³¹P NMR ANALYSIS OF COAL MOIETIES
BEARING -OH, -NH, AND -SH FUNCTIONS

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Quarterly Report

October 1, 1989 - December 31, 1989

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We began our work by derivatizing model carboxylic acid, phenols and alcohols with reagent 1a on the premise that since reagent 2 provided better ³¹P shift separation than 3a (presumably for steric reasons) the greater

bulk of 1a should constitute an even further improvement. This was definitely not the case (for reasons that are obscure) and it was deemed best not to synthesize 1b (which we were hoping would allow resolution of shifts due to enantiomeric sites in coal moieties. A second reason for abandoning this approach is that 3b, which like 1b is also chiral, additionally exists as two geometric isomers (cis and trans), thereby doubling the number of ³¹P nmr peaks to contend with (e.g., four peaks for an optically active alcohol). The third reason for dropping this strategy is that we have preliminary results that a ¹¹⁹Sn reagent will be far more promising.

Before describing the latter results, it should be mentioned that we were able to finish a study with 2¹ (preprint enclosed) wherein we were able to demonstrate that this reagent is to date the best phosphorus reagent for resolving the ³¹P nmr chemical shifts of a variety of compounds within a given functional group class, as well as for the separation of shift ranges among the various classes. We have also made a comparison of the viabilities of reagents 2 and 3a for the quantitative analysis of a model mixture of phenols and to a low temperature pyrolysis condensate of an

Illinois No. 6 coal sample.² Serendipitously, reagent 3a reacts with water to give the product in reaction 1. This reaction can be used to quantitate

water in coal extracts because a) its chemical shift is well separated from other derivatized coal moieties, b) the reaction is quantitative in the presence of excess reagent, and c) there are two nmr-active nuclei per product molecule contributing to the intensity of the ^{31}P nmr peak for each molecule of H_2O , thus providing excellent quantitation.³ Further efforts along these fruitful pathways are being pursued.

The chemical shift of the ^{119}Sn nucleus is in general more sensitive to its chemical environment than ^{31}P . An initial problem was the design of a reagent that reacts with labile hydrogen functional groups under mild conditions, e.g.:

The new reagent 4, which we have recently synthesized by two routes, appears to fulfill this requirement:

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 display 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 a 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 tendency 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 4 in pyridine in order to establish a data base.

REFERENCES

1. Lensink, C. and Verkade, J. G., submitted to Energy and Fuels.
2. Lensink, C. and Verkade, J. G., manuscript for Energy and Fuels in progress.
3. Reinartz, K. and Verkade, J. G., presented at the International Chemical Congress of Pacific Basin Societies, Meeting Abstracts, INOR 596, Honolulu, December, 1989.

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