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FINAL TECHNICAL REPORT

September 1, 1992 through December 31, 1993

Project Title: **PROTOCOLS FOR THE SELECTIVE CLEAVAGE OF CARBON-SULFUR BONDS IN COAL**

DE-FC22-92PC92521

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ABSTRACT

Summarized in this FINAL TECHNICAL REPORT for our project "Protocols for the Selective Cleavage of Carbon-Sulfur Bonds in Coal" are results of research pertaining to chemical reactions that aim to selectively cleave C-S bonds in model compounds as well as Illinois coal. Chemical reactions that result in carbon-sulfur bond cleavage are an essential aspect of any protocol designed to remove organic sulfur from coal. In the second year of our project "Protocols for the Selective Cleavage of Carbon-Sulfur Bonds in Coal" we have completed investigations of reactions in which organic sulfur-containing coal model compounds are subjected to different conditions of temperature, solvent mixtures, reagents, and radiation. We have also undertaken a series of reactions in which physically cleaned Illinois coal has been subjected to many of the same reaction conditions that were shown, via the use of model sulfides, to result in substantial C-S bond cleavage and or sulfur oxidation. Therefore, summarized in this final report are results of our investigations of the photooxidation reactions of coal model sulfones and sulfides; the photolytic desulfurization of coal; and various other topics, including a summary of our endeavors aimed at initiating C-S bond cleavage reactions using oxidation/chlorination/desulfurization protocols, and various tellurium reagents.

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EXECUTIVE SUMMARY

The following sets of experiments were slated for completion during the two-year funding period for "Protocols for the Selective Cleavage of Carbon-Sulfur Bonds in Coal":

•1. Allow various coal model compounds (species that contain aliphatic and aromatic C-S bonds) to be subjected to various conditions. The variables in these studies include different substrates, solvents, bases, added reagents (catalysts, oxidizing agents, electron acceptors), temperature and pressure. Photochemical reactions of these coal model compounds will also be studied by varying the wavelength of light, using various solvents with or without sensitizers, oxidizing the compounds and subsequently hydrolyzing the products of the reaction.

•2. Subject coal and coal model compounds to ultrasonic irradiation for different periods of time. The effects of adding catalysts or oxidizing agents will also be determined. Different substrates, solvents and oxidizing agents, along with ultrasonic irradiation, altogether will form a matrix of results that will allow determination of optimum conditions that will accomplish the desired C-S bond cleavage on coal samples.

•3. Heat the coal model compounds containing both aliphatic and aromatic sulfur, oxygen, carbon, and nitrogen at various temperatures, using a Differential Scanning Calorimeter(DSC). Observe the transitions in the sample brought about by C-S, C-O, C-C and C-N bond cleavages.

•4. Investigate differences in the bond strengths in the radical cations derived from coal model compounds 10-phenylthio-9-methylanthracene and 9-phenylthiomethyl-anthracene. We will attempt to ascertain the differences in reactivities of different types (i.e. aromatic or aliphatic carbon) of carbon-sulfur bonds, under various reaction conditions, and correlate these differences with their respective bond strengths.

This document constitutes our final report on this project. Results gained during the present reporting period include the following:

- Mixtures of BPS and NaOH/KOH, when heated for three hours at a final temperature of 330^{o}C and final pressure of 250 psi, remains largely unchanged, when the reaction is carried out in THF, morpholine, or quinoline.
- Benzyl phenyl sulfide (BPS) was converted to its sulfone (benzyl phenyl sulfone). The sulfone was then chlorinated with N-chlorosuccinimide, forming α-chloro-benzyl phenyl

sulfone. The resulting α-chloro-benzyl phenyl sulfone was subjected to room temperature hydrolysis by allowing it to react with NH_3 in water. Benzaldehyde was isolated in 40% yield. Also observed was phenyl disulfide.

- Benzyl phenyl sulfide, when treated with N-chloro-succinimide followed by ammonium hydroxide, forms benzaldehyde and dibenzyl disulfide, in near quantitative yields.
- NaTeH, when allowed to react with dibenzothiophene sulfone at temperatures less than 220°C, does not react. Dibenzothiophene sulfone, when allowed to react with tellurium powder alone, is recovered unchanged. When NaTeH was allowed to react with dibenzothiophene sulfone at temperatures greater than 220°C, C-S bond cleavage was observed. Products isolated include dibenzothiophene as well as the tellurium analogue of dibenzothiophene. In addition, NaTeH, when allowed to react with benzyl phenyl sulfone, forms the corresponding sulfide in high yields.
- Dibenzothiophene sulfone, when allowed to react with a mixture of $NiCl_2$ and $NaBH_4$ (at ca. 15°C for one hour), was transformed (in 30% yield) into biphenyl.
- Dibenzothiophene sulfone, after thorough mixing and grinding, was allowed to react with sodium borohydride, at temperatures ranging from 300 to 500°C. Isolated and identified by NMR and MS were biphenyl and dibenzothiophene, in yields (based on starting sulfone) that range from 30 to 80%. The formation of hydrogen sulfide in these reactions was confirmed by testing with lead acetate paper (the characteristic odor of hydrogen sulfide was also present). Other unidentified products were also formed in these reactions. Tha addition of tellurium to these reactions appears to assist desulfurization as the formation of dibenzotellurophene was noted.
- Photooxidations of phenyl sulfide, benzyl phenyl sulfide, thiophene, benzothiophene, and dibenzothiophene have been carried out under five sets of reaction conditions, all of which include irradiation of the sulfide with a Hanovia lamp: (a) adding oxygen in the presence of Rose Bengal in methanol solution; (b) adding oxygen in the presence of 9,10-dicyanoanthracene in acetonitrile solution; (c) adding oxygen in the presence of anthracene in acetonitrile solution; (d) adding oxygen in the presence of no sensitizer in several solvents; and (e) "blank" studies in which the sulfides were irradiated for similar time periods in the same solvents as those mentioned previously in the *absence* of oxygen. Results from these experiments suggest that electron transfer-mediated photooxidations (i.e. those in which 9,10-dicyanoanthracene or anthracene was used as a sensitizer) were more likely to occur (using the present set of sulfides) than the Rose Bengal-mediated reactions. Results from experiments in which benzyl phenyl sulfide and dibenzothiphene were photooxidized in the absence of sensitizer indicates that these substrates are quite reactive

in our photooxidative protocol. In essence, they appear to react with molecular oxygen, in the presence of light, without any added catalyst, forming both the analogous sulfoxides and sulfones. Finally, experiments carried out in which the sulfides were subjected to the Hanovia lamp in the absence of oxygen reveal that little or no reaction occurs. In other words, the oxygen is essential in these transformations.

- IBC-108 has been subjected to the same photooxidative protocol that we have developed in our work with the sulfide model compounds. The photooxidation protocol, when carried out in acetonitrile, appears to result in a 10% reduction in the organic sulfur content of the coal. When carried out in other solvents (such as pyridine, dimethyl sulfoxide, and methanol), the desulfurization occurs to a much greater extent (ca. 70%). These experiments have now been confirmed and rechecked; the results are valid. The integrity of the photooxidized coal was verified using differential scanning calorimetric (DSC) techniques as well as experiments that probed the reflectance and fluorencence properties of the samples, and therefore their maceral composition. Analysis of results from all of these experiments indicates that the photooxidation treatment does not substantially overwhelm or degrade the backbone of the coal macromolecule, for experiments carried out in a variety of solvents. For example, maximum reflectivity data for untreated IBC-108 and photooxidized IBC-108 (0.65 and 0.97, respectively) strongly suggest that the photoxidation treatment does not result in any structural compromise of the coal sample. In other words, the reacted coal is still coal. The increase in reflectance is probably indicative of oxygen crosslinks in the sample. FInally, the photooxidized coal was also inspected visually with the aid of a light microscope. These inspections revealed that the vitrinite present in photooxidized IBC-108 is **not** substantially degraded.

OBJECTIVES

Our long range objective in the research funded by ICCI has been to carry out experiments that will aid in solving the problem of coal desulfurization--from the perspective of inventing, understanding, and perfecting new carbon-sulfur bond breaking chemical reactions. Experiments carried out during the past three months included studies of reactions in which base mixtures were allowed to react with sulfur-containing coal model compounds under high temperature (Parr bomb) conditions. Additional experiments carried out during the present reporting period were aimed at cleaving carbon sulfur bonds in α-chlorosulfones,with the aid of various tellurium-based reagents. Other experiments carried out during this reporting period included studies of photochemical and photo-oxidation reactions of sulfur-containing coal model compounds in the presence/absence of sensitizers. It is our objective to develop a set of low-temperature reaction conditions that will enable substantial C-S bond cleavage to be affected in Illinois coal. The described experiments are the first steps in achieving some understanding at the molecular level of a newly-invented process. Details of photooxidative experiments involving IBC-108 are also found in this summary.

Examination of the four tasks listed below reveals details of the experiments planned to aid in the efforts to reach the stated objective:

TASK 1: Carry out experiments that aim to selectively cleave C-S bonds in coal model compounds benzyl phenyl sulfide, phenyl sulfide and dibenzothiophene, as well as physically cleaned Illinois coal. Main thrusts of these investigations include radical- and Lewis acid-initiated, as well as caustic- and photooxidatively-assisted C-S bond cleavages.

TASK 2: Evaluate the effect of ultrasonic radiation on the effectiveness of several C-S bond cleavage protocols.

TASK 3: Utilize differential scanning calorimetry (DSC) techniques in examinations of various methods of cleaving C-S bonds in coal model compounds, as well as gaining understanding of the degree of depolymerization in Illinois coals (coals that contain varying amounts of organic and inorganic sulfur) when these coals are subjected to depolymerization protocols. Also planned are DSC studies of several Illinois coals subjected to a variety of pretreatment conditions.

TASK 4: Carry out experiments that enable determinations of the bond energies for aliphatic and aromatic C-S bonds in the radical ions derived from several coal model compounds. Communicate these results to the coal-desulfurization community through publications in scientific journals.

INTRODUCTION AND BACKGROUND

The organic sulfur found in coal consists primarily of sulfur atoms covalently bonded to aliphatic or aromatic carbon atoms contained in the backbone of the coal macromolecule (there may be a small percentage of S—S and S—H bonds in coal as well). The sulfur present in Illinois coal is problematic because the combustion of high-sulfur coal results in the formation of species implicated in environmental problems related to acid rain. The relevance and significance of the experiments planned for the present funding period is perhaps best described by acknowledgment of the following two statements:

(a) In order to remove the organic sulfur from coal, carbon-sulfur bonds must be broken.
(b) Chemists' knowledge and awareness of reactions that lead to the selective cleavage of carbon-sulfur bonds, and in particular, sulfur atoms bonded to sp^2 (i.e. aryl) carbon atoms, is limited.

The experiments outlined in the four TASKS listed earlier in this final report are aimed at developing an increased understanding of methods that enable cleavage of C-S bonds. The longer term goal of these experiments is the invention of new chemical reactions, or perfection of existing chemical reactions. The attainment of reaction conditions that allow the selective cleavage of carbon-sulfur bonds in coal and coal model compounds is therefore the main goal of "PROTOCOLS FOR THE SELECTIVE CLEAVAGE OF CARBON-SULFUR BONDS IN COAL". An important outcome of these studies is the resulting increase in chemists' knowledge of carbon-sulfur bond cleavage reactions. Successful completion (successful in terms of affecting carbon-sulfur bond cleavages) of the studies described in this proposal thus increases the likelihood of the deployment of a simple and cost-effective protocol designed to remove organic sulfur from Illinois coal.

Much of the coal mined in Illinois suffers from its high sulfur content. Methods have been developed that are quite effective at removing the inorganic sulfur from coal. Unfortunately, the problem of organic sulfur present in Illinois coal remains to be solved. A major reason for the lack of progress in the area of organic sulfur removal is the lack of knowledge concerning carbon-sulfur bond cleavage reactions. Completion of the experiments outlined in TASKS 1-4 will at least partly remedy this situation. It is our desire to convert what we learn from these studies of carbon-sulfur bond breaking reactions into a simple protocol that will offer a reasonable and economically viable solution to the problems of using Illinois coal.

The experiments summarized in this final report are best described as fundamental studies of carbon-sulfur bond cleavage reactions, using both coal and model compounds. At present, none of these experiments describe a process that is cost-effective in terms of removing organic sulfur from coal. It is our desire to develop a practical carbon-sulfur bond-breaking technology from the research described in this proposal, and transition this new technology to the Illinois coal community.

EXPERIMENTAL PROCEDURES

TASKS 1-4 describe experiments that have synthetic, colorimetric, and electrochemical components. The synthetic component of our work is typical of the procedures that practicing organic chemists follow. A uv-visible spectrophotometer is utilized in the collection of appropriate acid-base and kinetic data.

Other experimental techniques and apparatus utilized in our work during the past three months include a Parr high pressure reactor vessel, GC techniques, FT-NMR techniques, DSC techniques, as well as other chromatographic techniques.

RESULTS AND DISCUSSION

TASK 1: Carry out experiments that aim to selectively cleave C-S bonds in coal model compounds benzyl phenyl sulfide, phenyl sulfide and dibenzothiophene, as well as physically cleaned Illinois coal. Main thrusts of these investigations include photo-oxidatively assisted C-S bond cleavage reactions.

1.1. CHEMICAL DESULFURIZATION OF COAL MODEL SULFIDES

- Introduction

As far as coal is concerned, it is likely that sulfides are the primary functional group that contain organic sulfur.. During the past 24 months of ICCI funding for this project, we have carried out several different reactions that aimed to thermally cleave C-S bonds in model sulfides such as benzyl phenyl sulfide (BPS). In many of these reactions, substantial degradation of the BPS was observed. Unfortunately, the product that results from these reactions often includes substantial (i.e. greater than 50%) amounts of intractable tars. When carried out in typical organic solvents, the products of reactions between BPS and caustics were particularly difficult to evaluate and identify. We therefore felt it was important to determine the maximum time and temperature at which little or no reaction occurred when BPS was allowed to react with caustic.

In other experiments, we have developed a new strategy for breaking aliphatic C-S bonds which involves chlorination followed by hydrolysis. Results from these experiments are also found in this section.

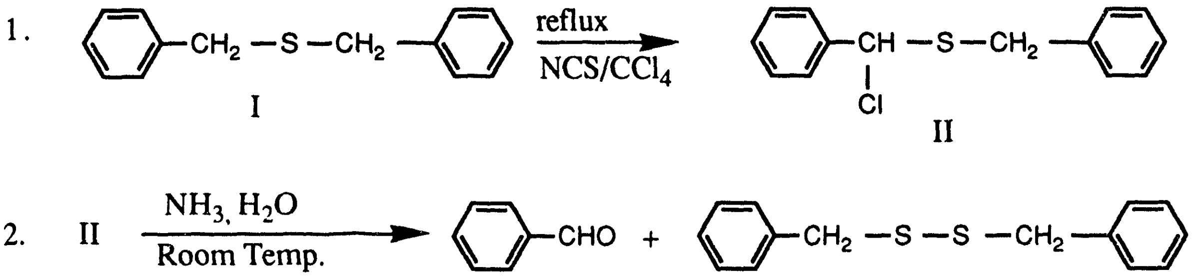
- Results

CAUSTIC/THERMOLYSIS PROTOCOL

In separate experiments, benzyl phenyl sulfide was allowed to react with KOH/NaOH mixtures, in THF, morpholine, and quinoline solvents, for 3 hrs. The final temperature for these reactions was 330°C; the final pressure was 250 psi. The main conclusion to be drawn from these experiments is that benzyl phenyl sulfide was recovered essentially unchanged in all of these reactions. It may therefore be possible to carry out similar reactions at slightly higher temperatures in an effort to study the transformation of BPS into other products and identify these products in reactions in which the mass balances can be accurately accounted.

CHLORINATION/HYDROLYSIS PROTOCOL

The reaction between dibenzyl sulfide (I) and N-chlorosuccinimide (NCS) followed by treatment of ammonium hydroxide showed that the carbon and sulfur bond was broken with one product being benzaldehyde and another product being dibenzyl disulfide.



In a related reaction, benzyl phenyl sulfide, when treated with N-chlorosuccinimide followed by ammonium hydroxide, forms benzaldehyde and dibenzyl disulfide, in near quantitative yields.

That the chlorination of the aliphatic carbon is an essential part of this reaction was verified by monitoring similar reactions in which phenyl sulfide was used as a substrate. In this reaction, we now believe, with the aid of TLC analyses, that approximately 20% of the starting material has been transformed into as yet unidentified products.

1.2. CHEMICAL DESULFURIZATION OF COAL MODEL SULFONES

- Introduction

It is also likely that sulfides and their *oxides* exist in coal. We have therefore added sulfones to our list of coal desulfurization model compounds. As described in previous quarterly reports, we have investigated tellurium-based reagents in reactions that aim to cleave C-S bonds as well as chlorination/hydrolysis protocols. In this report, additional results are described for these and related reactions. Also found in this section are initial results from reactions in which $NiCl_2$ was used as a reagent to cleave C-S bonds in organic sulfones.

- Results

CHLORINATION/HYDROLYSIS PROTOCOL

The substrate α-chloro-benzyl phenyl sulfone was subjected to room temperature hydrolysis by allowing it to react with NH_3 in water. Benzaldehyde was isolated in 40% yield. Also observed was phenyl disulfide.

TELLURIUM PROTOCOL

The utility of NaTeH as a reagent in C-S bond cleavage reactions has also been investigated. We first allowed $NaBH_4$ to react with dibenzothiophene sulfone. There was no reaction observed. We then allowed the same sulfone to react with a mixture of $NaBH_4$ and tellurium. Below $220^{o}C$, we observed no reaction. However, upon heating up to $500^{o}C$, we observed that biphenyl formed in 20-30% yields, while dibenzothiophene was formed in yields of about 30%. There are several more (as yet) unidentified products in this reaction.

When allowed to react with NaTeH at $300^{o}C$, dibenzothiophene sulfone formed substantial amounts of biphenyl, dibenzothiophene, and the tellurium analogue of dibenzothiophene. The products of these reactions have been isolated and confirmed by NMR, GC, and MS.

SODIUM BOROHYDRIDE PROTOCOL

4-Chlorophenyl sulfone was allowed to react with sodium borohydride under an argon atmosphere at about $240^{o}C$, TLC monitoring of the reaction mixture indicates that the sulfone degraded and formed 4-chlorophenyl sulfide and 4-chlorophenyl disulfide, among other products.

Phenyl sulfone was also allwed to react with sodium borohydride under an argon atmosphere at about $330^{o}C$ for 30 minutes. Probable products in this reaction are phenyl sulfide and diphenyl sulfide.

NICKEL CHLORIDE/SODIUM BOROHYDRIDE PROTOCOL

Benzothiophene sulfone was allowed to react, at ca. 15°C and 1 hour, with a mixture of $NiCl_2$ and $NaBH_4$. *Isolated* as a main product (ca. 30% yield) in this reaction was biphenyl, indicative of substantial C-S bond cleavage and extrusion of SO_2.

1.3. PHOTOOXIDATION OF ORGANIC SULFIDES

As described in prior quarterly reports, experiments have been carried out for the series of the coal model sulfides (phenyl sulfide, benzyl phenyl sulfide, dibenzothiophene, thiophene, and benzothiophene).

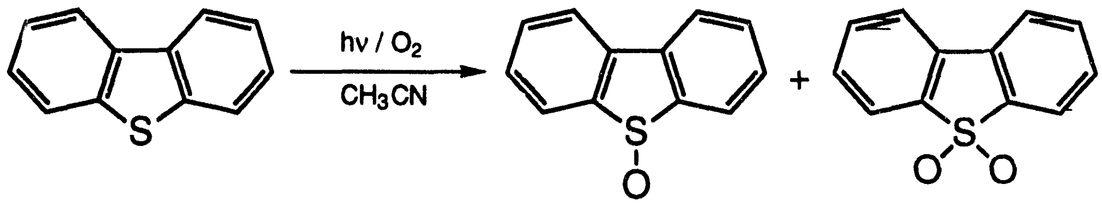
Of particular interest to us was the photooxidation of dibenzothiophene (DBT). As reported previously, this compound when irradiated for 22 hours, in the presence of 9,10-dicyanoanthracene (DCA) and oxygen, yielded oxygenated products (dibenzothiophene sulfoxide (DBTO) and dibenzothiophene sulfone ($DBTO_2$)) with about 60% yield. The yields were only slightly lower when anthracene was used as a sensitizer. This result is particularly interesting from the point of view of coal chemistry since polyaromatic hydrocarbons (potential electron transfer sensitizers) are abundant in coal. Our previously reported results indicate that singlet oxygen is probably not involved in this reaction since formation of the oxygenated products is not retarded by the addition of the $^1O_2$ quencher - β-carotene.

Interestingly, when no sensitizer was used, and dibenzothiophene was exposed to oxygen and light only, dibenzothiophene was isolated with 15% yield.

The acetonitrile used in our experiments was 99% pure. The one percent of impurities could be a source of the sensitizer. To evaluate this possibility 99.9% (HPLC grade) solvent was used in the experiments described in these report. The results of the photooxygenations of DBT are summarized in Table 1 (next page).

Furthermore, the role of molecular oxygen was evaluated for all the compounds studied by carrying their oxidations in the absence of light, with all other conditions unchanged.

TABLE 1



CONDITIONS	YIELDS [%]	
DCA sens./99% solvent	33	28
DCA sens./99.9% solvent	29	41
AN sens./99% solvent	37	11
no sens./99% solvent	15	0
no sens./99.9% solvent	28	13
β-carotene/99% solvent	11	0
no light/99% solvent	0	0
no oxygen/99.9% solvent	0	0

- Results

The same light source (200 W, medium pressure, Conrad-Hanovia 654A36 lamp, filtered through the Pyrex 7740 absorption sleeve) and standard photochemical reactor were used as described in previous reports. Oxygen was bubbled through 150 ml of the 0.01 M solution of the sulfide in acetonitrile. Sensitizer concentration was 0.0001 M. Reactions were monitored by GC and TLC. Products were isolated by column chromatography or by centrifugal, preparative, thin layer chromatography using a Harrison Research Chromatotron (Model 7924T). The separated compounds were then characterized by GC, TLC, and ^{1}H and ^{13}C NMR (DMSO-D$_6$ solution).

Three experiments have been carried out for dibenzothiophene. First, 22 hour unsensitized photooxidation was carried out in HPLC grade acetonitrile (99.9%) pure. The reaction gave unexpected results. The yields of oxygenated products instead of being lower were significantly higher than those obtained in 99% pure solvent. The yield for DBTO was 28% and for DBTO$_2$ 13%. About 50% of the substrate was recovered.

DCA sensitized photooxidation of DBT, in HPLC grade solvent, was carried out to evaluate the role of the solvent quality on the sensitized reaction. In the 22 hour reaction the yield of DBTO was 29% and DBTO$_2$ 41%. 9% of DBT was recovered. Thus, only the sulfone formation seemed to be enhanced when acetonitrile of higher purity was used. However, the increase of the total yield of the oxygenated products was not as dramatic as in the unsensitized reaction. The purity of acetonitrile probably plays important role in stabilization of the intermediate [DBT$^{+\bullet}$ O$_2^{-\bullet}$], formed in the unsensitized reaction.

The third reaction involved 22 hours of bubbling of oxygen through the acetonitrile (99.9% pure) solution of DBT but without irradiation. 95% of DBT remained unreacted (GC) and no other compounds were detected by GC or NMR in the product mixture.

Similar results were obtained for other model sulfides exposed to the same conditions[1]. Their conversions were low (GC) and only traces of unidentified products were detected.

This work shows that dibenzothiophene *alone*, in the present of light and oxygen, when dissolved in acetonitrile, is converted to the corresponding sulfoxide (in 28% isolated yield) and sulfone (in 13% isolated yield).

The results are important from the point of view that coal undergoes changes upon weathering, and that much of the chemistry associated with the weathering of coal may in fact be catalyzed by light.

1.4. PHOTOOXIDATION OF IBC-108 COAL

That light and oxygen (in the presence of sensitizer) can cleave or transform chemical bonds points to the power of these reagents in certain reactions. Published reports claim that atmospheric weathering leads to desulfurization of coal.[2] This observation was followed by laboratory experiments in which samples of coal were desulfurized in a two stage process (photooxidation and hydrolysis of products).[3] Up to 35% reduction in sulfur was reported when coal samples (suspensions in ethanol) were irradiated at 254 nm and then hydrolyzed.

In our attempts to achieve coal desulfurization via a photoxidative process, we have exposed IBC-108 to the standard unsensitized photooxidative conditions followed by hydrolysis in NaOH solution.

Results

The experiments were carried out as described previously. A sample of IBC 108 (250 mg) was suspended in 150 ml of a given solvent, and irradiated for 72 hours. The coal-acetonitrile suspension was stirred with a magnetic stirrer and agitated by oxygen that was delivered through teflon tubing. A 200 W medium pressure Conrad-Hanovia lamp, modified by a Pyrex 7740 light filter, was used as a light source. After the irradiation was completed the coal was filtered, weighed, and vacuum dried at 130°C.

The most recent quarterly report indicated that IBC-108, when subjected to photooxidative conditions in acetonitrile

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[1] Reaction times were equal to those of the photolytic runs i.e.: 75 minutes for PS, 1 hour for BPS and 5 hours for BT.

[2] Chandra, D.; Chakrabarti, J. N.; Swamy, Y. V. *Fuel* **1982**, *61*, 204.

[3] Mathur,V. K.; Murphy, S. *Am.Chem.Soc.Div.Fuel Chem.* **1988**, *33* (1), 232.

solution, was desulufized to the extent of about 10%. Hydrolysis of the photooxidized coal resulted in an additional 10% desulfurization.

We can now report results of the quantitative sulfur analysis for similar experiments in which pyridine, dimethyl sulfoxide, and methanol were used as solvents in the photooxidative protocols. In the Table below, Rob Bartelsmeyer of Carterville IL carried out the sulfur analyses.

Table I. Sulfur Analyses of IBC-108 Coal. Determination of the Effect of Photooxidation.

sample and description	% sulfur
IBC-108 photooxidized coal (pyridine)	0.3
IBC-108 photooxidized coal (DMSO)	0.7-0.8
IBC-108 photooxidized coal (MeOH)	0.5-0.6
IBC-108 (untreated)	2.5-2.7

Inspection of the data in Table I reveals that these experiments result in organic sulfur decreases by ca. 70% as a result of photooxidation alone. Of note is that the photooxidative procedure renders about 30-50% of the coal soluble in the respective solvents. In other words, the photooxidation process leaves about 50-70% (by weight) insoluble material that served as samples for the sulfur content as well as the fluorescence and reflectivity experiments.

TASK 2:Evaluate the effect of ultrasonic radiation on the effectiveness of several C-S bond cleavage protocols.

RESULTS: No experiments were undertaken for this task for this period.

TASK 3: Utilize differential scanning calorimetry (DSC) techniques in examinations of various methods of cleaving C-S bonds in coal model compounds, as well as gaining understanding of the degree of depolymerization in Illinois coals (coals that contain varying amounts of organic and inorganic sulfur) when these coals are subjected to depolymerization protocols. Also planned are DSC studies of several Illinois coals subjected to a variety of pretreatment conditions.

*RESULTS:*Our DSC-based experiments have been carried out on IBC-108 itself, as well as photooxidized IBC-108. Our intent in these experiments is to determine what it is that the DSC-based results can tell us about coal, as well as how our photooxidative protocol changes the thermal properties of IBC-108.

The results of these experiments are problematic as far as their analysis is concerned. In the following discussion, all of the comments pertain to the dashed lines in Figures 1-3. Shown in Figure 1 is the hard-copy output from an experiment in which untreated IBC-108 was subjected to the DSC experiment. Inspection of the dashed line in Figure 1 reveals that it possesses a maximum at ca. 100°C (probably due to the presence of water) and a minimum at about 450°C. Above 450°C, the curve continues to rise upward. As stated previously, the main goal of these experiments is the determination of the effect of photooxidation (and/or subsequent hydrolysis) on the starting IBC-108 coal. Therefore, the curve in Figure 1 is most important in terms of comparison with data obtained on photooxidized and hydrolyzed iBC-108 samples (Figures 2 and 3, respectively). Inspection of Figure 2 (a plot of heat vs temperature for *photooxidized* IBC-108) reveals the aforementioned maximum at ca. 100°C (again probably due to the presence of water), an inflection point at about 350°C, and a minimum at about 500°C. After 500°C, the curve rises upward. Comparison of Figures 1 and 2 strongly suggests that photooxidation of IBC-108 does not overwhelmingly change the nature of the coal macromolecule, at least for the samples that have been examined to date. Shown in Figure 3 is a plot of heat vs. temperature for an IBC-108 sample that has been subjected to *hydrolysis* reaction conditions. Inspection of Figure 3 reveals the same downward curve above 100°C, an inflection point at about 400°C, and a minimum at about 500°C. As in Figures 1 and 2, the curve rises upward above 500°C. At this time we interpret the similarity in these data to mean that the photooxidative and hydrolysis processes utilized in this work do not overwhelmingly change the nature of the coal macromolecule, at least for the samples that we have examined to date. It is likely that the aforementioned inflection point is the result of some moderate depolymerization of the coal macromolecule that results from the photooxidative process.

It is probably most appropriate to discuss additional analyses of the photooxidized coal in this section of the report. A central issue regarding the photooxidization protocol is the determination of the degree of degradation/crosslinking of the treated coal. Therefore, the reflectance and fluorescence properties of untreated IBC-108 were analyzed side-by-side with IBC-108 that was subjected to photooxidation and subsequent hydrolysis.

A white/blue light maceral analysis of IBC-108 and photooxidized (in methanol) IBC-108 was carried out. The untreated 108 possessed (by volume) ca. 5% vitrinite, 5% inertinite, and 90% vitrinite, while the photooxidized sample possessed ca. <0.5% vitrinite, 11% inertinite, and 88% vitrinite. The petrographic composition data indicate that

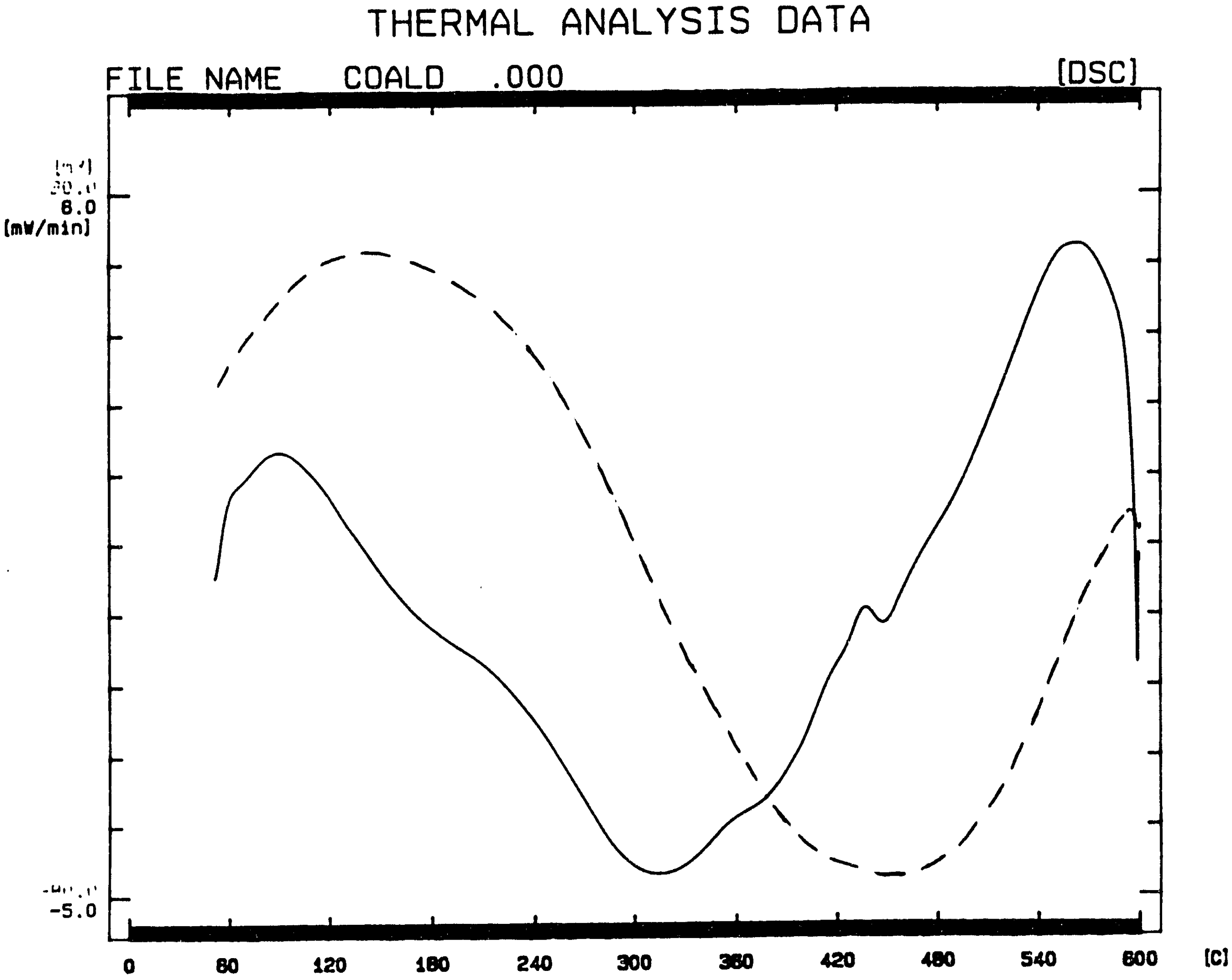


Figure 1. Hardcopy Output from DSC experiment completed on IBC-108.

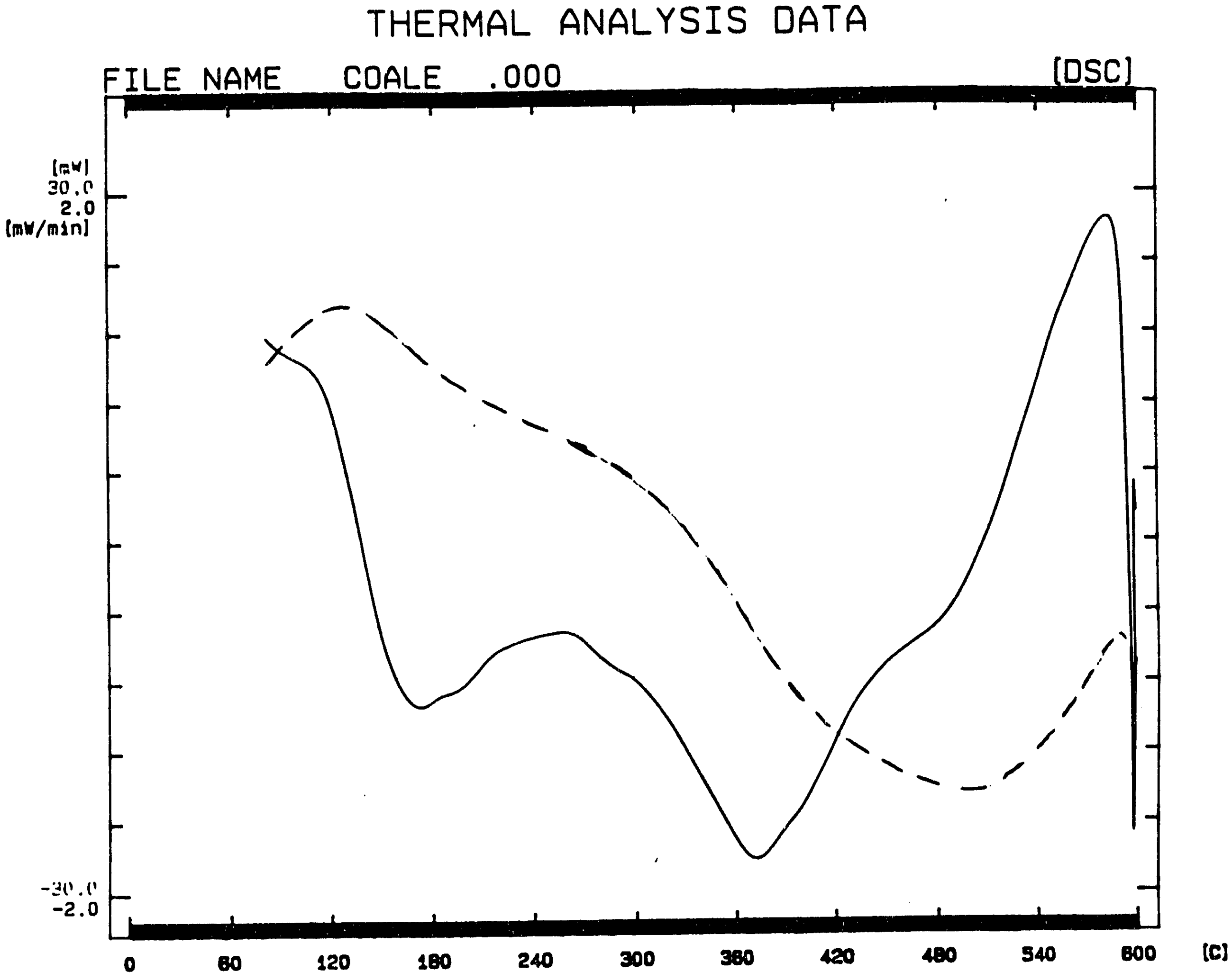


Figure 2. Hardcopy Output from DSC experiment completed on *photooxidized* IBC-108.

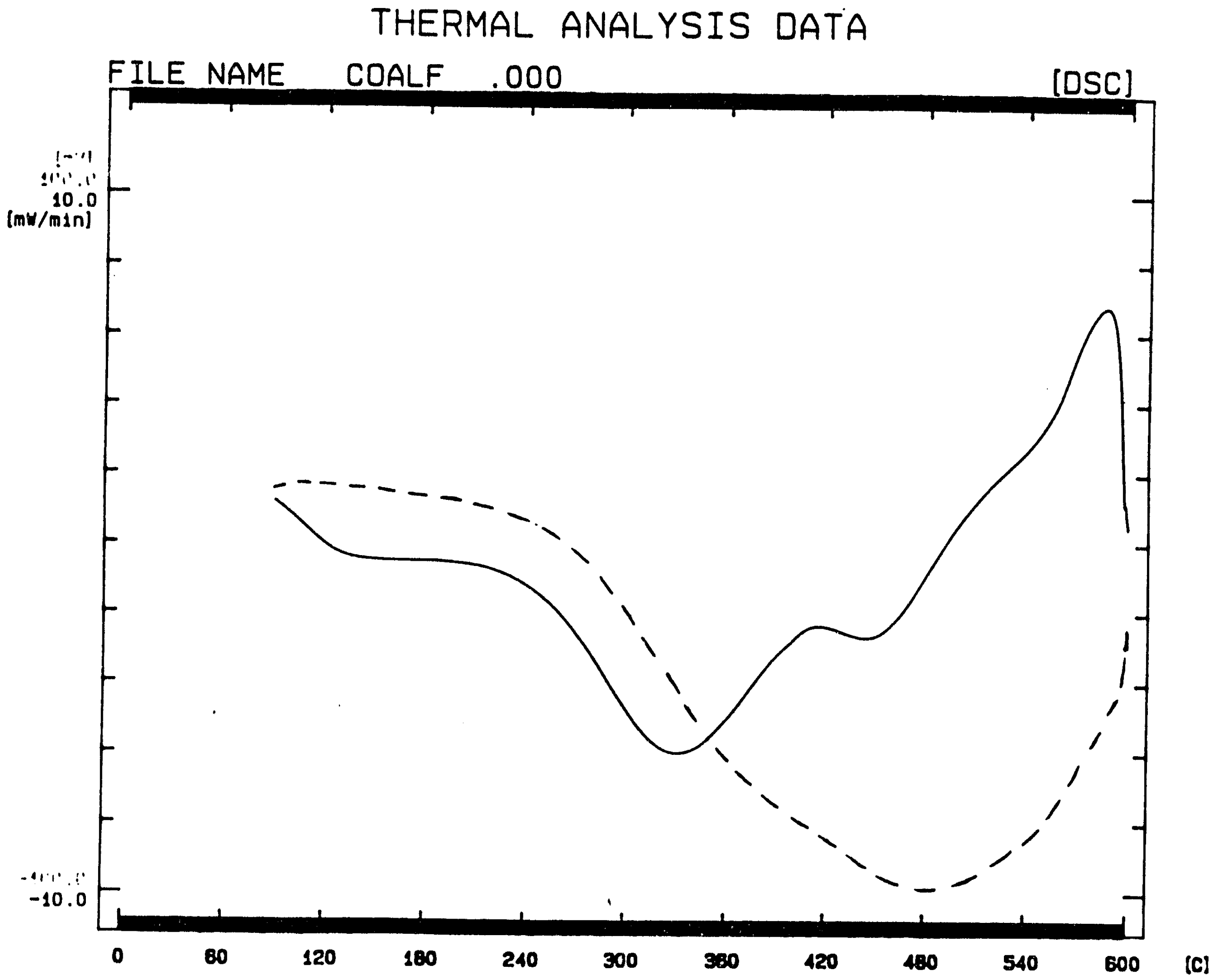


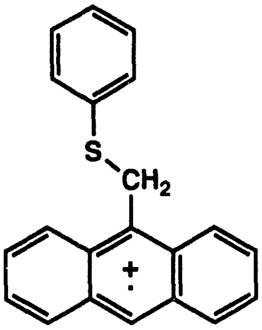
Figure 3. Hardcopy Output from DSC experiment completed on *hydrolyzed* IBC-108.

the photooxidation process reduces the exinite (or the ability to observe it) but increases the inertinite maceral content in the coal.

Maximum reflectance data for untreated IBC-108 and photooxidized IBC-108 (0.65 and 0.97, respectively) indicate that the photooxidized coal is "still coal" with little loss of the structural integrity possessed by the original sample. The slight increase is probably associated with some additional crosslink that results from the incorporation of oxygen into the backbone of the coal. Microscopic analysis of the photooxidized 108 also indicates that the vitrinite is not substantially degraded upon photooxidation.

TASK 4: Carry out experiments that enable determinations of the bond energies for aliphatic and aromatic C-S bonds in the radical ions derived from several coal model compounds. Communicate these results to the coal-desulfurization community through publications in scientific journals.

RESULTS: Rather involved experiments involving photomodulated voltammetry have been completed in attempts to determine redox potentials for electron transfer reactions involving various organic radicals and cations. The essence of these experiments is that we are trying to perfect a device which will enable us to evaluate redox potentials for transient organic species. We have now evaluated the C-S bond strengths in molecules such as **4** and **5**,***relative to*** the C-S bond strengths in the neutral (reduced) analogues of **4** and **5** (i.e. 9-phenylthiomethylanthracene and 9-phenylthiofluorene, respectively). The C-S bonds in **4** and **5** are about 10 and 25 kcal/mol weaker than the identical bonds in their neutral analogues. These data are important because species such as **4** and **5** are likely intermediates in radical-cation assisted desulfurization processes. The data suggest that the 1-electron oxidation of aromatic substrates such as 9-phenylthiomethylanthracene and 9-phenylthiofluorene **does not** result in an overwhelmingly large reduction in the C-S bond



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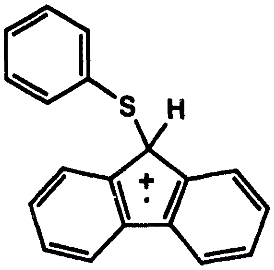

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strengths for these species. It is thought that C-S bond cleavage is an essential part in any protocol that attempts to remove organic sulfur from Illinois coal.

RESEARCH OUTLOOK

In the area of photooxidations of Illinois coal and organic sulfides, my research group and I have made important and real progress in areas that logically lead to new experiments in coal chemistry. We plan to write a proposal to ICCI in the spring of 1994 that aims to further our results in this area.

Equipment Inventory
September 1, 1992, through August 31, 1993

Project Title: "Protocols for the Selective Cleavage of Carbon-Sulfur Bonds in Coal"
Principal Investigator: Mark J. Bausch
Organization: Southern Illinois University at Carbondale
Department: Chemistry and Biochemistry

List of Equipment Purchased

<u>NONE DURING THIS FUNDING PERIOD</u>

List of Publications and Presentations

JOURNAL ARTICLES

NONE DURING THIS FUNDING PERIOD.

PRESENTATIONS OR CONFERENCE PAPERS

Bausch, M.J. November 1992 "Photooxidations of Organic Sulfides and Related Topics." Seminar Speaker, University of Kentucky.

Bausch, M.J. January 1993 "Photooxidations of Organic Sulfides." Seminar Speaker, Lehigh University.

Bausch, M.J. April 1993 "An Overview of the Research In the Bausch Group at SIU.", Exxon Chemical Company, New Jersey.

Bausch, M.J. August 1993 "Protocols for the Selective Cleavage of Carbon-Sulfur Bonds in Coal.", Annual Illinois Coal Contractors Meeting, Urbana IL.

PROJECT MANAGEMENT REPORT
September 1, 1992 through December 31, 1993

Project Title: **PROTOCOLS FOR THE SELECTIVE CLEAVAGE OF CARBON-SULFUR BONDS IN COAL**

Principal Investigator: M. J. Bausch
Department of Chemistry & Biochemistry
Southern Illinois University at Carbondale
Carbondale, Illinois 62901
618-453-6461
Project Manager: Ken Ho, Illinois Clean Coal Institute

COMMENTS

All milestones met with the exception of Milestone I.

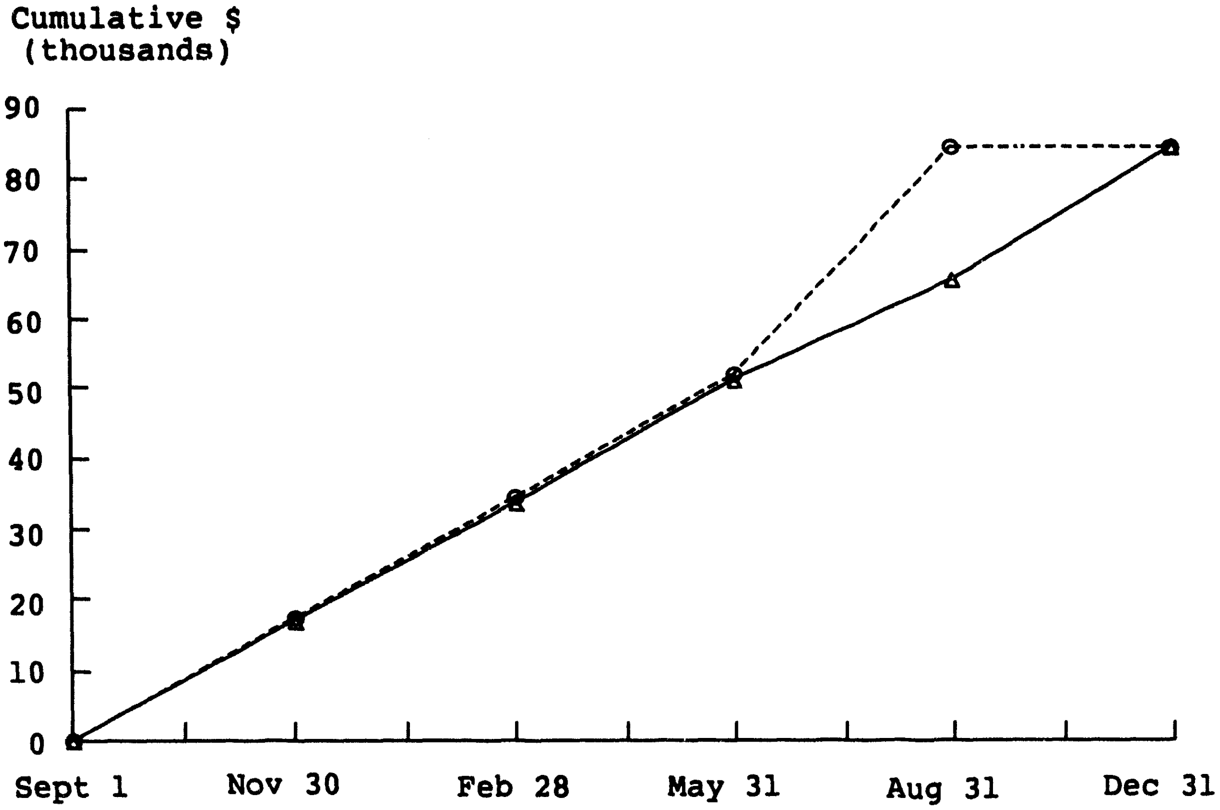
Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1992	Projected	12,250	1,636	0	500	1,500	1,589	17,475
to Nov. 30, 1992	Estimated Actual	12,250	1,636	0	0	1,500	1,539	16,925
Sept. 1, 1992	Projected	24,500	3,272	0	500	3,000	3,127	34,399
to Feb. 28, 1993	Estimated Actual	24,500	3,272	0	0	3,000	3,077	33,849
Sept. 1, 1992	Projected	36,750	4,908	500	500	4,500	4,716	51,874
to May 31, 1993	Estimated Actual	36,750	4,908	500	0	4,500	4,666	51,324
Sept. 1, 1992	Projected	62,955	6,545	1,000	0	6,000	7,700	84,700
to Aug. 31, 1993	Estimated Actual	48,955	4,908	850	0	5,000	5,971	65,684
Sept. 1, 1992	Projected	62,955	6,545	1,000	0	6,000	7,700	84,700
to Dec. 31, 1993	Estimated Actual	62,955	6,545	1,000	0	6,000	7,700	84,700

*Cumulative by quarter.

COSTS BY QUARTER

Protocols for the Selective Cleavage of
Carbon-Sulfur Bonds in Coal



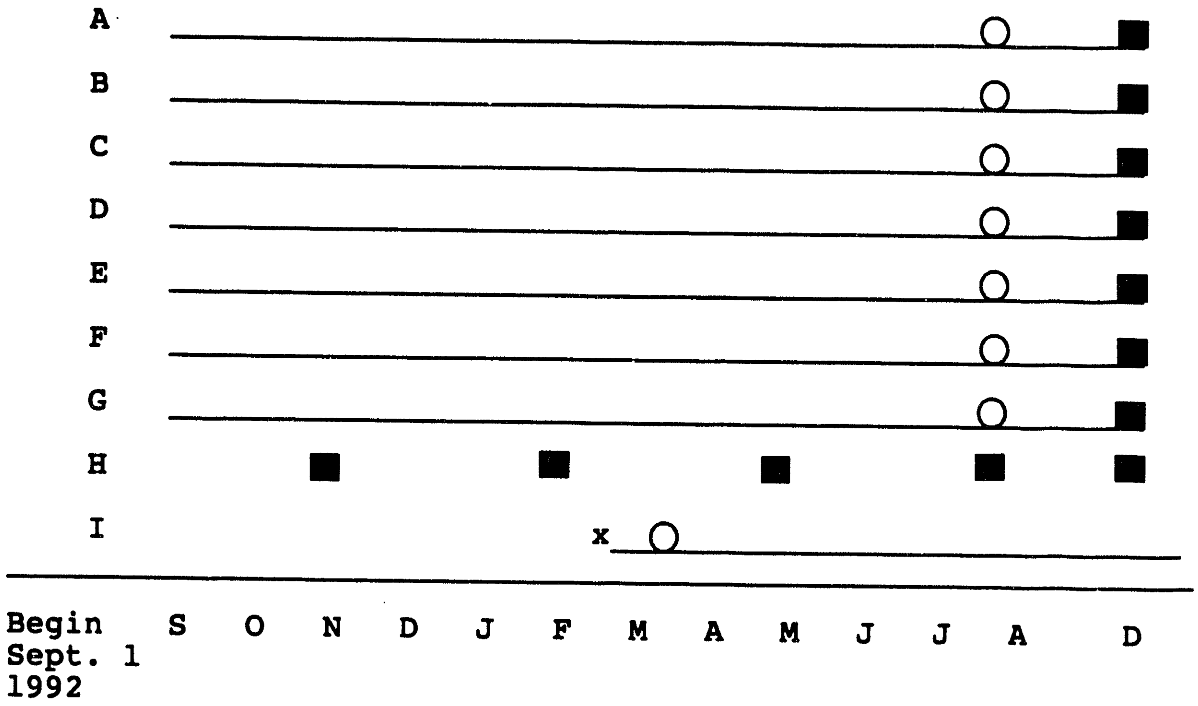
Months and Quarters

O = Projected Expenditures ---------

Δ = Estimated Actual Expenditures ________

Total Illinois Clean Coal Institute Award $84,700

SCHEDULE OF PROJECT MILESTONES



Milestones:

A. Post-doctoral research associate employed
B. Graduate research assistant employed
C. Graduate research assistant employed
D. Task 1 undertaken; second Bausch group Task 1 review 2/1/93
E. Task 2 undertaken; second Bausch group Task 2 review 3/1/93
F. Task 3 undertaken; second Bausch group Task 3 review 4/1/93
G. Task 4 undertaken; second Bausch group Task 4 review 5/1/93
H. Technical reports and project management reports prepared and submitted
I. Publication prepared and submitted: "Lewis Acid-Promoted C-S Bond Cleavage Chemistry"

Mark Bausch
PROTOCOLS FOR THE SELECTIVE CLEAVAGE OF CARBON-SULFUR BONDS IN COAL

HAZARDOUS WASTE REPORT
September 1, 1992 through December 31, 1993

EPA Hazardous Waste Number	Chemical/Solvent	Hazard Code	Amount Used (L)
U002	Acetone	I	1
U003	Acentonitrile	I,T	4
U037	Benzene, Chloro-		0.1
U070	Benzene, 1,2-dichloro-		0
U056	Benzene, hexahydro-	I	0.1
U220	Benzene, methyl-		3
U044	Chloroform		2
U135	Hydrogen sulfide (H_2S)		Trace
U154	Methyl alcohol	I	3
U138	Methyl iodide		0.05
U188	Phenol		0.05
U196	Pyridine		2

All hazardous wastes listed above were turned over to the SIUC Center for Environmental Health and Safety. They were disposed of in accordance with the EPA/SIUC approved disposal plan. For additional information, please contact James Tyrrell, Director, Center for Environmental Health and Safety, (618) 536-7511.

DATE FILMED

5/31/94

END