DOE/PC/91334--T21

DOE/PC/91334--T21

DE92 007871

TECHNICAL REPORT

September 1 through November 20, 1991

Project Title: VHF EPR Analysis of Organic Sulfur in Coal
DE-FG22-91PC91334
Principal Investigator: R. B. Clarkson, UIUC
Co-Principal Investigator: R. L. Belford, UIUC
Project Monitor: Dr. Ken Ho, CRSC

ABSTRACT

This report covers progress made in the first yearly quarter of a two year investigation using novel, very high frequency electron paramagnetic resonance (VHF EPR) spectroscopy techniques and instrumentation (one of only two W-band spectrometers in existence) developed earlier by these authors, to conduct further qualitative and quantitative studies of heteroatomic organic molecules in coal with particular emphasis on sulfur. Previous W-band (96 GHz) work is being extended to studies of new model compounds as well as coal and desulfurized coal samples. Typically, the model compounds under investigation and their analogues are found in coals as stable free radicals which give rise to an EPR signal.

The preparation of radicals from compounds having widely varying structures and physical properties in a stable environment has long been a very difficult task. To address this problem, the refinement of several new and very useful methods of preparing of these stable free radicals in various glasses, at catalytic surfaces, and in solution, are presented in this first report. Free radical generation was accomplished by both UV photolysis as well as chemical oxidation/reduction techniques. By these methods, over 25 new compounds, often commercially derived from coal extracts, have been prepared and studied by conventional X-band EPR (9 Ghz). Several representative W-band spectra are also presented.

DISCLAIMER

This project is funded by the U. S. Department of Energy (PETC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared program.

EXECUTIVE SUMMARY

This program addresses the need for innovative approaches to characterize the organic sulfur in Illinois Basin coals by means of high frequency electron paramagnetic resonance (VHF-EPR) spectroscopy operating at W-band microwave frequencies (96 GHz). This instrument is one of only two such instruments in the world, and the only one in the U.S.A. [1]. This instrument has shown unique sensitivity to heteroatoms in coal, and we believe the technique can be successfully applied for the **non-destructive, direct determination of organic sulfur in coal.** Preliminary data from Illinois coals and separated macerals indicate that **the method also may be able to distinguish aromatic from aliphatic sulfur, and may be useful in assessing the extent of conjugation in aromatic portions of the coal.**

In order to illustrate the advantage of higher frequency EPR, consider Figure 1, which shows EPR spectra of an Illinois #6 whole coal taken at three different microwave frequencies: 9, 35, and 96 GHz. At 96 GHz, a new feature characteristic of sulfur is resolved.

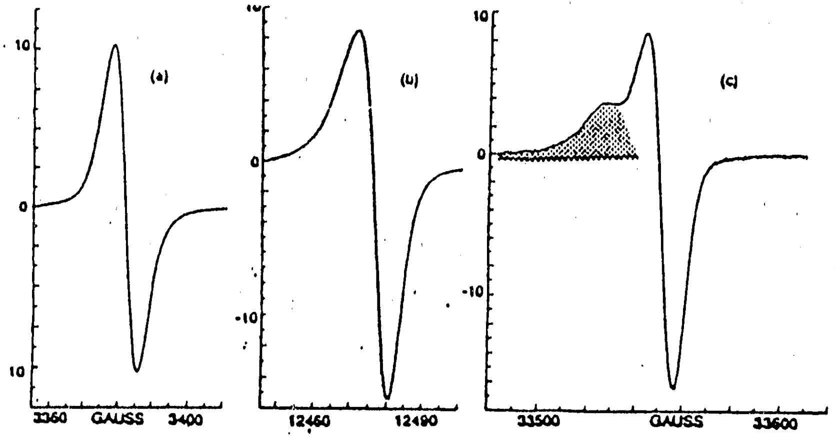


Figure 1. EPR spectra of a whole Illinois #6 coal taken at (a) 9 GHz, (b) 35 GHz, and (c) 96 GHz[1]. Highlighted portion of (c) is due to S (and perhaps O).

In the lower frequency spectra, sulfur atoms shift the EPR resonance line, but the shift is too small to be readily resolved. In order to **resolve** the effect of sulfur, higher field strengths and frequencies must be used. The resonance occurring at lower field strength is highlighted in Figure 1(c) and is due to heteroatoms such as sulfur and oxygen. In coal, this signal is largely the result of organic sulfur. The goal of our current work is to develop a non-destructive spectroscopic technique to resolve qualitatively and quantitatively the molecular forms of organic sulfur in coal that are responsible for these spectra. To that end, a number of coals, inertinites, chars, and model thiophenic compounds continue to be studied using the W-band spectrometer under a variety of conditions.

Because the information about the amount and chemical forms of organic sulfur in coal contained in VHF EPR spectra is new, it is very important that we develop correct interpretations of these data. To accomplish this task, we continued this quarter to pursue the chemistry of synthetic thiophenic systems which mimic the properties of aromatic organic sulfur in coal. Over thirty new compounds were studied. In addition to improving and perfecting the previously reported methods of preparation utilizing boric acid glass matrix isolation of the compounds followed by UV irradiation, we are developing other methods to insure production of only the radical species we desire and minimize side products. We also have begun to develop synthetic

---

[1] Clarkson, R. B., Wang, W., Nilges, M. J., and Belford, R. L. In Processing and Utilization of High-Sulfur Coal; Markuszewski, R. and Wheelock, T. D., Eds; Elsevier: New York, 1990.

methods for producing radical preparations of smaller sulfur-containing compounds (thiophene, benzothiophene) which are harder to form from parent compounds. The goal of Phase II work continues to be the elucidation of relationships between molecular structure and VHF EPR spectra that will allow us to make more accurate and insightful interpretations of the data from coal.

The unique instrument is one of only two such devices in the world, and the only one currently operating in the U.S.A. Much effort has been devoted to the development of a high quality W-band EPR spectrometer. Funding obtained from the CRSC over the preceding (1990-91) period allocated for improvement of this instrument provided for lower-noise detectors and sources, resulting in at least a five-fold improvement in signal to noise ratio, as shown in figure 2. This improvement is very important to the success of the project for the remainder of the current grant period.

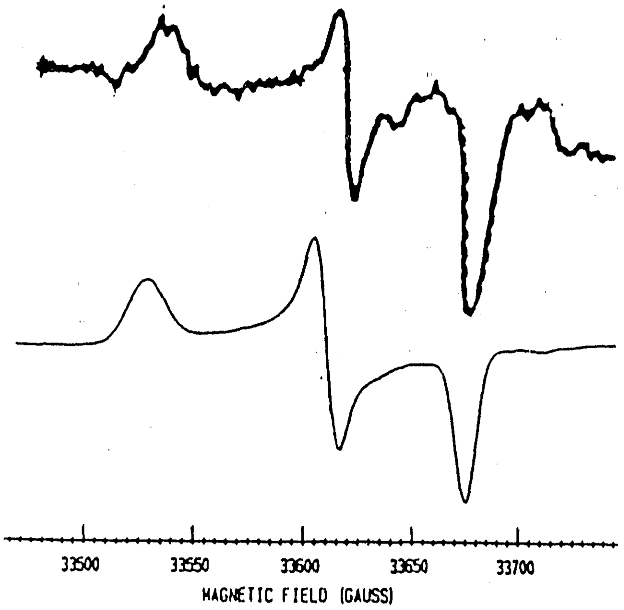


Figure 2. Experimental W-band EPR spectra of dibenzothiophene radical. Upper trace: spectrum acquired before the recent spectrometer improvements. Lower trace acquired under same conditions after spectrometer improvements.

OBJECTIVES

In accordance with the four initially proposed phases of the project, the long term objectives are:

1) Develop a detailed understanding of VHF EPR spectra of organic sulfur species in coal from experimental and theoretical studies of model compounds. (Phase I)

2) Obtain VHF EPR spectra of coal, solvent extracted coal, and separated macerals. (Phase II)

3) Using the results from 1) and 2), determine aromatic cluster size distribution and compare with NMR data. (Phase III)

4) Analyze desulfurized coal for quantitative, and structural changes in aromatic sulfur. (Phase IV)

The first quarter has been successful in proportionally advancing towards meeting the first goal. The second quarter will continue with the study of model compounds (phase I) as well as begin phases II and III. Coal samples will first be prepared under nitrogen and X-band spectra will be acquired and examined. Chemical analysis of all premium coals will be conducted. W-band spectroscopy of premium coal will begin to be acquired as well. In addition, solvent extraction and maceral separation will begin, along with the acquisition of model desulfurized coal compounds.

EXPERIMENTAL PROCEDURES

A. Design and Building of the W-band VHF EPR spectrometer The rather simple resonance lineshapes at 9 and 35 GHz represent the state-of-the-art for the EPR of coal before the development of the W-band spectrometer. The key to our work plan is the W-band spectrometer. This unique instrument has been built over the last three years, and now incorporates several important technical innovations that make it well-suited for the present research work.

B. Preparation of Ultra-Pure Thiophenes

The spectra of thiophene model compounds have shown secondary resonances that raised serious questions regarding the nature of products formed in our synthesis. Our most favored technique is to dissolve compounds in molten boric acid, after which the melt is allowed to cool into a glass. Samples then are UV irradiated for 15 minutes to produce matrix isolated radicals. The concern over minor products included the possibility that diradical species were forming, a situation which could lead to erroneous spectral interpretations.

Ultra-pure boric acid was first melted to form a glass, and the blank material was UV irradiated to insure that no background signals were forming. After this, our focus turned to possible impurities in the starting thiophenic compounds purchased from Aldrich Chemical Co. We therefore obtained small quantities of recrystallized thiophenes, and repeated the preparation. Spectra at W-band from these preparations showed almost no secondary resonances.

In order to study the effects of electron delocalization on the magnitude of g-anisotropy in thiophenic systems, we need to synthesize stable radicals of materials with boiling points that are too low for the conventional boric acid preparation. Thiophene and benzothiophene cannot easily be incorporated into molten boric acid, so several new preparative routes are currently being investigated. One technique involves placing the desired starting material together with boric acid in a pressure pellet, which then is crimp sealed and heated to produce the matrix isolated thiophenes. Another technique is to dissolve the starting thiophene in rigorously dehydrated sulfuric acid. The solution then is frozen at liquid nitrogen temperatures and UV irradiated to produce radicals. In this second preparation, the sample must remain at 77K after irradiation in order to preserve the radicals. At present, neither of the techniques has produced samples of acceptable concentration for our work, but both have produced radicals. We are now optimizing both methods in order to allow the study of the homologous series of thiophenes from C_4H_4S to $C_{16}H_{10}S$ and larger thiophenes.

C. Preparation of thiophene model systems

Pure samples of dibenzothiophene (DBT) and benzonaphthothiophene (BNT) were purchased from Aldrich Chemical. Cation radicals of these materials, in addition to dibenzofuran (DBF), were prepared by two alternate routes. Each method was developed to produce stable populations of pure cation radicals in a powder or glassy matrix, thus duplicating the disordered state of chemical species in coal. It is essential that this disorder criterion be met for our model systems to provide accurate spectral information that directly relates to spectra from coal without theoretical intervention.

Method 1. Preparation on Houdry catalyst.

In this approach, our method utilizes the oxidation catalyst Houdry M-26, a silica-alumina catalyst developed for petroleum cracking. This catalyst is first activated by calcining in air at 650°C for 12 hours. Alternatively, the catalyst may be activated by heating to the same temperature in a vacuum. Following activation, the catalyst is transferred in a closed tube to a glove bag, where it is opened under an atmosphere of dry oxygen. In the glove bag, an amount of the desired thiophenic sulfur compound is added to the Houdry to make a powdered mixture that is 0.2% by weight in the thiophenic species.

The powder then is placed in a 1mm O.D. quartz tube that has been sealed to a ground glass joint suitable for attachment to a high vacuum system. A stopcock at the top of the apparatus is closed, and the device removed from the glove bag and placed on a vacuum line, where it is opened and evacuated to $P < 10^{-5}$ Torr for several hours. Then the sample stopcock is closed and the sample slowly is heated to the melting point. Sublimation of the thiophenic compound results in an even adsorption throughout the Houdry catalyst, where electron transfer produces a cation radical species (DBT+, BNT+, or DBF+). The small quartz capillary holding the sample then is flame sealed, and is ready for examination in the W-band EPR spectrometer.

Method 2. Preparation in Boric Acid Glass by UV Irradiation

Powdered boric acid and the desired thiophenic compound are mixed together in a 1:1000 ratio by weight. The powder then is heated slowly to the melting point of boric acid (ca. 180°C). The glass is allowed to cool, broken into small fragments, and loaded into a quartz sample tube. The tube is placed in a Ray-O-Net irradiation unit and subjected to UV irradiation and 254 nm for 30 minutes. After this, the sample is removed, sealed with high-purity mass spectrograph grease, and taken to the W-band spectrometer for analysis.

In order to study sulfur containing organic (SCO) model compounds by EPR, stable free radicals have to be generated each from its own precursor. The preparation procedure is by no means trivial. It often involves a great deal of complexity in systems or processes, either physical or chemical.

Considerable effort has been devoted to the chemistry of synthesizing and spectroscopic characterization of SCO radicals. Each preparation technique must be evaluated in terms of the chemical uniformity of the free radical distribution, concentration, matrix interference, complexity of preparation, and of course EPR signal intensity. Following is a summary of these preparation procedures with some literature references. Note that an extensive bibliography review was conducted this quarter to support this study.

CHOICE OF THE SCO COMPOUND

Some three dozen obtainable SCO compounds were selected based on their representation of typical organic sulfur moieties in coal and/or their own scientific merits. Here are ten homologous series SCO compounds studied or being studied. A list of the structure, full and abbreviated name of those compounds can be found in Appendix A.

Series #1---Fused aromatic thiophenes: THI, BTH, DBT, BNT
Series #2---Fused aromatic furans: FUR, BFU, DBF, BNF
Series #3---Alkyl thiophenes: THI, DMT, ETH, BUT, HET, DET, DOT
Series #4---Alkyl furans: FUR, DMF, EFU, BUF
Series #5---Benzothiophene derivatives: BTH, MBT, MBI
Series #6---Benzofuran derivatives: BFU, MBF, EBF, MBX
Series #7---Two heteroatoms in a ring: THA, TXO, MBI, MBX
Series #8---Pure hydrocarbons: DHA, BFL, PYL
Series #9---Sulfide and disulfide: DPS, PDS
Series #10--Interesting others: TAA, PCZ, BCA

All the above compounds have been located and purchased from a number of commercial sources (e.g. Aldrich, TCI, Lancaster, ICN Biomedical, Eastman Kodak, etc). Gas chromatography (GC) has shown some impurity in each of a number of these compounds, in which case the compound will be either repurified or commercially synthesised in purer form prior to final spectroscopic study. In addition, several other SCO compounds will be custom-synthesized to fill in some gaps in the series or extend these homologous series.

An extensive literature search has been conducted to determine what EPR spectroscopy of these model compounds may have been done. The search logic was set up this way so that each EPR (ESR, electron paramagnetic resonance, electron spin resonance, ESE, ENDOR, etc) study of the title compound results in a hit. If the number of the hit is greater than one, a further (narrow-down) search of g-anisotropy was requested, and this almost always results in zero hit--little or virtually no work has been done on studying structure--g-anisotropy relationship, for the very understandable reason stated earlier in our report. On the other hand, if the number of hits is zero, than an expanded search was requested to bring some relevant information in the context of coal and radical research.

CHOICE OF THE SUBSTRATE

A relatively inert substrate or dilutant matrix is required to disperse free radicals so as to prevent chemical interactions as well as spectroscopic spin-exchange anomalies. The substrate must also however facilitate electron transfer by acting as a Lewis acid in order to make stable ionic radicals. These solid matrix preparations yield randomly oriented, dilute, and rigid trapped radical species such as are found in coal. A variety of substrates have been used. These can be classified into three types: solution; surface; solid matrix.

Solution

Conc. H_2SO_4[2-3] etc
Na/DME or K/THF[4] etc
$AlCl_3$/Nitromethane[5] etc

Surface

Zeolite,[6] H-Mordenite,[7] or hectorite[8], etc
Alumina[9] or Alumina/silica (e.g. Houdry HM-46[10]), etc
Boric Acid Powder (BAP) or Boric Oxide Powder (BOP)[11]

Solid matrix

Frozen glass of all above mentioned solution[12]
Solidified molten glass of Boric Acid Glass (BAG)[13-14] or Boric oxide Glass (BOG)[15], etc
Some other low melting-point solid matrices such as BX_3 $(X=I)$[16], or paraffin wax[17], etc
Co-crystallization of SCO and substrate, either in crystalline form or in polycrystalline form. Pure SCO single crystal without substrate could be studied but would be outside the scope of this project.

CHOICE OF THE METHOD

Radicals can be generated by any one or combination of the following methods: First, chemical oxidation/reduction (see footnotes) which can be done with concentrated sulfuric acid, an alkaline metal in an appropriate solvent, surface of a catalyst or reaction with an another radical.[18] Second, electrochemical oxidation/reduction.[19] And third, Radiolysis or photolysis. A large portion of all work were done this way. THI and FUR were studied in Freon at 77K by γ-ray irradiation.[20] UV photolysis or UV flash Photolysis seem to be a popular way to generate radical ions. It is also the preparation technique we investigated quite intensively.
More than thirty compounds have been prepared by BAG-UV method. In addition, several other preparation procedure were also investigated. These are summarized in the table below.

---

[2] H. J. Shine, in "Organic Sulfur Chemistry," M. J. Janssen, (Editor), Interscience, New York, N.Y. 1967
[3] IERC
[4] H. Bock, et al, Phosphorous and Sulfur, 14, 211 (1983)
[5] L. Lunazzi, et al, Tetrahedron Letters, 36, 3847 (1972)
[6] B. Hwang et al, Zeolites, 10, 101 (1990)
[7] A. V. Kucherov, et al React. Kinet. Catal. Letter, 28, 301 (1985)
[8] T. J. Pinnavaria, J. Phys. Chem. 78, 994 (1974)
[9] W. Wang et al, IERC and this project
[10] W. Wang, et al, IERC and this project
[11] W. Wang, et al, IERC and this project
[12] e.g. frozen PYL/H2SO4 solution, IERC
[13] Z. H. Khan, et al, Can. J. Chem. 52, 827-828, 1974
[14] W. Wang, et al, IERC and this project
[15] W. Wang, et al, IERC and this project
[16] W. Wang, et al, IERC and this project
[17] W. Wang, et al, IERC and this project
[18] B. C. Gilbert, J. Chem. Soc., Perkins II, 207 (1981)
[19] B. A. Kowert, et al, J. Amer. Chem. Soc. 94,5538 (1972)
[20] D. N. Ramakristra Rao, et al, J. Chem. Soc, Perkin II, 1983 (Unfortunately, no g value were reported, not even to mention the g-anisotropy)

	Photolysis	Chemical Oxidation
Soln./Frozen Soln.	----------	PYL/H2SO4
Surface	Series #1/BOP-UV THI/Alumina-UV	THI/Alumina
Matrix Isolation	Series #1-#9/BAG-UV Series #1,#2,#8/BOG-UV Series #1/BI3-UV Series #1/Paraffin Wax-UV	

A full set of experimental parameters affecting the radical generation or EPR signal has been probed, which is highlighted in the following sections.

EXPERIMENTAL PARAMETERS AFFECTING RADICAL PREPARATION AND DETECTION

Take a typical process of generating BNT cation radical from BNT in BAG using UV photolysis (BNT/BAG-UV) as an example. The following factors have been identified to affecting either the radical generation or the EPR spectrum.

Purity of BNT

Highest commercially available degrees of purity were obtained for BNT; others might require some purification procedure such as chromatography, recrystallization, sublimation, and so on.

Purity of BA

Four different degree as high as 99.999% were tested; we found in most cases the purity of 99.99% to be sufficient. Elemental analyses of the BA and BAG as well as BOG were performed to ensure there was no significant interaction between the boron compound and reaction vessel like Pyrex test tube.

Mole ratio of BNT to BA

This is an important parameter. A range of 10^{-5} to 10^{-1} has been systematically covered, depending on the SCO. A typical mole ratio (concentration) is 10^{-3}.

Melting temperature and pressure of BA or BNT/BA mixture

Our Thermogravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC) confirmed that three de-moisturized ortho boric acids H_3BO_3 or $B(OH)_3$ lost three waters becoming $B_2O_3(OH)_3$ at around ca. 130 °C, then becoming meta boric acid HBO_2. Upon heating at even higher temperature, ca. 400 °C, meta boric acid becomes boron oxide B_2O_3. Later EPR experiments demonstrated that both BAG and BOG and probably the intermediate boron acid forms are good electron acceptors (Lewis acids).

Since some of the SCO compounds have rather low boiling-points, various scheme were attempted to increase the efficiency of BAG procedure. High pressure stainless steel capsules were used. The results, however, differ little from those of open vessel (one atmosphere).

When and how to add BNT to BA molten glass

BNT has a high melting point of 188-190 °C, so the BA has to be heated above 190 °C. For a compound with such a high melting point, it doesn't matter when the BNT is added to the BA, before heating or after BA becomes molten. But for some other SCO's which don't have such high melting points, it was determined that mixing SCO after the BA was melted served better.

How to do glassing

The molten mixture was then vortexed to maximize the dispersion of the BNT in molten BA, then cooled down either by air or cold water. The cooling rate seemed not to have any discernible effect on the EPR spectrum. Realizing that a molecularly dispersed BNT/BAG mixture might be quite important to our study, we also tried some other methods which will be reported later.

UV irradiation wavelengths and durations as well as temperature

Three different UV wavelengths, 254 nm, 300 nm, 350 nm, have been systematically tested on series #1. The shortest one, 254 nm, gave best EPR signal overall. UV-visible spectra of Series #1 plus a few other compounds like PYL have been obtained both in hexane and concentrated sulfuric acid.

The concentration of organo-sulfur radicals in BAG was found to correlate positively with the duration of UV irradiation. Thus, longer time of exposure to UV is favor for those compounds with low quantum or chemical efficiency. However, prolonged UV irradiation does generate some defects either in fused silica or BAG (BOG also) or both. So sometimes a trade-off was needed. Nevertheless, we have studied those centers in our control sample by EPR. The results have been used assisting our characterization of SCO radicals.

Temperature also plays a role here. We are investigating UV irradiation at 77K to increase the lifetime of some radicals.

The sensitivity, resolution, and spectral lineshape, which contain rich information on the structure and dynamics of radicals, are directly or indirectly related to a set of EPR experimental conditions under which the experiments were performed and the spectra were recorded. We have carefully studied these conditions in order to ensure adequate S/N while maintaining the best resolution and true spectral lineshape. This is necessary for correct simulation and interpretation of the spectra during the later phases of this project.

Microwave frequency

At least two microwave frequencies, X-band (9.5 GHz) and W-band (95 GHz) have been or are being applied to the very same sample. The frequency dependent part and frequency invariant part of spin hamiltonian can be separated by this multifrequency approach. Most organic free radicals have little g-strain, resulting in dramatic enhancement in spectral resolution because of the ten-fold dispersion in electron Zeeman coupling. We have found that g-factor, and hence the microwave frequency, is the most important experimental parameter of all: for most SCO radicals (except THA), no g-anisotropy can be measured or deduced from X-band spectra, yet almost all can be measured or deduced from W-band spectra. Representative spectra have been presented in previous reports, and many more will be described in subsequent quarterly reports.

Microwave power level

Preliminary results on the spectral saturation behavior of these organic radicals in different substrate were obtained. Care has been taken to avoid saturation by keeping the microwave power below ca. 0.5 milliwatts, as it has proven to be very important to some radicals like PYL.

Other EPR experimental parameters

Other parameters which we have investigated and need to monitor are modulation amplitude, temperature, radical concentration, changes in Q (quality factor) due to dielectric loss from certain substrate, choice of g standard or absolute g measurement, matrix effect, possible $\Delta M = \pm 2$ transitions, etc.

RESULTS AND DISCUSSION

In the space allotted to this report we can show only selected results. Tables 2 and 3 show the measured EPR spectral g tensor values for several of the compounds under investigation. It is clear that all the g anisotropy is too small to resolve at X-band, although the average g sometimes does give one a hint of it. On the other hand, W-band results clearly demonstrated that the small g anisotropy can be resolved. The g shift, XY g anisotropy generally follow the trends one expects. The detailed simulation of the spectrum and interpretation of those EPR parameters and spin Hamiltonian parameters are the subjects of ongoing research and will be reported later.

In terms of chemical preparation, the most versatile one is still BAG-UV, but it has the shortcoming of being troublesome for low-boiling-point SCOs. The BOG-UV method is worse than BAG-UV in that sense. Paraffin wax and BI_3 are not good matrices, not because of the severe matrix interference but because they are not good Lewis acids.

CONCLUSIONS AND RECOMMENDATIONS

The development of chemical procedures to synthesize reliable models of thiophenic and other sulfur-containing organic species in coal has been a year-long effort starting in the 1990-91 grant period and extending through this quarter. We believe that the fruits of this effort will provide extremely useful information needed to interpret the VHF EPR spectra from coal. Overall, we have learned this quarter that the BAG-UV method yields the highest concentrations of the least-contaminated species for the higher-boiling model compounds, while adsorption on catalyst particles followed by UV irradiation is most promising for low-boiling compounds. With the elimination of secondary resonance peaks in the spectra of radical thiophenic systems, we have the necessary information to proceed with confidence in this experimental and theoretical phase of the work. During the next quarter, we will continue to optimize the synthesis of low molecular-weight models but place more emphasis on the evaluation of spectral data using computational simulations and comparison of homologous series. The development of model compounds has progressed considerably over the past quarter. We are now in a position to intensify our focus on the spectroscopy of these compounds at W- and X- bands.

Routine W-band spectral analysis soon should begin on Illinois Coal Bank, and Argon Premium coal samples, as projected in the time line. Later in this grant year, desulfurized coals from researchers who have used a variety of methods will be studied to determine the type of sulfur removed (ie. aliphatic vs aromatic), and the effectiveness of each technique. In the last quarter, we will attempt to locate "before and after" coal samples that have been subjected to microbial cleaning, in order to evaluate what forms of organic sulfur this procedure attacks. We also will continue to work on the low-temperature pyrolysis study, in order to gain a clearer understanding of the effects of modest temperatures on the sulfur composition and structure of Illinois coals.

Table 1: List of model coal compounds and abbreviations

ABREVIATIONS OF THIOPHENIC COMPOUNDS

NUMBER	ABBR	NAME	SERIES
1	EBF	2-Ethylbenzofuran	6
2	MBF	2-Methylbenzofuran	6
3	MBI	2-Methylbenzothiazol	5
4	MBX	2-Methylbenzoxazol	6
5	3MBT	3-Methylbenzo[b]thiophene	5
6	5MBT	5-Methylbenzo[b]thiophene	5
7	BCA	2-Benzofurancarboxylic Acid	6
8	BFL	2,3-Benzofluorene	8
9	BNT	1,2-Benzodiphenylene Sulfide	1
10	BTH	Thianaphthene	1,5
11	BFU	2-n-Butylfuran	2,4
12	BUT	2-n-Butylthiophene	3
13	DBF	Dibenzofuran	2
14	DBT	Dibenzothiophene	1
15	DET	3-n-Decylthiophene	3
16	DFS	Difurfuryl Sulphide	9,10
17	DHA	9,10-Dihydroanthracene	8
18	DMF	2,5-Dimethylfuran	4
19	DMT	2,5-Dimethylthiophene	3
20	DOT	3-n-dodecylthiophene	3
21	DPS	Diphenyl Sulphide	9
22	EFU	2-Ethylfuran	4
23	ETH	2-Ethylthiophene	3
24	FUR	Furan	2,4
25	HET	3-n-Hexylthiophene	3
26	PCZ	9-Phenylcarbazole	9
27	PDS	Phenyl Disulfide	9
28	PYL	Perylene	8
29	TAA	2-Thiophene Acetic Acid	9
30	THA	Thianthrene	7
31	THI	Thiophene	1,3
32	TXO	Thioxanthene-9-one	7

TABLE 2. MEASURED X-BAND EPR PARAMETERS OF THIOPHENIC RADICALS[1]

ABBR	g AVERAGE <g>	WIDTH gauss	INT. a.u.	C. INT. a.u.
DMT	2.00284	5.3	1.4E-4	3.6E-4
DMF	2.00276	5.3	8.6E-5	4.1E-5
ETH	2.00354	16	1.6E-4	4.8E-4
BUT	2.00403	7.9	-	-
BUF	2.00338	19	4.4E-4	2.1E-3
MBT	2.00471	9.5	-	-
MBF	2.00483	19	1.1E-3	5.9E-3
MBI	2.00511	11	1.6E-4	4.8E-4
MBX	2.00399	16	2.1E-3	1.2E-2
DHA	2.00305	9.7	2.5E-4	1.0E-3
EBF	2.00345	24	2.1E-3	5.7E-3
DET	2.00367	11	2.2E-4	5.9E-4
HET	2.00347	11	4.5E-4	1.2E-3
BNT	2.00407	9.6	8.4E-4	9.2E-3
BTH	2.00383	15	5.0E-4	1.4E-3
THI	2.00336	11	4.0E-4	1.1E-3
DBF	2.00247	19.4	1.1E-3	7.9E-3
THA	2.00779	19.5	5.5E-3	3.9E-2
PYL	2.00258	12.3	7.7E-5	2.4E-4
DBT	2.00602	10.2	5.4E-5	3.9E-4
DPS	2.00444	6.9	5.5E-3	1.5E-3
EFU	2.00120	12	-	-
BFL	2.00317	15	6.9E-3	9.6E-4
DPS	2.00790	11.7	8.1E-3	-

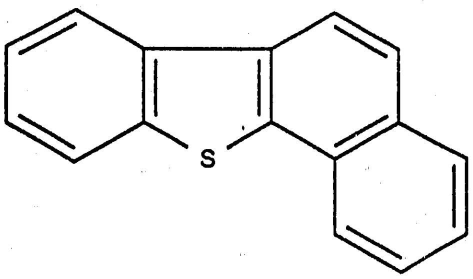
---

[1] WIDTH IS OVERALL SPECTRAL WIDTH,
INT. IS SCALED DOUBLE INTEGRATION,
C.INT. = (INT. OF THE SAMPLE -INT. OF BAG)/INT. OF STRONG PITCH

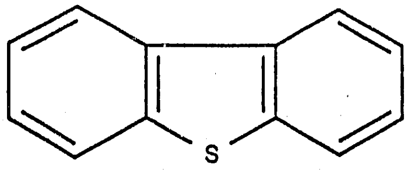
TABLE 3. MEASURED W-BAND EPR PARAMETERS

Compound	g_{shift}	g_{x-y}	$g_{(x+y)/2-z}$	ΔH_x	ΔH_y	ΔH_z	
BNT	18	29	27	24	14	19	
DBT	42	50	64	18	12	12	
BTH	13				40.47		
THI	13				26.10		
THA	59	54	88	6	7	5	
PYL	3	0	3	-	-	-	a=3.46

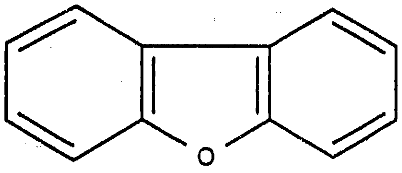
APPENDIX A LIST OF STRUCTURE AND OUR ABBREVIATION OF SULFUR CONTAINING ORGANIC COMPOUND INVESTIGATED



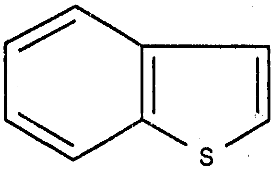
BNT



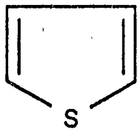
DBT



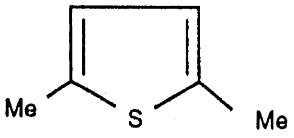
DBF



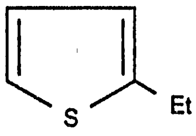
BTH



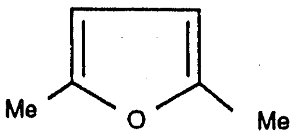
THI



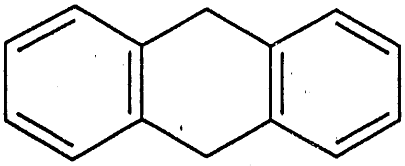
DMT



ETH



DMF

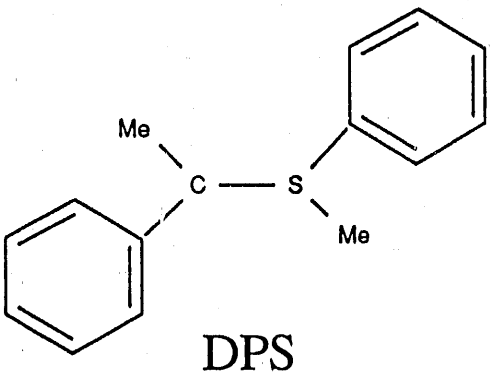


DHA

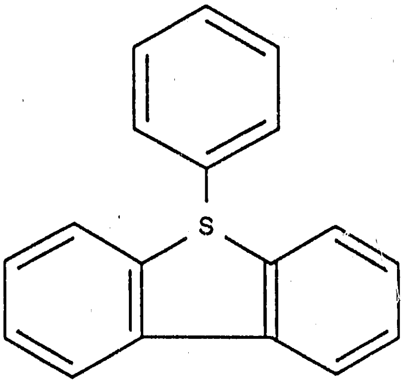
$(CH_3CH_2)_{11})_2S$

DS

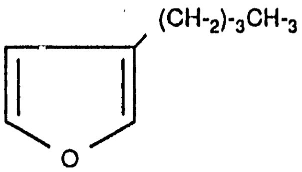
2



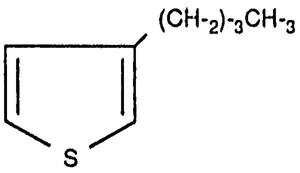
DPS



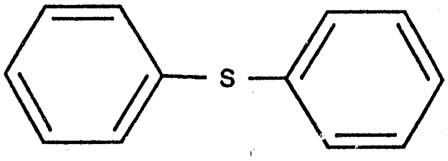
PCZ



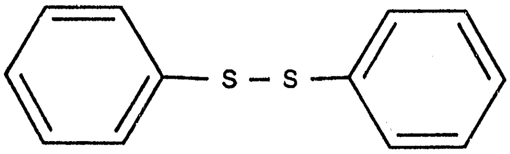
BUF



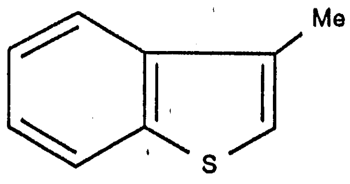
BUT



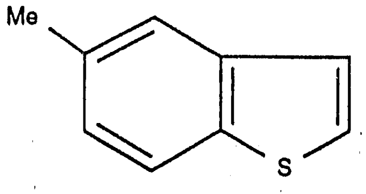
DPS



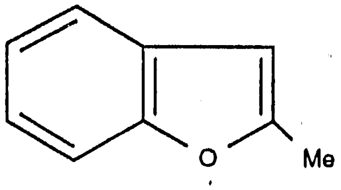
PDS



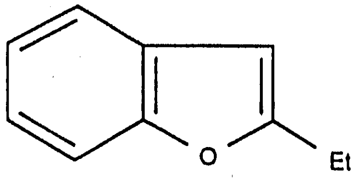
3MBT



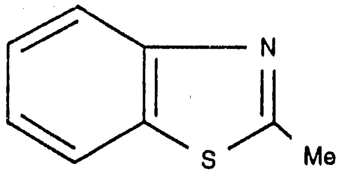
5MBT



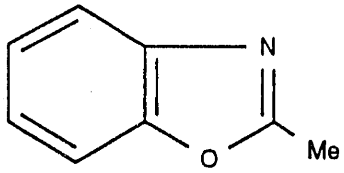
2MBF



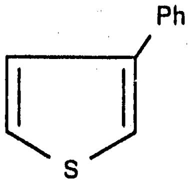
2EBF



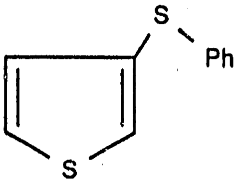
2MBT



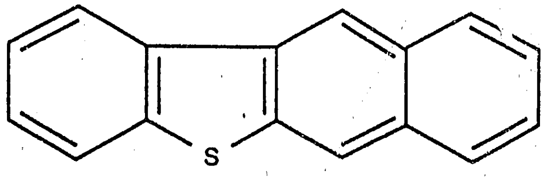
2MBX



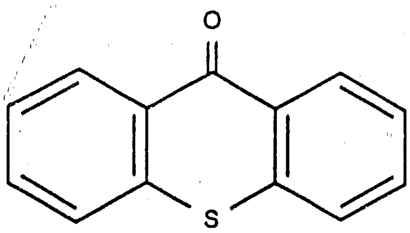
PHT



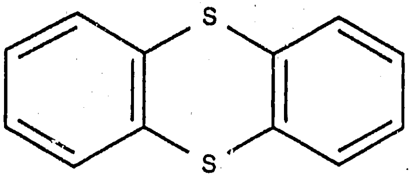
PTT



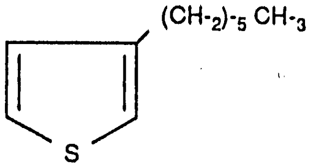
BFL



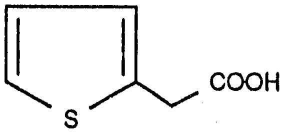
TXO



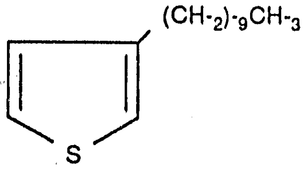
THA



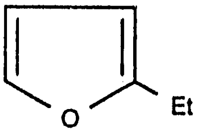
HET



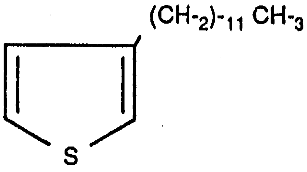
TAA



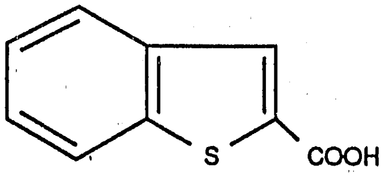
DET



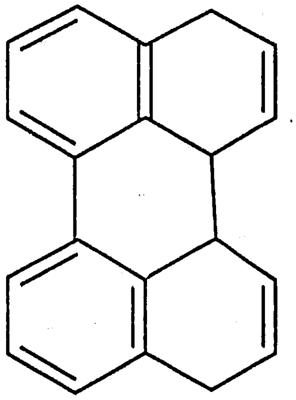
EFU



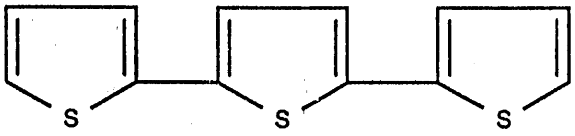
DOT



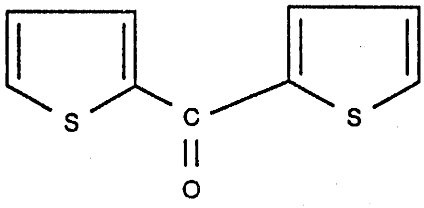
BCA



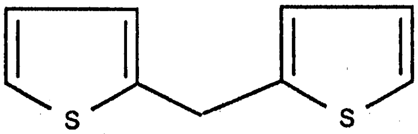
PYL



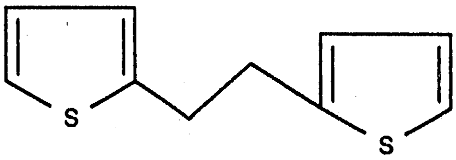
TET



THT



MDT



DFS

PROJECT MANAGEMENT REPORT

September 1 through November 20, 1991

Project Title: VHF EPR Analysis of Organic Sulfur in Coal

Principal Investigator: R. B. Clarkson, UIUC
Co-Principal Investigator: R. L. Belford, UIUC
Project Monitor: Dr. Ken Ho, CRSC

COMMENTS

The budget for this first quarter report is on schedule.

This project is funded by the U. S. Department of Energy (PETC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared program.

END

DATE
FILMED

4/02/92

I