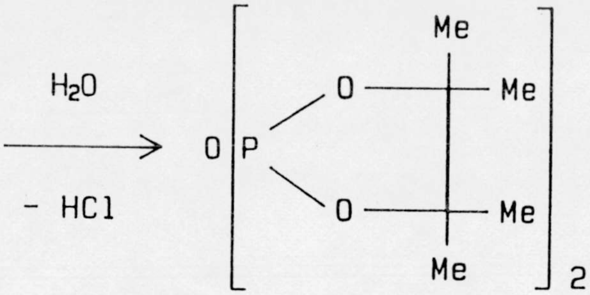


31-P = 132.82 ppm (2)

coals are the ASTM thermogravimetric procedure,[8] microwave absorption[9] or transmission,[10] capacitance measurements,[11] gamma-ray backscattering,[11,12] IR spectroscopy[13], and thermalization of fast neutrons.[14] A gas chromatographic-mass spectral technique involving $^{16}O/^{18}O$ exchange has also been reported recently.[15] NMR techniques appear to have been restricted to some early ^1H resonance measurements.[16] To our knowledge, no reports have appeared in which heteronuclear NMR spectroscopy has been applied to determine moisture in pyridine extracts of coal.

ACCOMPLISHMENTS

Because Dr. Reinartz, Dr. C. Lensink's replacement, began work on the project three months after Dr. Lensink's departure, the goals for Phases II-IV as set out in the January 20, 1989, WAS document are delayed by approximately one quarter.

Using reagent 2, we determined the moisture contents of pyridine extracts of several coals and have submitted our preliminary findings for presentation at the Pacifichem Meeting in December.[16] In one procedure, the coal extract is prepared by heating the sample in pyridine for two hours. To a 2.0 ml aliquot of the supernatant is added 20 to 45 mg of $Cr(acac)_3$ as a relaxagent and 0.2 mL of 2. The ^{31}P NMR peak areas corresponding to the excess reagent and the product shown in reaction (1) were then measured by integration on the NMR spectrometer. Table I contains data we have recently obtained by this ^{31}P NMR procedure, which compare favorably with our analyses of the moisture content carried out by the standard ASTM method. We are currently establishing the reproducibility of our method. We will then repeat the procedure on experiments with Argonne premium coal samples.

Table I. Moisture Contents of Coals.

	% Moisture Determined by	
Coal	^{31}P NMR	ASTM D3302
Illinois #6 16-02-86 40-200 mesh	3.06	3.14
Lower Kittanning -80 mesh	0.48	0.51
Illinois #6 01-24-89 -80 mesh	2.26	1.97

Initially, we chose to investigate pyridine extracts of coals for four reasons: 1) Pyridine is a base which assists reaction (1) shown on page 3 by forming a soluble hydrochloride salt; 2) Pyridine is a convenient and good extracting solvent; 3) Pyridine does not react with reagent **2** or its hydrolysis product; 4) Pyridine readily dissolves moisture. From our preliminary results, it appears that our method has at least three advantages: 1) Each water molecule produces two NMR-active, 100% abundant ^{31}P nuclei in the product in reaction (1) giving a substantial peak for easy integration; 2) Pyridine apparently extracts moisture quite quantitatively; 3) Because our method is easily carried out in an inert atmosphere and at room temperature, oxidation and loss of volatiles other than water (both being possible sources of error in the thermogravimetric ASTM method) are avoided.

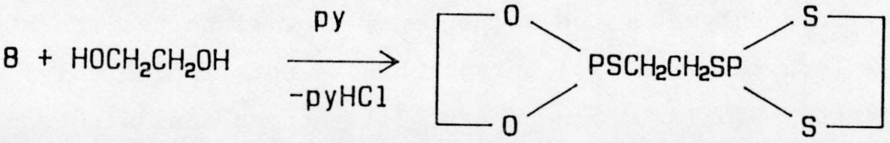
During the next quarter we plan to extend this method to determining the surface moisture in solid coals. This will be done by reacting **2** with the surface moisture accumulated by thermally dried coals in the standard gravimetric method.[17] We will then measure this water content by ^{31}P NMR spectroscopy in a solvent (such as pentane) that dissolves the hydrolysis product of **2** (see reaction (1)) but which does not (appreciably) extract coal components. Similar measurements will then be done with non-predried coals and a comparison of the data made with the dried/re-moisturized samples. If the data compare favorably, our method would be faster as well as non-destructive since no heating would be involved.

As an extension of our continued search for new and better reagents, the new derivatizing agent **15** was synthesized[18] in order to evaluate the influence of unsaturation on the separation in ^{31}P NMR peaks of derivatized model compounds. As can be seen from Table II, this reagent unfortunately does not constitute enough of an improvement to warrant its synthesis (which is more labor-intensive than **2** or **8**). We still plan to synthesize **16** and **17** to see if the improvement afforded by incorporation of sulfur atoms over oxygen atoms in the ring system of a reagent is augmented by the presence of selenium atoms.

Table II. Comparison of ^{31}P NMR Chemical Shifts of Model Compounds Derivatized with Reagents **15**, **8**, or **2**.

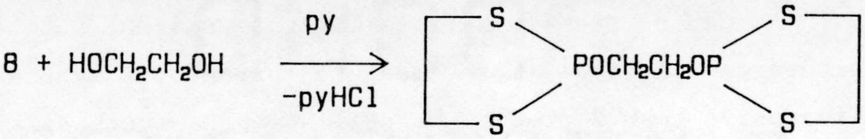
Model Compounds	Reagents 15	 8	 2
2-propanethiol	111.58	102.16	201.7
ℓ-menthol	133.12	151.78	135.9
2-methyl-cinnamic acid	144.38	153.19	127.99
2,6-dimethyl-aniline	88.87	103.88	--
methanol	131.00	145.98	133.3

In a previous publication,[7] we showed that the model diol ethylene glycol reacts with reagent **8** in pyridine according to reaction (3). This reaction involves a transesterification as well as derivatization. Dr. Reinartz has recently discovered that this reaction begins to occur only



(3)

when the molar ratio of **8** to diol decreases to 2:1. As long as **8** is present in large excess (i.e., our normal conditions for derivatizing pyridine extracts of coal) only the expected derivatization reaction (4) takes place. At high ethylene glycol concentrations, complete transesterification occurs,



(4)

as evidenced by the stench of liberated $HSCH_2CH_2SH$. In the case of the diol $HOCHMeCH_2OH$, partial transesterification becomes evident at a ratio of **8**/diol of 4:1. Other difunctional systems such as oxalic acid are also under investigation.

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