DOE/PC/30088-4

Coal-Transformation Chemistry

Fourth Quarterly Progress Report

Leon M. Stock, Principal Investigator

D.A. Blain, C.I. Handy, P. Heimann, C.B. Huang, H.-H. King,

W. Landschulz, and R.S. Willis

Research Students

University of Chicago

Chicago, Illinois 60637

Prepared for the

Department of Energy

Under Contract #DE-AC22-80PC30088

I. ABSTRACT

Pyrene, perylene, anthracene, 9,10-diphenylanthracene, naphthalene and biphenyl have been employed as electron transfer agents in the reduction of Illinois No. 6 coal with potassium in tetrahydrofuran. These electron transfer agents are about equally effective for the reduction of this coal at short reaction times (3 hours). At intermediate reaction times (45 hours), there are major differences in the degree of the reduction reaction. Biphenyl and naphthalene are much more effective reagents than anthracene or 9,10-diphenylanthracene. At very long reaction times (100 hours), the differences in the effectiveness of these hydrocarbons have been leveled somewhat. We conclude that the anions of biphenyl and naphthalene achieve a greater degree of electron transfer to the coal molecules and that the use of these anions enhances the fragmentation reactions of the coal. This work is described in Part A.

Illinois No. 6 bituminous coal and Colorado subbituminous coal were reacted with potassium dissolved in a mixture of monoglyme and triglyme at -50°C. The reduction reaction proceeded via solvated electrons rather than by an electron transfer reaction. The coals were then alkylated with methyl iodide and their solubilities in tetrahydrofuran were determined. The Illinois coal reductively alkylated via solvated electrons was considerably less soluble in tetrahydrofuran than the same coal reductively alkylated with potassium and naphthalene in tetrahydrofuran. These results indicate that the use of metals dissolved in etheral solutions is not as effective as the use of a metal and an electron transfer agent for the conversion of Illinois No. 6 coal to a soluble product. The reductive alkylation of a subbituminous coal with potassium in an etheral solvent was also studied. In this case, only a low yield of soluble alkylated product was obtained. There are no notable differences in the course of the dissolving metal reaction compared to the reaction with potassium and an electron transfer agent in tetrahydrofuran. These results are discussed in Part B.

A sample of Illinois No. 6 coal which had been reductively butylated with n-butyl-1-^{13}C iodide was hydrolyzed. Carbon nmr spectroscopy of the hydrolyzed coal revealed that the resonances previously assigned either to the presence of n-butyl carboxylates or to n-butyl tertiary ethers were removed. This observation provides definite evidence that only carboxylates were present in the original alkylated product. The results are reported in Part C.

Selective alkylation of the acidic hydroxyl groups in Illinois No. 6 coal was carried out using tetrabutylammonium hydroxide as a phase transfer catalyst and iodomethane or 1-iodobutane as alkylating agent as described by Liotta. The tetrahydrofuran solubility of the product was significantly improved in a reaction where reductively butylated coal was subsequently methylated using Liotta's procedure. The selective alkylation reaction was found to be effective, as regards the solubilization of coal, when a tetrahydrofuran-insoluble coal reductive alkylate residue was brought into reaction with the reagents tetrabutylammonium hydroxide and 1-iodobutane. This work is discussed in Part D.

The infrared spectra of raw Illinois No. 6 and Colorado coals and some of their alkylates were studied on a comparative basis. The spectra show that the relative intensities of the O-H and aliphatic C-H stretching frequencies are significantly different before and after alkylation and that an absorption near 1730 cm^{-1} assigned to carboxylic esters appears upon selective alkylation. These spectra are shown in Part D.

The reactions of phenol with sodium sulfide at 400°C producing thiophenol, the stability of thiophenol at 400°C, and the influence of sulfur compounds on the deuterium-hydrogen exchange reactions between tetralin-d_{12} and diphenylmethane are discussed in Part E. The results indicate that mercaptans and mixtures of sodium sulfide with 1-naphthol or 2-naphthol accelerate the exchange reaction, but that sodium sulfide, phenol, 1-naphthol, or 2-naphthol do not increase the rate of the exchange reaction. Tentative conclusions concerning the influence of inorganic sulfides on the exchange reactions are presented in Part E.

II. OBJECTIVE AND SCOPE OF WORK

A. Objective

The objective of this research is to define the structural features of coal which are important in conversion processes.

B. Scope of Work

TASK 1 Solubilization Reactions

The objective of this task is the development of methods for the conversion of coal molecules to soluble materials. Methods for the non-selective and selective conversion of coal to polyanions and for the conversion of the polyanions to soluble products will be investigated.

TASK 2 Quantitative Analysis

The objective of this task is the development of semiquantitative methods for the determination of the course of the alkylation reactions and other significant processes through the use of isotopic labels and other appropriate analytical procedures including chromatography and spectroscopy.

TASK 3 Application of the Procedure

The procedures developed in tasks 1 and 2 will be applied in a study of the structure and reactivity of a selected group of coals, coal macerals, and coal products.

TASK 4 The Chemistry of Liquefaction

The objective of this task is the elucidation of the chemical reactions that occur to initiate and sustain the liquefaction reaction. The reactions of molecules with deuterium atom labels will be studied to probe the course of these reactions.

III. SUMMARY OF PROGRESS

A. Work During This Quarter

Six electron transfer agents have been investigated for use in the reductive alkylation reaction by determination of the rate of formation of the

$$\text{Coal} \xrightarrow[\text{Electron Transfer Agent}]{K} \text{Coal polyanion}$$

coal polyanion. The rate data obtained for this heterogeneous reaction indicate that the electron transfer agents show different degrees of effectiveness at different stages of the reaction. It is clear, however, that biphenyl and naphthalene form the most thermodynamically unstable and most kinetically reactive anions. The rates of reduction and the quantity of soluble product obtained from these compounds are much greater than for the other hydrocarbons used in this study.

Illinois No. 6 bituminous and Colorado subbituminous coals were reduced with potassium followed by alkylation with methyl iodide in a mixture of ethylene glycol dimethyl ether and triethylene glycol dimethyl ether at -50°C. The solubility of these reductively alkylated coals in tetrahydrofuran was determined.

Illinois No. 6 coal which had been reductively butylated with n-butyl-1-^{13}C iodide was hydrolyzed with tetrabutylammonium hydroxide for the purposes of studying the importance of n-butyl carboxylates versus n-butyl tertiary ethers in the tetrahydrofuran soluble coal product. It was found that n-butyl carboxylates are present in the alkylated products while butyl tertiary ethers are not.

Illinois No. 6 coal was selectively alkylated according to a procedure outlined by Liotta. The infrared spectra of unreacted Illinois No. 6 coal, unreacted Colorado coal and their alkylation products were recorded to characterize the coals and the coal products more completely.

The exchange reactions of tetralin-d_{12} with diphenylmethane at 400°C are accelerated by combinations of 1- and 2-naphthol and sodium sulfide, naphthalenethiol, or combination of phenol and sodium sulfide. Under these experimental conditions, phenol reacts with sodium sulfide to form thiophenol and a trace of diphenyl sulfide.

B. Summary of Progress to Date

TASK 1 Solubilization Reactions

Six compounds: pyrene, perylene, anthracene, 9,10-diphenylanthracene, naphthalene, and biphenyl have been examined as electron transfer reagents in the reductive alkylation of Illinois No. 6 coal. The results indicate that naphthalene and biphenyl are the most suitable electron transfer agents for the rapid reduction of this coal and for the formation of soluble alkylated products.

Our work has shown that by reacting Illinois No. 6 coal with K/$C_{10}H_8$/THF/n-BuI over 50% of the reductively alkylated coal was soluble in THF. The same results were obtained when methyl iodide was the alkylating agent. When a Colorado subbituminous coal was reacted under the same conditions, there was much less solubilization. When the insoluble Colorado coal residue was reacted under the same conditions, significantly more solubilization occurred.

Work has continued with regard to the elucidation of entities important in the solubilization of coal by reductive alkylations. To that end, it has been established that whereas butyl carboxylates are formed in the reductive butylation of Illinois No. 6 coal, butyl tertiary ethers, are not formed in the reaction.

The reactions of lithium, sodium, and potassium with Illinois No. 6 coal in liquid ammonia were examined. The polyanions were then alkylated with n-butyl iodide. It was observed that lithium and potassium were about equally effective at -33° and that these metals were both more effective than sodium under these conditions.

The research work has also established that Illinois No. 6 coal reacts with potassium in liquid ammonia at -78°, -33°, and 25°. The coal anions prepared in this way are readily alkylated. Essentially the same amount of soluble alkylated products are obtained at each temperature. The coal anion was prepared in liquid ammonia at -33° and 25°. It was then reacted with n-butyl chloride, bromide, and iodide. The iodide was more effective for the conversion of the coal to a soluble product than either of the other two halides. It was also established that the use of a cosolvent during the alkylation and the use of longer reaction times were beneficial for the formation of the greatest amount of soluble product. The information thus far obtained establishes that the reductive alkylation reaction can be effectively performed at -33° or at 25°, that potassium is a more generally effective reagent and that butyl iodide is an effective alkylating agent. When the various reaction parameters are optimized the Illinois No. 6 coal is converted into a butylated product which is about 55% soluble in tetrahydrofuran.

Our research work has established that Colorado coal requires a greater quantity of potassium per gram of coal than Illinois No. 6 coal, in order to yield an alkylated product of comparable tetrahydrofuran solubility. It is possible to conclude that increased concentrations of potassium in liquid ammonia and longer alkylation times, favor greater solubility of Colorado subbituminous B coal.

Recent investigations have confirmed that Colorado subbituminous coal has a greater carboxylic acid content than Illinois No. 6 coal. This explains why upon alkylation more esters are formed from Colorado coal, whereas Illinois No. 6 bituminous coal under similar conditions yields more ethers.

TASK 3 Application of the Procedures

The information concerning the structure and chemical reactions of Illinois No. 6 coal has been assembled and critically analyzed. A structure for Illinois No. 6 coal that is compatible with the proton and carbon nmr spectra obtained for solid state samples and with chemical reaction data for oxidation under several different kinds of conditions, for reductive alkylation and for tetralin-d_{12} exchange reactions has been proposed by L.B. Alemany.

TASK 4 The Chemistry of Liquefaction

The significance of phenolic compounds and benzoic acid derivatives as acidic reagents at 400° has been examined. Study of the exchange reactions of tetralin-d_{12} and diphenylmethane in the presence and absence of these compounds and appropriate product studies have clearly established that phenol does not serve as an acid under the experimental conditions. Rather, the phenolic compounds undergo exchange via a free radical pathway.

The reduction of styrene by tetralin at 400°C has been investigated. An unusually complex reaction mixture was obtained. The observations indicate the complexity of the organic reactions of even relatively simple molecules at high temperature. It is particularly significant to note that recombination reactions can lead to adducts which can fragment by facile β-scission reactions to yield diverse products. For example, styrene reacts with tetralin to give 11% 1,3-diphenylpropane, 4% 1-methyltetralin, and 7% 1-methylnaphthalene.

The effects of organic additives on the reduction of E-stilbene by tetralin at 400°C have been studied. Additives such as coal, benzyl phenyl sulfide, 9,10-anthraquinone, and tetracene in low concentration greatly accelerate the rate of reduction of E-stilbene by tetralin.

The significance of the concerted pericyclic reaction in the coal liquefaction has been examined. Study of the thermal hydrogen atom transfer reactions of reactive donors, tetralin, 1,2- and 1,4-dihydronaphthalene with anthracene, phenanthrene and E-stilbene suggested that the free radical pathway is more likely. The reduction of tetracene and E-stilbene by a mixture of donor and deuterated donor provided further experimental support. The deuterium distribution of the produced 5,12-dihydrotetracene is $d_0:d_1:d_2:d_3:d_4=$ 54:24:19:2:1 with tetralin as donor, 56:27:12:4:1 with 1,2-dihydronaphthalene as donor, 42:34:18:5:1 with 1,4-dihydronaphthalene as donor. The deuterium distribution of 1,2-diphenylethane, produced by the reduction of E-stilbene with 1,2-dihydronaphthalene, is $d_0:d_1:d_2:d_3:d_4$ = 62:29:7:1:0.

Sodium sulfide reacted with phenol to produce thiophenol (6%), and diphenyl sulfide (0.5%) at 400°C in 4 hrs. It was found that thiophenol was not stable at 400°C, about 75% thiophenol decomposed to form diphenyl sulfide (30%) during the reaction conditions. Mercaptans and combinations of naphthol and sodium sulfide accelerated the deuterium-hydrogen exchange reaction at 400°C. The combination of phenol and sodium sulfide did not affect the exchange reaction in 30 min but it accelerated the exchange reaction in one hour. Chars did not increase the rate of the exchange reaction between tetralin-d_{12} and diphenylmethane.

IV. DISCUSSION OF TECHNICAL PROGRESS

PART A

The Reactivity of Electron Transfer Agents

by Phillip Heimann

Introduction

The electron transfer agents plays an important role in the reductive alkylation reaction. The results shown in Table Al indicate that the less thermodynamically stable biphenyl anions are more effective for the formation of soluble coal alkylate than naphthalene or anthracene.

$$\text{Coal} \xrightarrow[\text{ArH,THF}]{\text{K}} \xrightarrow{\text{BuI}} \text{Coal(Bu)}_n$$

Table Al. The Influence of Electron Transfer Agents on Formation of Soluble Alkylated Product from Illinois No. 6 Coal[a]

Aromatic Compound	Reduction Potential, v	Conversion to THF Soluble Product,%
Biphenyl	2.70	58
Naphthalene	2.50	52
Anthracene	1.90	41

[a] Unpublished results obtained previously in this study.

The results presented in the table may be indicative of a general trend. These findings suggest a new approach for the study of the reactivity of coal molecules. Specifically, the reactivity of a coal may be gauged by the rate of the electron transfer reaction and by the extent of the electron transfer reaction. To test this idea, we have investigated the rates of formation of the coal polyanions using biphenyl, anthracene, phenanthrene, pyrene, and perylene as the electron transfer reagents. We have also compared the reactivity of anthracene and 9,10-diphenylanthracene to assess the impact of the steric requirements of the electron transfer reagent on the process. More specifically, 9,10-diphenylanthracene is about 13.5 x 8.0 x 3.5Å. This large molecule would experience more difficulty than anthracene in traversing the small pore structure of the coal. Consequently, if the reaction proceeds by a short range contact reaction between the electron transfer agent and the aromatic residues in the coal, then it must be anticipated that the reaction between these bulky molecules and the coal compound would be distinctly less rapid than the reaction of anthracene with the same coal. On the other hand, electron transfer reactions may occur with the aromatic compounds on the exterior surface of the solid coal with rapid electron transfer reactions to propel the electron to the interior of the coal structure. Bond cleavage reactions in the interior would then unravel the structure with the ultimate collapse of the matrix. A process of this kind would not be slowed appreciably by the bulky phenyl groups on the meso positions of anthracene. Thus, we sought information concerning the significance of surface to interior electron transfer reactions relative to the transport of the electron transfer reagent to the interior of the coal matrix via the pore structure. The general significance of this problem has been discussed in detail by Larsen and his associates (A1).

Accordingly, we have examined the rates of reaction of potassium and pyrene, perylene, 9,10-diphenylanthracene, anthracene, and biphenyl with Illinois No. 6 coal.

Experimental Procedure

The reaction solvent, tetrahydrofuran was purified by refluxing it for 4 hours over lithium aluminum hydride prior to distillation. The Illinois No. 6 coal was ground in a ball mill to -325 mesh. It was dried in a vacuum oven for 15 hours prior to use. The electron transfer agents used in these experiments were purified in the customary way.

A pair of identical experiments were carried out concurrently for each hydrocarbon. In each experiment, potassium and the electron transfer agent were stirred in tetrahydrofuran under an atmosphere of argon, but coal was added to only one of the reaction solutions. The reaction solutions were assembled in a glove bag in an argon atmosphere.

In a typical procedure, the electron transfer agent (3.10 to 3.15 mmoles) was dissolved in THF (55 mL). For perylene 115 mL of THF were used because of its limited solubility. After being rinsed twice in THF, potassium (1 to 1.05 g) was added. The apparatus was removed from the glove bag and argon was slowly passed through the apparatus for the course of the reaction, 5 days. For the reactions with coal, a dumper was connected to the reaction flask. The dried Illinois No. 6 coal (1 to 1.01 g) was added to the reaction solution 3 to 4 hours after the reaction between potassium and the electron transfer agent had been initiated.

The progress of the reaction was followed by titration. One mL aliquots were withdrawn by syringe from the vigorously stirred solution and were quenched in 30 ml of distilled water. The titrations were performed on a pH meter with 0.0503 N HCl. For a typical control reaction, aliquots were taken on the first day at 0.33, 0.67, 1.33, 2, 4, and 8 hours and after 1,2,3,4 and 5 days. For a typical coal reaction, aliquots were withdrawn at 0.5, 1,2,3, 3.5, 4, 4.5, 6 and 9 hours and after 1,2,3,4 and 5 days. On the final day of each experiment with coal, two titrations were performed, the second titration was performed on an aliquot taken from a reaction mixture in which the solid coal particles had been allowed to settle to the bottom of the flask.

Figure A1.--The titration curve for the reaction of potassium with biphenyl alone (B) and with biphenyl and Illinois No. 6 coal (C) are shown. The equivalence levels for the conversion of biphenyl to biphenyl(-2) and to biphenyl(-1) are also noted by the straight lines.

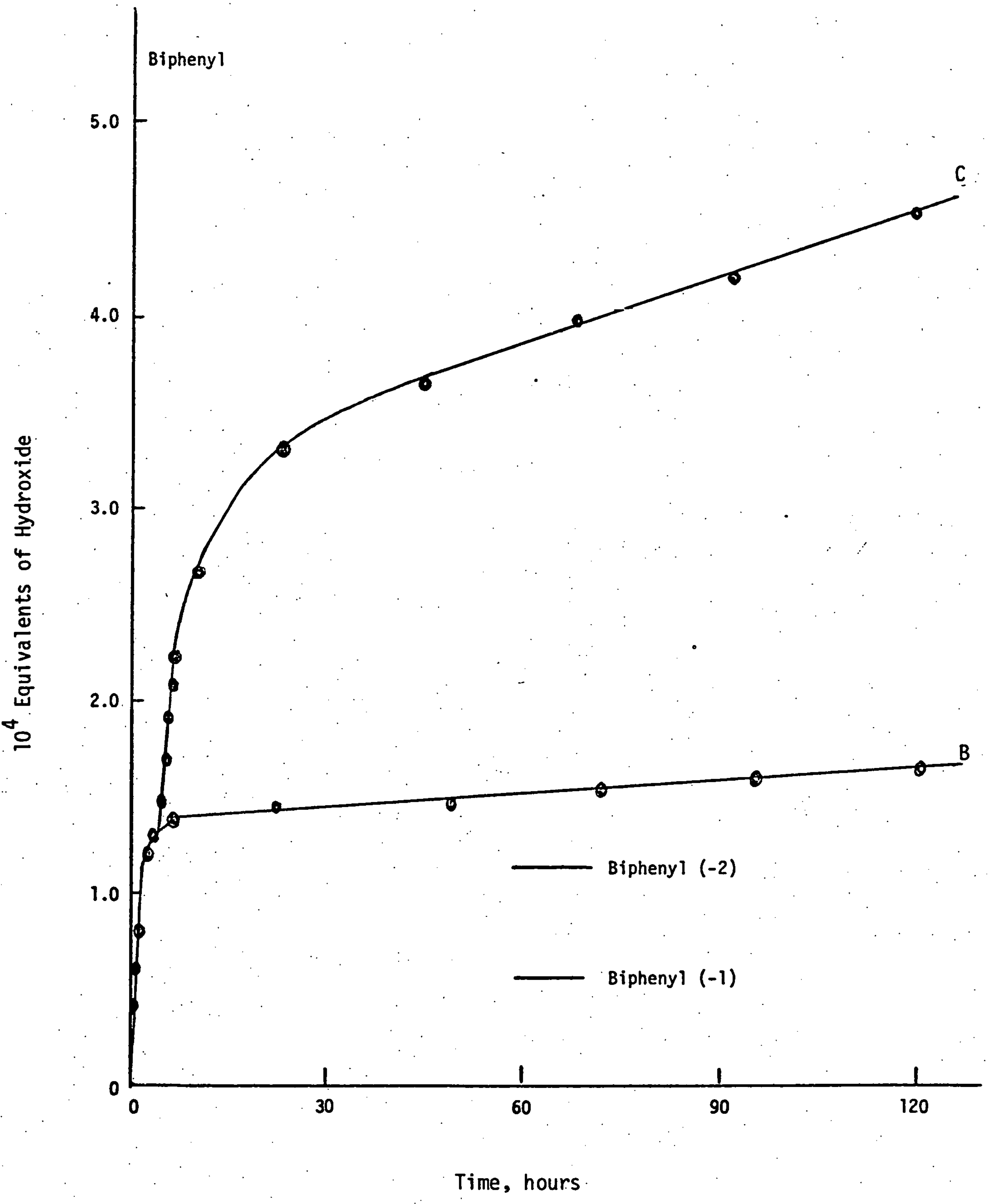


Figure A2.--The titration curve for the reaction of potassium with perylene alone (B) and the perylene and Illinois No. 6 coal (C) are shown. The equivalence levels for the conversion of perylene to perylene(-2) and perylene(-1) are also noted by the straight lines.

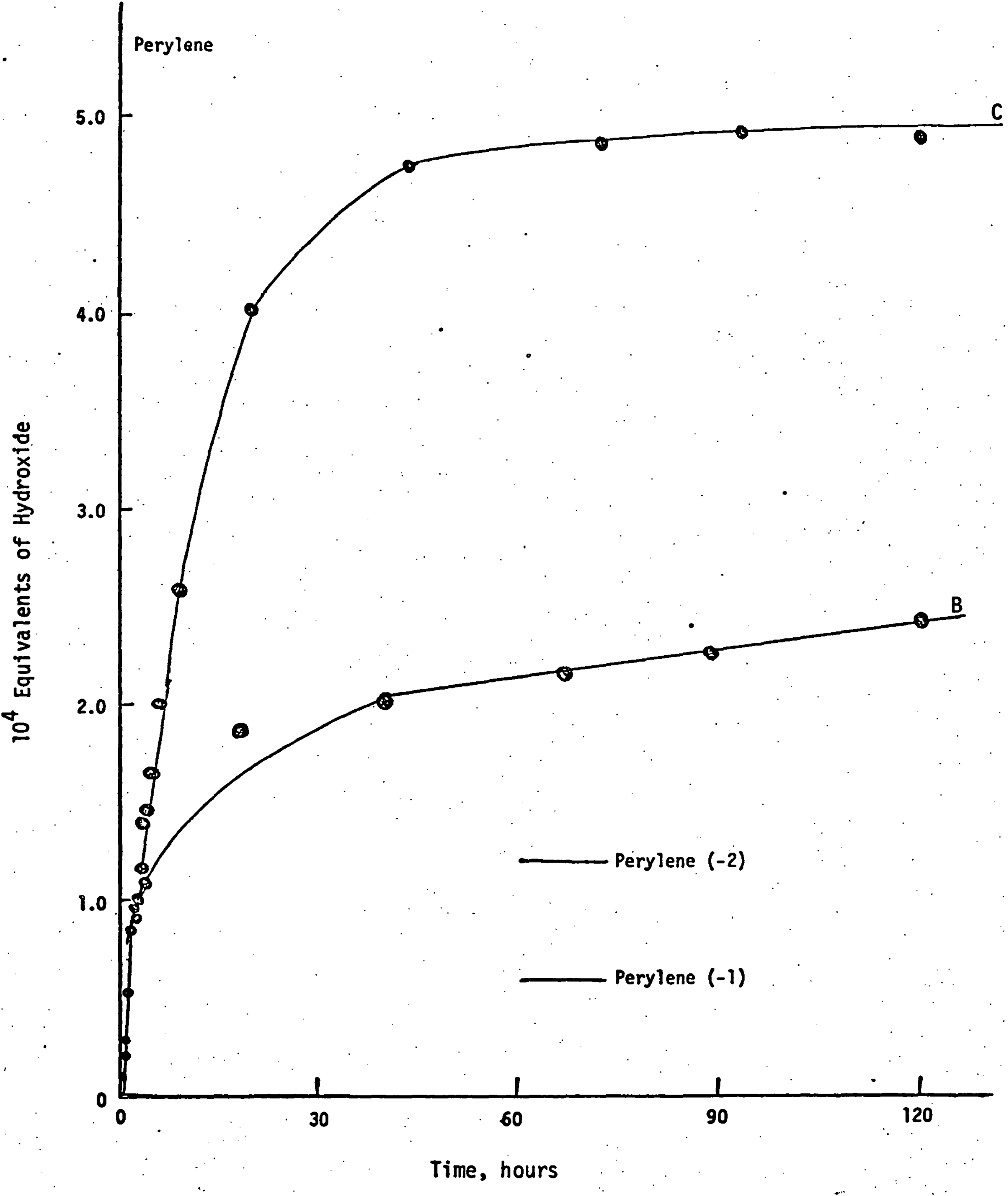


Figure A3.--The titration curve for the reaction of potassium with 9,10-diphenylanthracene alone (B) and the 9,10-diphenylanthracene and Illinois No. 6 coal (C) are shown. The equivalence levels for the conversion of 9,10-diphenylanthracene to 9,10-diphenylanthracene(-2) and 9,10-diphenylanthracene(-1) are also noted by the straight lines.

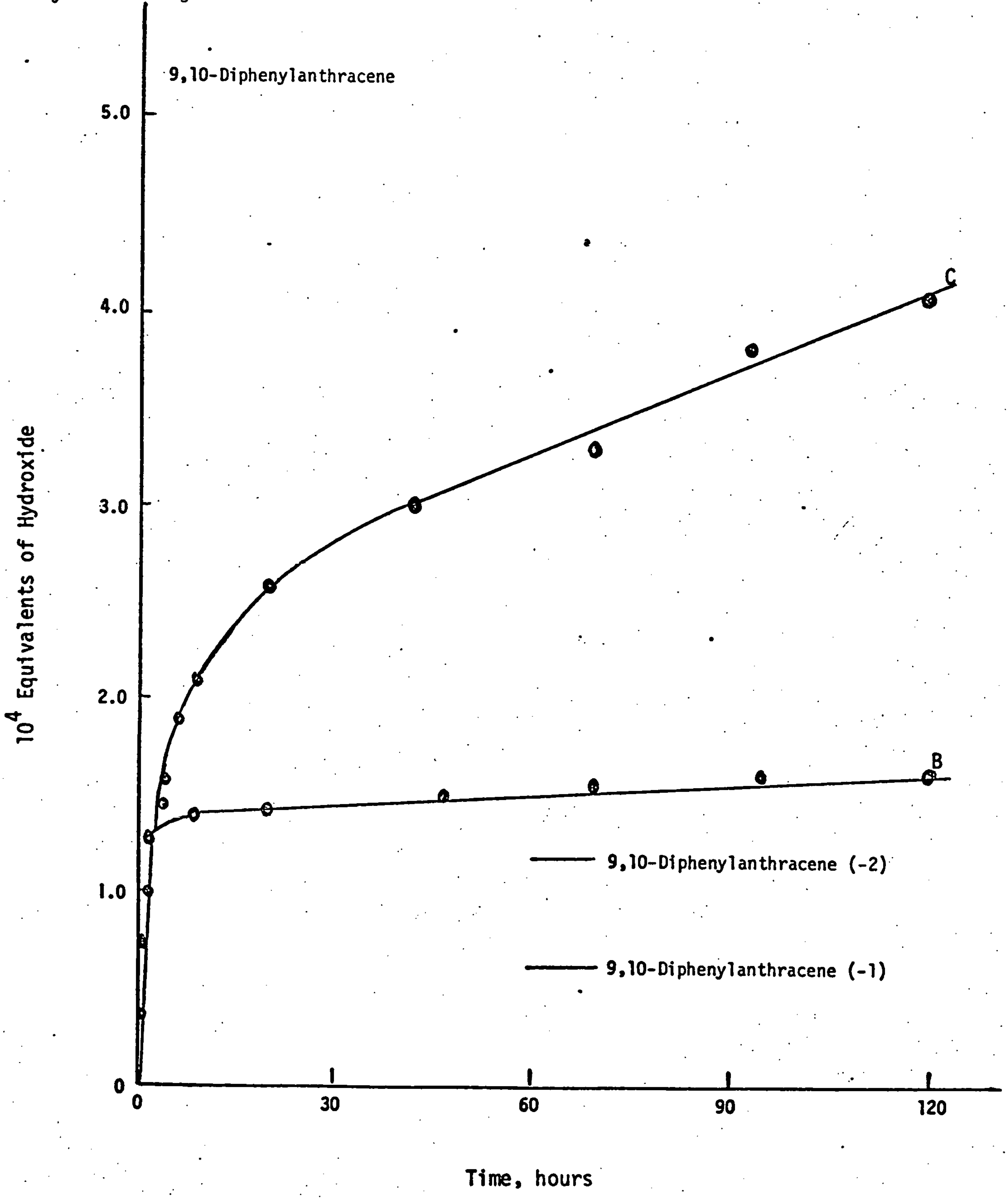


Figure A4.--The titration curve for the reaction of potassium with anthracene alone (B) and the anthracene and Illinois No. 6 coal (C) are shown. The equivalence levels for the conversion of anthracene to anthracene(-2) and anthracene(-1) are also noted by the straight lines.

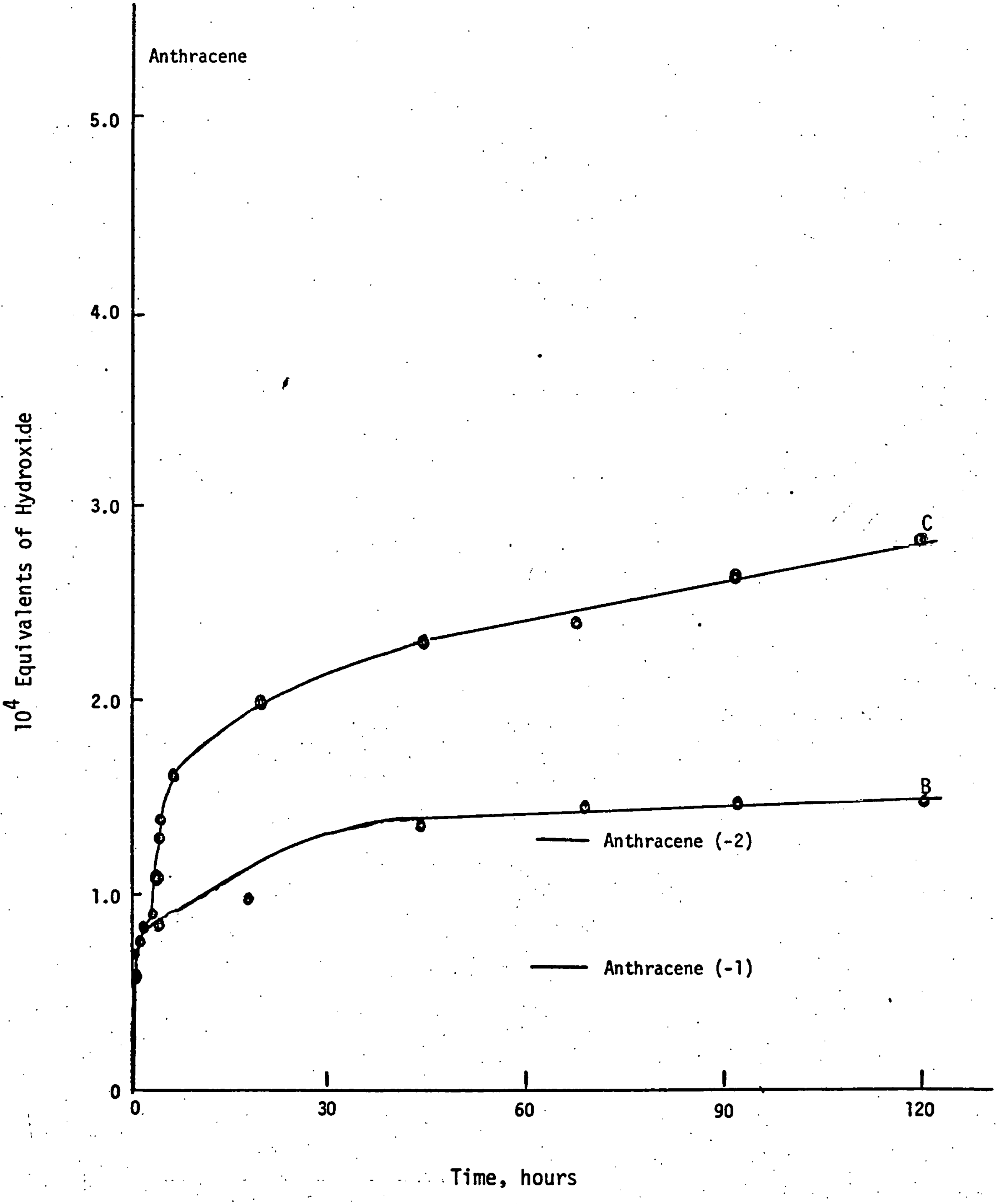
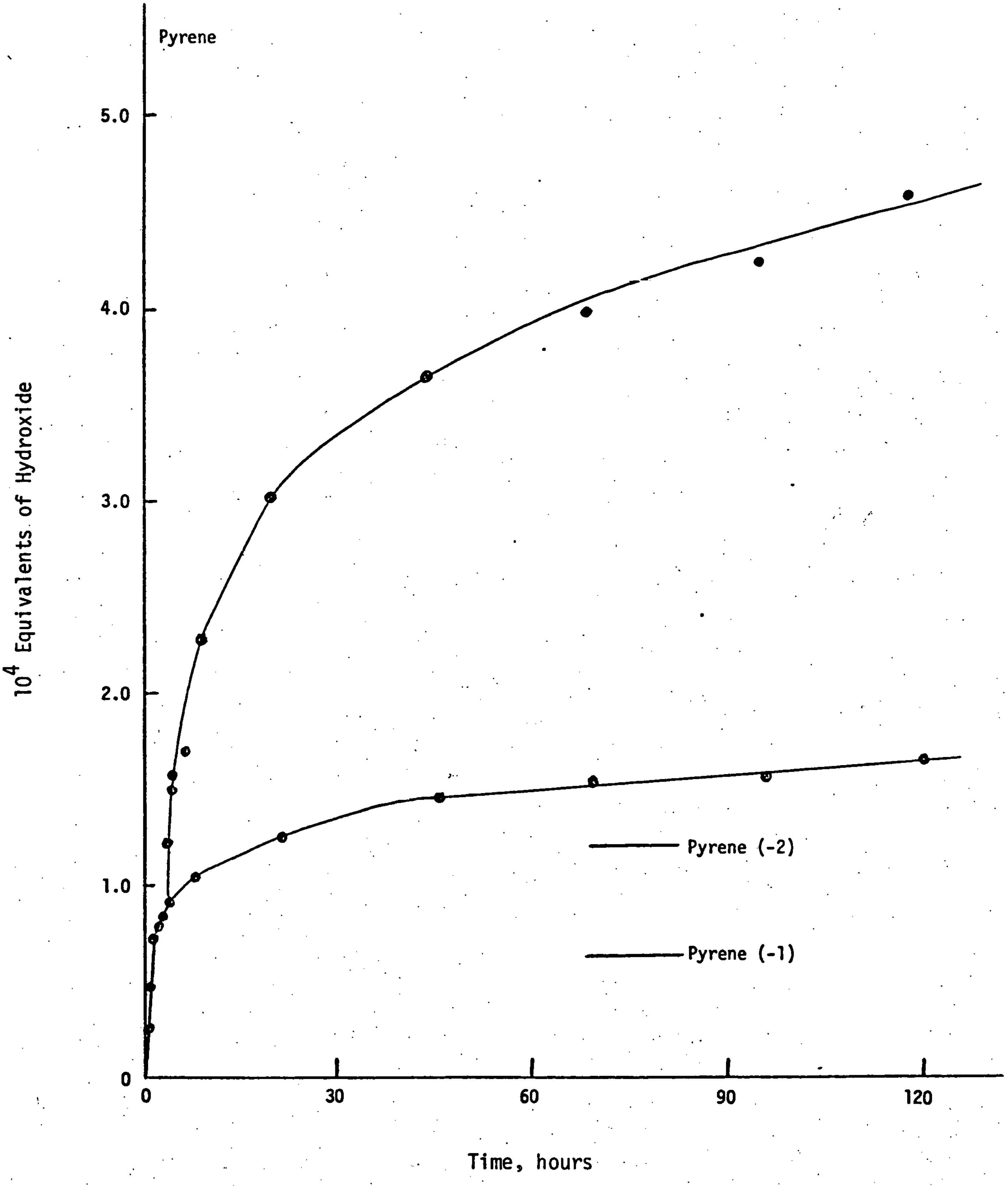


Figure A5. The titration curve for the reaction of potassium with pyrene alone (B) and the pyrene and Illinois No. 6 coal (C) are shown. The equivalence levels for the conversion of pyrene to pyrene(-2) and pyrene(-1) are also noted by the straight lines.



Results

Color changes accompanied all these reactions. The color of the negatively charged species was so intense that it could only be discerned by looking at the liquid rising up against the wall of the flask. The negatively charged naphthalene was dark green; the pyrene, cherry red; the perylene, purple; the 9,10-diphenylanthracene, blush purple, the anthracene, green; the biphenyl, blue-green.

When the coal was added, a second color change took place. The solution became almost colorless immediately after the addition of the coal. About 1.5 hours later the solution became greenish yellow.

The titration curves for biphenyl, anthracene, 9,10-diphenylanthracene, pyrene, and perylene are shown in Figures A1-A5. The results obtained previously for naphthalene are shown in Figure A6.

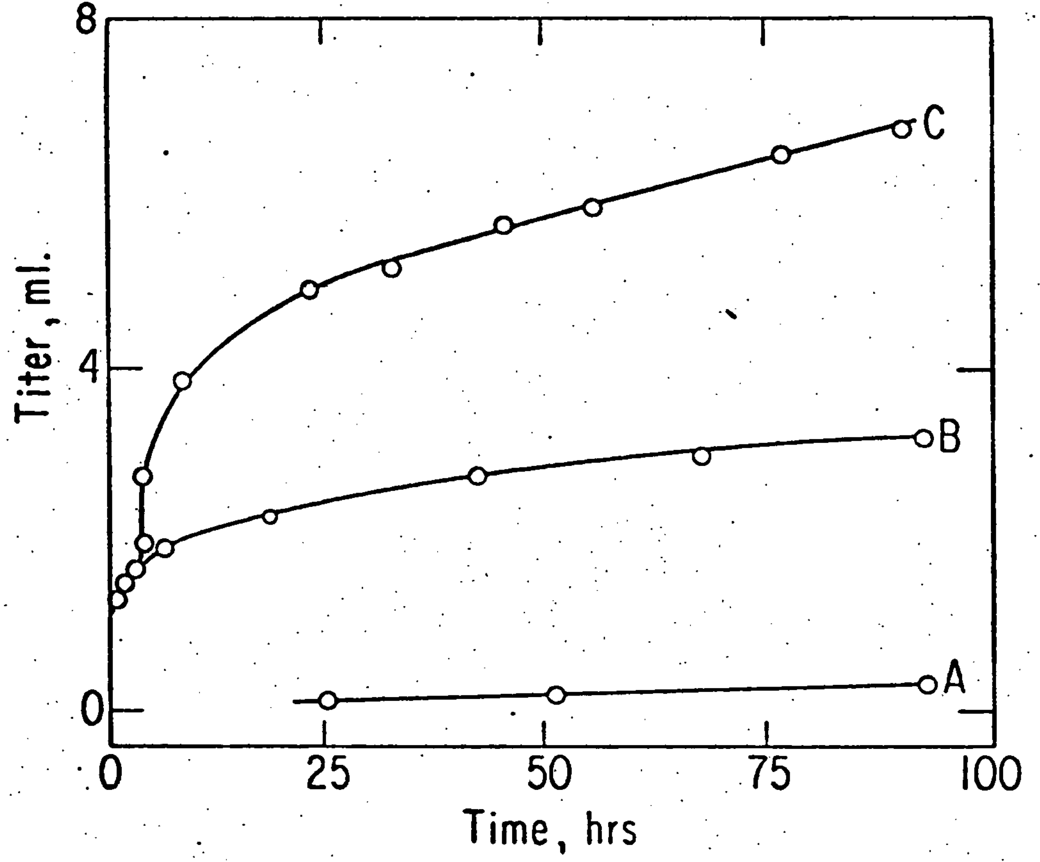


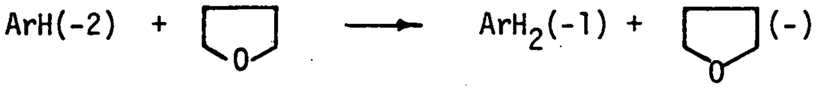
Figure A6--The rates of reduction of tetrahydrofuran (A), naphthalene (B), and Illinois No. 6 coal (C) are presented by a comparison of the titer required for aliquots of separate reaction mixtures over 100 hrs.

Discussion

All the electron transfer agents exhibited similar profiles. All exhibited a very fast initial rate which partially leveled off after three to four hours. After the coal was added, another sharp increase in rate occurred. Six hours after the coal was added, this burst also leveled off to a rate about 2 x 10^{-5} equiv OH^-/hr. The rate reduction of the coal slows considerably in five days. However, the rate of the reaction with coal is still about four times larger than the rate of the control reaction at the end of the experiment.

The titers observed in the control experiments indicate that all the electron transfer agents except perylene are reduced to a similar extent. These solutions contain 2.63 to 2.92 equivalents of latent hydroxide ion per molecule of the electron transfer agent. For perylene, this value is about 3.8.

Control experiments between potassium and tetrahydrofuran negate a direct reaction between these substances, Figure A6. However, a reaction may proceed in the presence of the electron transfer agent. The reaction of 5 mg of tetrahydrofuran in this way would accommodate the results of our experiments.



Perylene behaves quite differently. In the control experiments, this hydrocarbon acquires about 3.8 negative charges per molecule as judged by the titrimetric data. In the presence of coal, the potassium is completely consumed in 2 days as the perylene rather than the coal is reduced. Presumably, the coal molecules provide the protons necessary for the fuller reduction of this hydrocarbon.

The differences in reactivity of the electron transfer agents were estimated after 3, 45, and 120 hours from the difference in the titer for the reactions with and without coal. The results are presented in Table A2.

The results obtained for aliquots of the reaction mixture withdrawn three hours after the coal was added to the reaction mixture reveal that there are only modest variations in the reactivity of the electron transfer agents. Presumably, many of the rapid initial reactions occur between the acidic protons of the coal and the basic anions as illustrated for biphenyl(-2). At these short reaction times, therefore, there are no meaningful differences in reactivity.

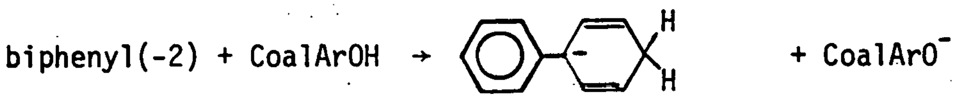


Table A2. The Influence of Electron Transfer Agents on Reduction of Illinois No. 6 Coal with Potassium in Tetrahydrofuran at 25°C.

	10^3 Meq of Base per Ml		
Compound	3 Hrs	45 Hrs	120 Hrs
Pyrene (-2.11)	88	221	294
Biphenyl (-2.70)	78	220	260
9,10-Diphenylanthracene	-	153	246
Naphthalene (-2.50)	78	115	209
Anthracene (-1.96)	74	100	136

Theory based on K is 0.491 Meq per Ml.

The extent of the reaction after 45 hours differs considerably. At this stage of the process, the reduction reactions initiated in the presence of pyrene and biphenyl have proceeded to a much greater extent than the reactions initiated in the presence of 9,10-diphenylanthracene, naphthalene and anthracene. Other information suggests that pyrene as perylene may be reduced under the experimental conditions (A2).

There are significant differences in the reactivity of the other electron transfer agents at the 45 hour point. The reactivity order observed for biphenyl > naphthalene > anthracene correlates very well with the reduction potentials for these hydrocarbons. This order is also observed at 120 hours. The rate data for these compounds also correlate well with the quantity of soluble product obtained in these reactions, Table A1. These data strongly suggest that the reaction is kinetically controlled at this time and that the less stable,more reactive anionic electron transfer agents are more effective for the reduction and depolymerization of the molecules in Illinois No. 6 coal as illustrated for ether cleavage.

$$\mathrm{ArH(-2) + Coal\text{-}O\text{-}Coal \rightarrow ArH + Coal(-1) + Coal\text{-}O^{-}}$$

After 120 hours, the situation has changed significantly. At this time, the differences in most of the electron transfer agents have been appreciably leveled. Only anthracene is significantly less reactive.

The leveling of the reactivity at 120 hours compared to 45 hours may be understood on the basis of the influence of the reduced coal molecules on the progress of the reaction. The anions, anion radicals, and dianions produced from the coal molecules must exert an important influence on the behavior of the other electron transfer agents in solution. We postulate that at long reaction times in the absence of excessive concentration of an added electron transfer agent the fragment coal molecules moderating the differences in reactivity of the added electron transfer agents and limiting the extent of the carbon-oxygen and carbon-carbon bond cleavage reactions in the case of Illinois No. 6 coal.

The rate data for 9,10-diphenylanthracene and anthracene suggest that steric factors do not play a major role. Indeed, the diphenylanthracene is more reactive than the unsubstituted compound. These results certainly suggest that the anionic electron transfer agents do not, of necessity, propagate the reaction through the small pores of the coal. Rather reaction models in which electron density is propagated from a surface acceptor to another acceptor in the interior of the coal by electron transfer without the further intervention of the electron transfer reagent (A3) or models in which molecular fragments of coal are peeled away from the solid as layers from an onion appear more compatible with these results. It is pertinent to note that the products obtained in the reductive alkylation reaction of the residue of a reductive alkylation are remarkably similar. This observation is, of course, most compatible with the latter interpretation.

Two aliquots, one from the stirred mixture and one from the unstirred mixture were withdrawn on the fifth day of the experiment. Typical results are summarized in Table A4.

Table A4. Distribution of Hydroxide Ion Forming Substances in Solid and Liquid Phases in Tetrahydrofuran at the End of the Reaction.

Compound	10^3 Meq of Base per Ml	
	120 Hours Solid and Liquid Phase	120 Hours Liquid Phase Only
Pyrene	459	70
Anthracene	285	40
Biphenyl	450	40

The results presented in Table A4 indicate that only a fraction of the basic anionic compounds are soluble in tetrahydrofuran. Thus, the subsequent alkylation reactions occur heterogeneously.

In summary, these results indicate that the least thermodynamically stable anion radicals and dianions are more effective for reduction of Illinois No. 6 coal. The reactivity of naphthalene and biphenyl illustrate this feature of the reaction. Second, the preliminary results obtained in the investigation of the role of steric factors on the reaction suggests that the dimensions of the electron transfer agent are not a critical factor in the success of the reaction. Rather, the reduction potential exerts a much more important effect. Finally, the reduced coal products are not soluble to an appreciable extent in the etheral solvent.

References

A1. J.W. Larsen, P. Choudhury, T. Greene, and E.W. Kuemmerle, Am. Chem. Soc., Fuel Division Preprints, 24, 197 (1979).

A2. The first and second reduction potentials for pyrene although somewhat less than those for perylene are more favorable than those for the other hydrocarbons examined in this study.

A3. The parameters which influence electron transport in solids have been studied in many laboratories. The rate of electron migration depends significantly upon the relative energy content of the donor and the acceptor and the distance between them. Electron propagation in anionic coal should be a relatively rapid process.

PART B

Reductive Alkylation of Coal via Solvated Electrons

by D.A. Blain and W.H. Landschulz

Introduction

From as early as 1959 it has been known that alkali metals dissolve slightly in ethers giving blue solutions. For example, potassium partially dissolves in monoglyme at several temperatures ranging from 0° to -50°C to give a characteristic deep blue solution. The temperature coefficient of solubility is negative in monoglyme (B1).

Recently Niemann and his coworkers were able to reduce a bituminous coal by adding the coal to a blue solution of potassium in a mixture of monoglyme and triglyme. These reactions were either quenched with a proton donor or with an alkyl halide (B2). In these reactions no electron transfer agent was necessary, so there was no possibility of naphthalene or other electron transfer agent being incorporated into the product (B3). Niemann and his coworkers studied their reductively alkylated coal by infrared and ^{13}C nmr spectroscopy. Their success prompted us to examine the suitability of the method for the reductive alkylation of Illinois No. 6 and Colorado subbituminous coals.

Experimental

The Colorado subbituminous B coal is from Seam No. 3 of the Laramie formation in Weld County, Colorado (B4).

Ultimate Analyses of Colorado Subbituminous Coal (Wt. %, dry basis)

Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen (by difference)	Ash
70.64	4.61	1.52	0.39	18.96	3.88

These figures give a % carbon (daf) = 73.5 compared to a % carbon (daf) = 77.2 for Illinois No. 6 coal.

Experimental Procedure

Monoglyme was refluxed over lithium aluminum hydride for four hours and distilled at atmospheric pressure. Triglyme was refluxed over lithium aluminum hydride for three hours at about 10 torr and then distilled at that pressure at 105°C. All reactions were run at -50°C under argon.

Triglyme (40 ml) and monoglyme (20 ml) were added to a flamed flask. After allowing the solvents to cool to -50°C, potassium (1 g per g of coal) was added, stirring (by a glass enclosed stir bar) was started, and within ten minutes the solutions had turned deep blue. Thirty minutes after the potassium had been added, the coal (< 325 mesh, Table B1) was added. Fifteen hours later, solid potassium remained. Distilled methyl iodide (2 moles methyl iodide per mole potassium) was added dropwise in monoglyme (10 ml) and the reaction was stirred for sixty more hours. The methyl iodide dissipated the blue color almost immediately.

The reactions were worked up by pouring the reaction mixture into distilled water (500 ml), acidifying with 2N hydrochloric acid, and then filtering through a glass frit. The coal was washed repeatedly with water to remove potassium iodide, dried, and weighed. In experiments 2 and 3 the coal was also washed with n-hexane to remove the residual triglyme not removed during the water washes. In all three experiments the coal alkylate was then repeatedly extracted with distilled tetrahydrofuran. The tetrahydrofuran soluble portion was filtered below 4-5.5μ and then freed of the solvent in a vacuum desiccator for 72 hours. The tetrahydrofuran insoluble portion was dried and weighed. Gel permeation chromatography (as described in previous Quarterly Progress Reports) was done on the soluble fraction from experiment 1 (Figure B1). Proton nmr spectra (270 and 500 MHz) were taken of the tetrahydrofuran soluble portions from experiments 1 and 3.

Results

The results obtained for reductive methylation using the solvated electron approach are summarized in Table B1. Figure B1 shows the gel permeation chromatography elution profile of the tetrahydrofuran soluble portion from experiment 1.

Discussion

Alkylating coal reductively in a blue solution of potassium dissolved in ether seems to be an excellent way to transform the coal into a soluble derivative. In this procedure solvated electrons are transferred directly to the coal, eliminating the need for an electron-transfer agent which complicates the isolation of the solubilized coal (B3). However, the use of this procedure with Illinois No. 6 coal provided 25 to 30% tetrahydrofuran soluble material. This conversion is only about 50% of the solubility realized in the reductive alkylation reaction using naphthalene.

The elution profiles obtained from gel permeation chromatography of reductively methylated Illinois No. 6 coal from the two systems are very similar (Figure B1). The profiles only differ in that there are more lower molecular weight fragments produced in the K/$C_{10}H_8$/THF system. This is consistent with the higher solubility obtained under these reaction conditions.

As discussed in the Third Quarterly Progress Report, the reductively alkylated Colorado subbituminous coal was significantly less soluble in tetrahydrofuran than the reductively alkylated Illinois bituminous coal. This is true both in the K/$C_{10}H_8$/THF system and in the K/monoglyme/triglyme system (Table B1). Subbituminous coal has a large amount of hydroxyl groups. It has been estimated that one-third of the total oxygen content is present as phenolic hydroxyl groups (B5). There are also more carboxylic acids present than in bituminous coal. When the coal is added to the solution of naphthalene anions and dianions, these relatively acidic protons will be donated by the coal, reducing the naphthalenes to dihydronaphthalenes and other by-products (B3). These reduction reactions reduce the concentration of the electron transfer reagent and inhibit the ability of naphthalene to serve as an electron transfer agent. The net result is a low solubility of the coal alkylate. The alkylated product obtained in a second pass reaction is much more soluble in tetrahydrofuran. Since most of the acidic protons from the coal were lost during the first pass reaction, the coal does not hamper the ability of naphthalene to serve as an electron transfer agent during the second pass reaction, resulting in more complete reductive alkylation.

Due to the relatively low solubility of coal reductively alkylated under blue solution conditions, the difficulty of totally removing the triglyme from the coal, and the wealth of data we already have from the K/$C_{10}H_8$/THF system (B6), we have decided to employ the K/$C_{10}H_8$/THF system for the spectroscopic investigation of Illinois No. 6, Colorado subbituminous and other coals.

References

B1. J.L. Down, J. Lewis, B. Moore, and G. Wilkinson, J. Chem. Soc., 3767 (1959).

B2. (a) K. Niemann, Ph.D., Thesis, University Bochum, 1977; (b) K. Niemann and H.-P. Hombach, Fuel, 58, 853 (1979); (c) K. Niemann and U.-B. Richter, Fuel, 58, 838 (1979); (d) M.W. Haenel, R. Mynott, K. Niemann, U.-B. Richter, and

Figure B1. Styragel Elution Profiles of Soluble, Methylated Illinois No. 6 Coal.

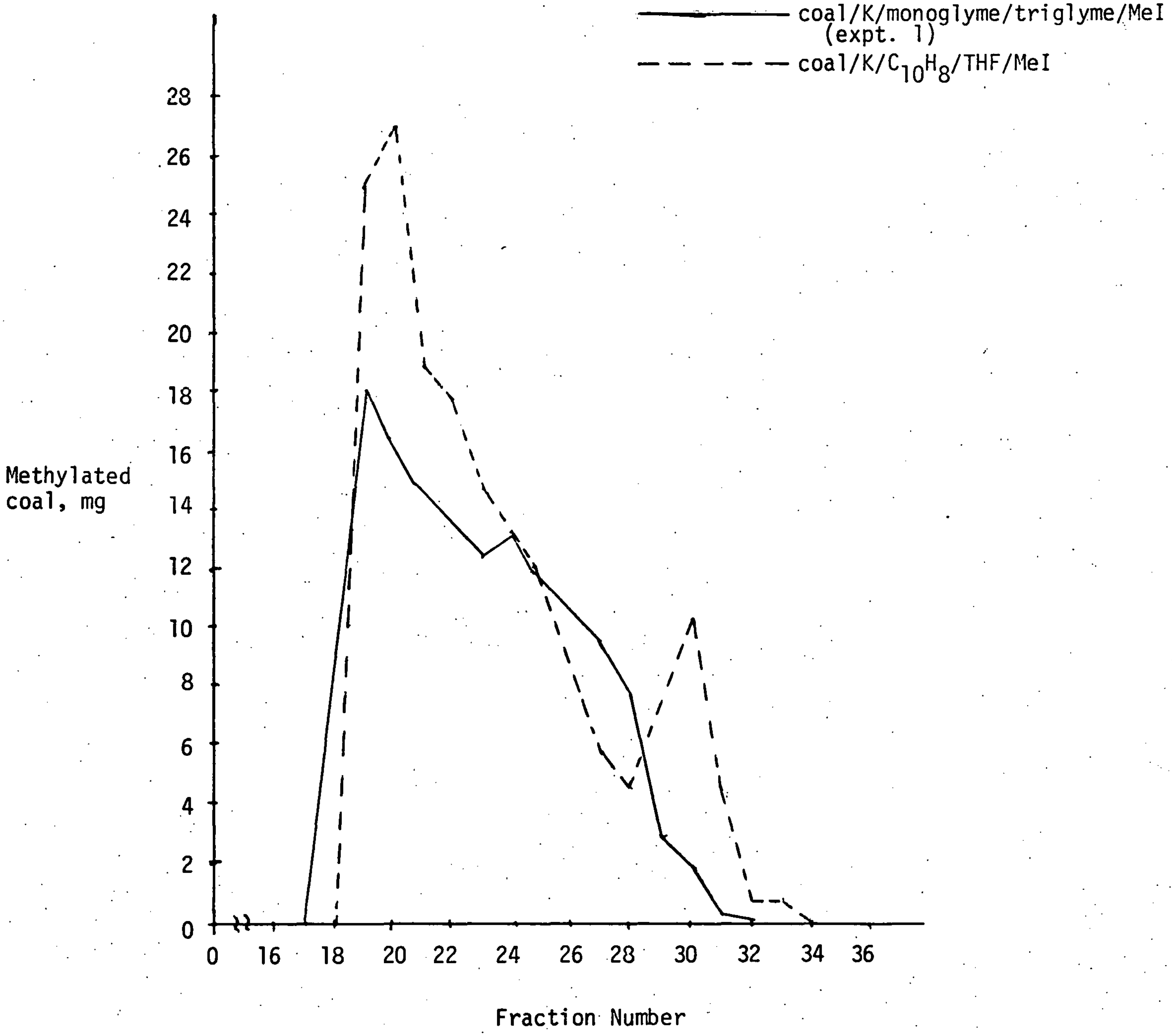


Table B1. Results for the Coal/K/Monoglyme/Triglyme/MeI Reactions

Expt.	Wt. of coal (g)	Wt. of coal alkylate (g)	Wt. of THF soluble material (g)	% THF solubility	$\frac{\text{Wt. of coal alkylate}}{\text{Wt. of coal}}$
1[a]	0.971	1.096	0.280	25.5	1.13
2[a]	0.460	0.510	0.106	20.8	1.11
3[b]	0.982	0.997	0.053	5.3	1.02

[a] Illinois No. 6 coal.

[b] Colorado coal.

L. Schanne, Angew. Chem. Int. Ed. Eng., 8, 636 (1980).

B3. J.A. Franz and W.E. Skiens, Fuel, 57, 502 (1978).

B4. Coal and ultimate analysis furnished by the Institute of Gas Technology, Chicago, Illinois.

B5. H.W. Sternberg and C.L. Delle Donne, Fuel, 53, 172 (1974).

B6. L.B. Alemany, Ph.D. Thesis, University of Chicago, 1980.

Summary of Progress to Date

Methods of elucidating structural information from spectroscopic techniques are being continued.

PART C

Hydrolysis of ^{13}C Enriched Butylated Coal

by Reid S. Willis

Introduction

In the past quarter, experiments have been carried out which provide information for further assignment of the most upfield resonance of the ^{13}C nmr of 1-^{13}C enriched butylated coal. The experiments demonstrate that these resonances are due mostly, if not exclusively to the presence of carboxylic esters.

Experimental Part

Hydrolysis of Butyl Benzoate--Butyl benzoate (.9 g, 5 mmol), tetrahydrofuran (15 ml) and tetrabutyl ammonium hydroxide (4 g, 40% in H_2O, 6.1 mmol) were added to a flask and the reaction mixture was stirred for 2.5 hours at room temperature before acidification with concentrated hydrochloric acid. The next day, the organic matter was extracted with ether which was subsequently dried over magnesium sulfate and removed. The white crystalline product (.6 g) was benzoic acid (100%).

Hydrolysis of Coal--A gel permeation chromatographic fraction (see reference C1) of tetrahydrofuran soluble, 1-^{13}C enriched butylated coal (fraction 14, 35 mg) was treated with tetrahydrofuran (2 ml) and tetrabutylammonium hydroxide (1 ml, 40% by weight in H_2O). This homogeneous mixture was allowed to stir at room temperature for 25 hours before it was acidified with 2N hydrochloric acid. The acidified coal was not soluble in solution. More water was added to the mixture and solid product was collected on a fritted funnel. The salts were washed away and the coal was dried under nitrogen overnight. All of the coal was dissolved in chloroform-d (99.8%) and ^{13}C nmr was taken of the sample (C2). The resonance at 64 ppm had been reduced virtually to baseline (see Figure C1). The infrared spectrum of the hydrolyzed coal shows a larger absorption at 3350 cm^{-1} than that of the nonhydrolyzed coal, indicating a stronger O-H absorption.

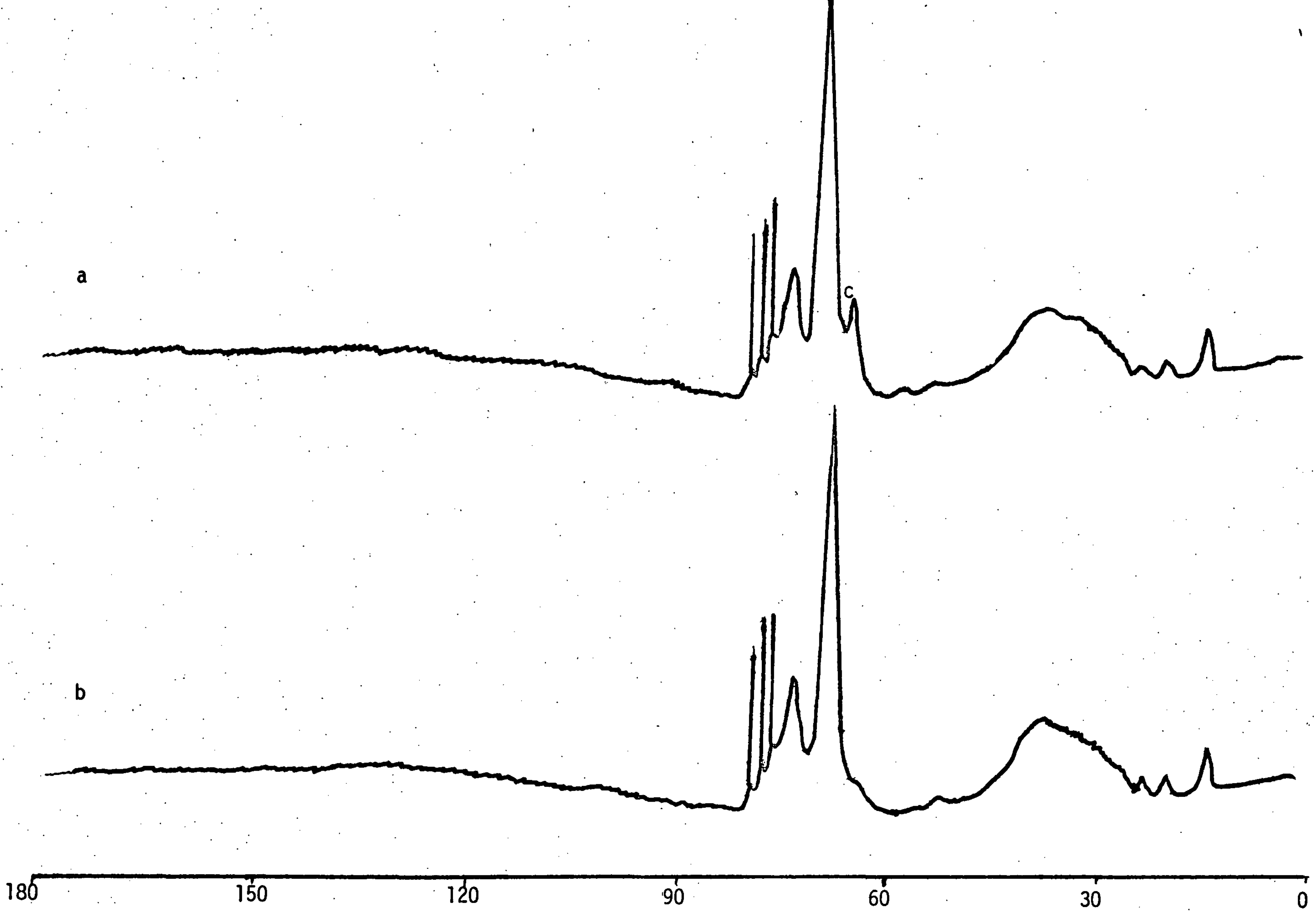


Figure C1--CMR (a) spectrum of Fraction 14 of coal alkylated with butyl-1-^{13}C iodide (ref. 4c); (b) spectrum of hydrolyzed Fraction 14; (c) resonance of butyl-1-^{13}C-carboxylates.

Results and Discussion

It has been suggested (C3) that the resonance in the region of interest (designated c in Figure C1) could be due to the presence of carboxylates or n-butyl tertiary alkyl ethers. We carried out a base catalyzed hydrolysis in order to selectively eliminate resonance due to the presence of carboxylates. As seen in Figure B1, the cmr spectrum of hydrolyzed 1-^{13}C enriched butylated coal, the signal intensity has been virtually, if not completely, eliminated; a decrease of 95 ± 5% of the original signed intensity is seen. The small residual intensity, if any, may be due to butyl tertiary ethers or residual butyl esters. These results suggest that the contribution of n-butyl tertiary ethers to the resonance of the unhydrolyzed coal is negligible and that the resonance is due almost exclusively to the presence of n-butyl carboyxlates.

It is apparent that chemical reactions involving ^{13}C enriched alkylated coal samples can be employed for elucidation of the structure of the coal product, particularly if the reaction is specific for one type of functionality in the coal. Presently, the importance of vinyl ethers in reductively butylated coal is being pursued. Since vinyl ethers cleave much more readily than aryl ethers, studies of cmr and infrared spectra of acid hydrolyzed ^{13}C enriched butylated coal may give some insight to the importance of vinyl butyl ethers in the coal product.

References

C1. Alemany, L.B., Ph.D. Thesis, p. 64; also see experiment 9B and Styragel Chromatography in experimental section.

C2. Ibid., p. 101; parameters used for nmr of hydrolyzed coal identical to Alemany's except that D5 was set at 1.5 seconds.

C3. Ibid., p. 123.

C4. Ibid., p. 105.

PART D

Alkylation of Coal and Infrared Spectroscopy of Coal Alkylates

by C.I. Handy

Introduction

During this quarter attention has been directed toward the selective alkylation of acidic hydroxyl groups present both in raw Illinois No. 6 coal and in Illinois No. 6 coal that had previously been reductively alkylated using potassium in liquid ammonia and methyl or butyl iodide. The selective alkylation was effected using n-butyl ammonium hydroxide as base and methyl or n-butyl iodide as alkylating agent according to Liotta's procedure (D1). The infrared spectra of raw Illinois No. 6 hvC bituminous and Colorado subbituminous B coals were recorded. In addition, selected samples of alkylated coals were examined by infrared spectroscopy.

Results

The results obtained for the experiments in which Illinois No. 6 coal was alkylated according to Liotta's method are summarized in Table D1. The infrared spectra of raw Illinois No. 6 and Colorado coals and some samples of reductively and/or selectively alkylated coals are shown in Figures D1 to D7.

Discussion

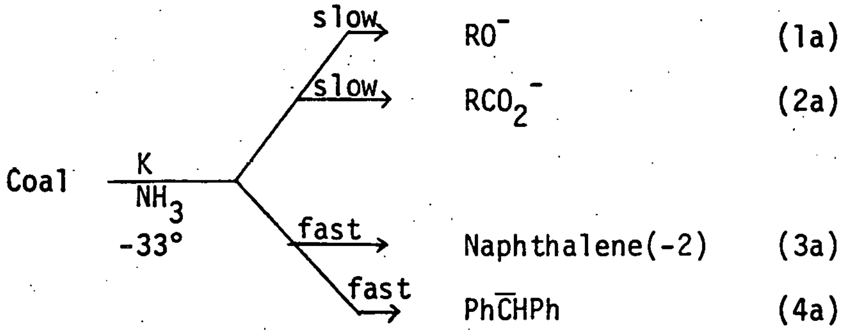
It is known that coal is reduced by potassium in liquid ammonia to yield the coal polyanions

$$nK + NH_3 \rightarrow nK^+ + (NH_3)_e^{-n}$$

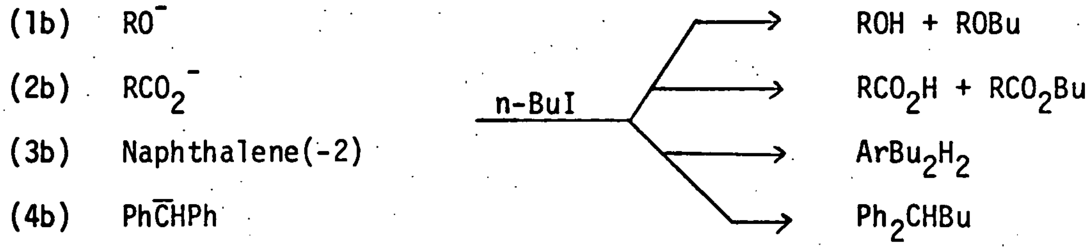
blue solvated electrons

$$Coal + (NH_3)_e^{-n} \rightarrow Coal^{-n} + NH_3$$

Many different anions exist in the solution as shown below.



Upon treatment with an alkylating agent, for example n-butyl iodide, species (1a) and (2a) would react slowly to form butyl ethers and butyl esters respectively. On the other hand the carbanions (3a) and (4a) would react more rapidly to form alkyl hydrocarbons such as $ArBu_2H_2$ and Ph_2CHBu, respectively.



We therefore rationalized that it would be worthwhile to attempt to increase the conversion of unreacted phenols and carboxylic acid moieties in the alkylated coals to their corresponding ethers and esters in a second reaction, so as to enhance the solubilization of coal in an etheral solvent such as tetrahydrofuran. The method developed by Liotta (D1, D2) was chosen because of its selective and specific nature and the mildness of its reaction conditions. Our results (Table D1) suggest that the second alkylation reaction does indeed facilitate the solubilization of reductively alkylated coal. The procedure is most effective when the reductively alkylated material is first isolated and only the tetrahydrofuran-insoluble part is used as the starting material in the second alkylation reaction (experiment 5, Table D1). The tetrahydrofuran solubility of the starting material increases to 21%. This result suggests that unreacted carboxyl or hydroxyl groups exist in the reductively alkylated coals and that prolonged reactions are necessary to complete the alkylation reaction.

(5a) $\mathrm{CoalOH} + \overset{+}{\mathrm{N}}\mathrm{Bu}_4\overset{-}{\mathrm{O}}\mathrm{H} \rightarrow \mathrm{Coal}\overset{-}{\mathrm{O}}\overset{+}{\mathrm{N}}\mathrm{Bu}_4 + \mathrm{H}_2\mathrm{O}$

(5b) $\mathrm{Coal}\overset{-}{\mathrm{O}}\overset{+}{\mathrm{N}}\mathrm{Bu}_4 + \mathrm{RI} \rightarrow \mathrm{CoalOR} + \overset{+}{\mathrm{N}}\mathrm{Bu}_4\mathrm{I}^-$

(6a) $\mathrm{CoalCOOH} + \overset{+}{\mathrm{N}}\mathrm{Bu}_4\overset{-}{\mathrm{O}}\mathrm{H} \rightarrow \mathrm{CoalCO}\overset{-}{\mathrm{O}}\overset{+}{\mathrm{N}}\mathrm{Bu}_4 + \mathrm{H}_2\mathrm{O}$

(6b) $\mathrm{CoalCO}\overset{-}{\mathrm{O}}\overset{+}{\mathrm{N}}\mathrm{Bu}_4 + \mathrm{RI} \rightarrow \mathrm{CoalCOOR} + \overset{+}{\mathrm{N}}\mathrm{Bu}_4\mathrm{I}^-$

As expected the gain in weight is greatest when reductively butylated coal is butylated again by the Liotta procedure (experiment 3, Table D1) and the weight gain is most modest when reductively methylated coal is methylated (experiment 4, Table D1). However, the tetrahydrofuran solubilities do not parallel the weight increases (experiments 2, 3 and 4, Table D1), the greatest solubility being realized when the reductively butylated coal is subsequently methylated.

The infrared spectra of dried raw Illinois No. 6 and Colorado coals show a prominent, broad O-H stretching frequency at 3300-3600 cm^{-1} (Figure D1). This absorption is considerably diminished but still present in the reductively alkylated coals showing that reductive alkylation does leave some alcohols, phenols and carboxylic acids unaltered. In contrast, the samples of Illinois No. 6 coal that underwent the Liotta reaction exhibit relatively small O-H stretching frequencies suggesting that selective alkylation of acidic hydroxyl groups has indeed occurred (Figures D6a, D6b, D7a). The C-H bands in the aliphatic region of the infrared spectra (2800-3000 cm^{-1}) are more intense relative to the O-H absorptions in the alkylated coals than in the unreacted coals (Figures D1 to D5). Both the unreacted and alkylated coals show a broad absorption about 1600 cm^{-1} which may be assigned to aromatic C=C stretching. The carbonyl stretching frequency of carboxylic acids which is located at approximately 1665-1700 cm^{-1} overlaps with the aromatic C=C absorption and consequently the absorption appears to be broad and not well defined. However, in the esterified samples (alkylated coals) this absorption shifts to higher frequencies of 1720-1740 cm^{-1} and can be discerned as a discrete absorption. The Colorado coal which has a relatively high oxygen content ($\sim$19%) upon reductive butylation yields a tetrahydrofuran-soluble product with a fairly strong absorption near 1730 cm^{-1} which is attributed to carboxylic esters (Figure D4b and D5b). Interestingly, this absorption is not as strong in the tetrahydrofuran-insoluble part of the product from Colorado coal, (Figures D4a and D5a) nor is it as intense in either the tetrahydrofuran-soluble or tetrahydrofuran-insoluble fractions obtained by reductive butylation of Illinois No. 6 coal whose oxygen content is lower ($\sim$12%) (Figures D2a-D3b). However, the tetrahydrofuran-

Table D1. Attempted Solubilization of Illinois No. 6 Coal by Selective Alkylation of Acidic Hydroxyl Groups.

Expt. No.	Wt. of coal, in g.	Reductive Alkylation	Product isolated	mmoles $\overset{+}{N}Bu_4\overline{O}H$ per g. coal	mmoles RI per g. coal	Wt. of coal alkylate in g.	Wt. of THF soluble product in g.	% THF solubility	$\frac{\text{Wt. of coal alkylate}}{\text{Wt of starting material}}$
1a	1.0439	No	-	3.0	7.7, MeI	1.3003	0.1169	9	1.25
1b	1.4341	No	-	3.2	3.1, BuI	2.0750	0.4822	23	1.45
2	0.8348	Yes, Bu	No	18.5	47.9, MeI	1.2354	0.7541	61	1.48
3	0.9399	Yes, Bu	No	24.7	46.7, BuI	1.4262	0.5581	39	1.52
4	0.8224	Yes, Me	No	93.9	97.7, MeI	1.0460	0.3768	36	1.27
5	1.4974 THF-insol. Bu-coal	Yes, Bu	Yes	4.7	15.2, BuI	1.6034	0.3425	21	1.07

Experiment 1b was carried out by A. Reed.

Figure D1a

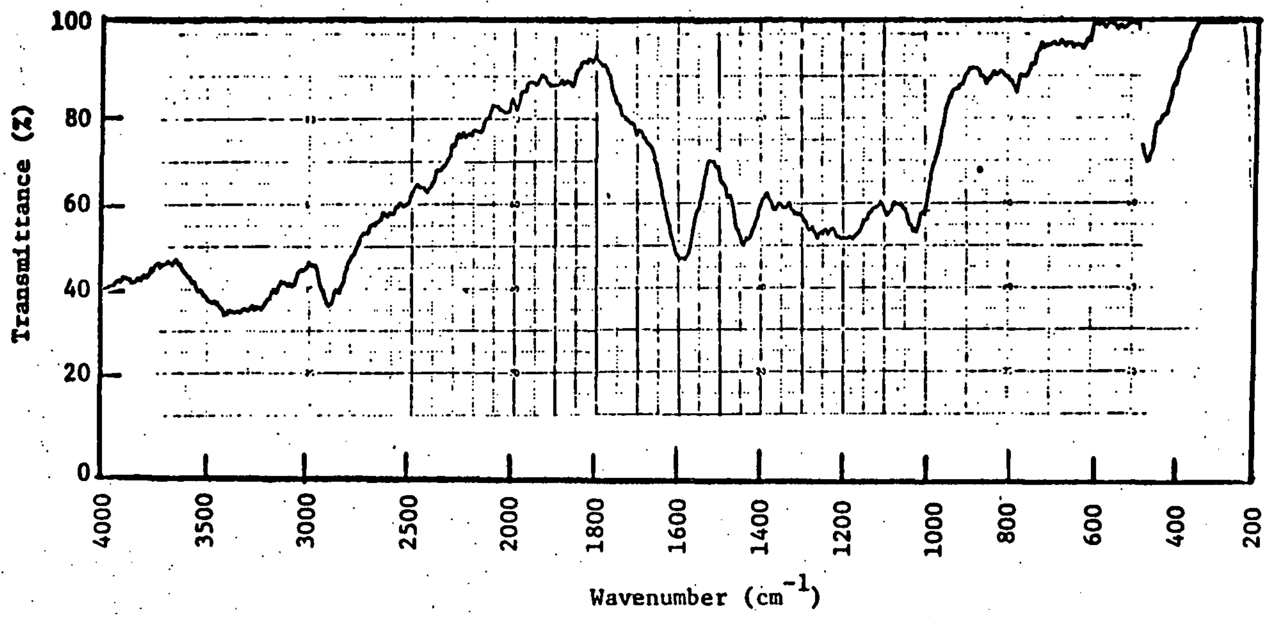


Figure D1b

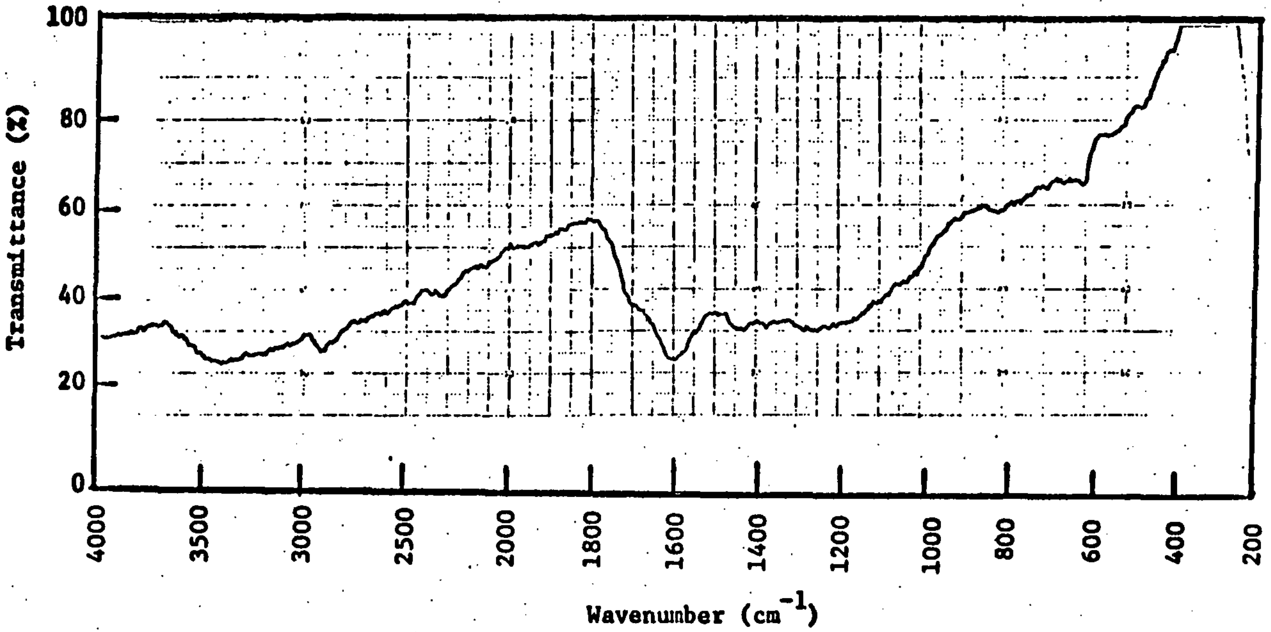


Figure D1a. The infrared spectrum of dried Illinois No. 6 coal.

Figure D1b.--The infrared spectrum of dried subbituminous Colorado coal.

Figure D2a

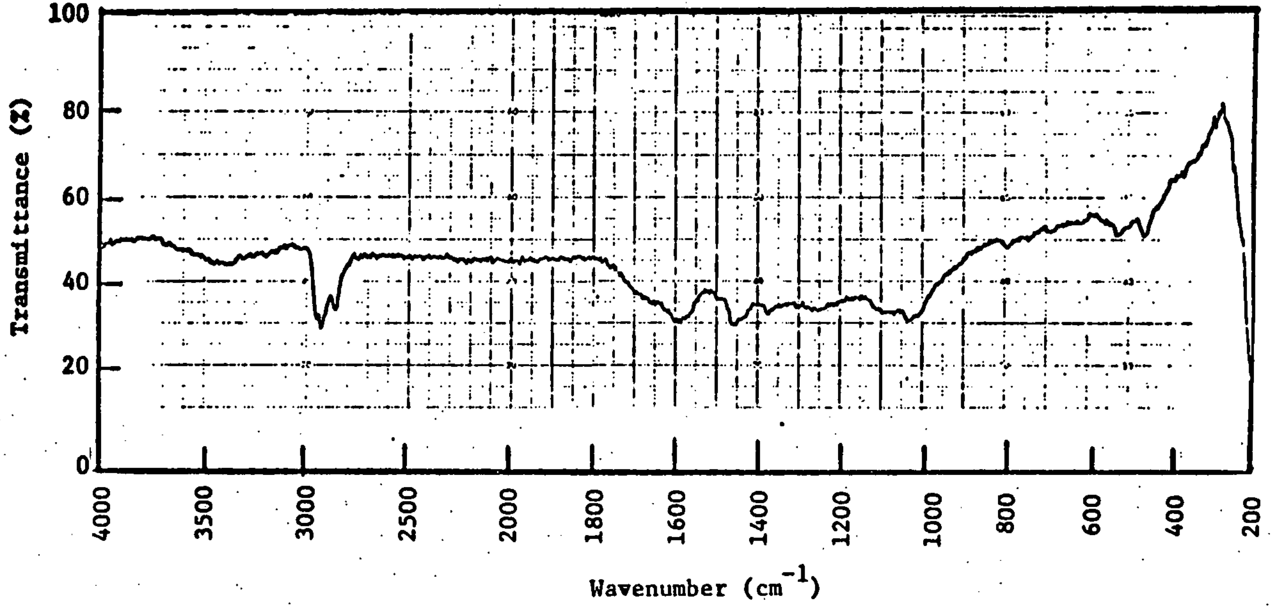


Figure D2b

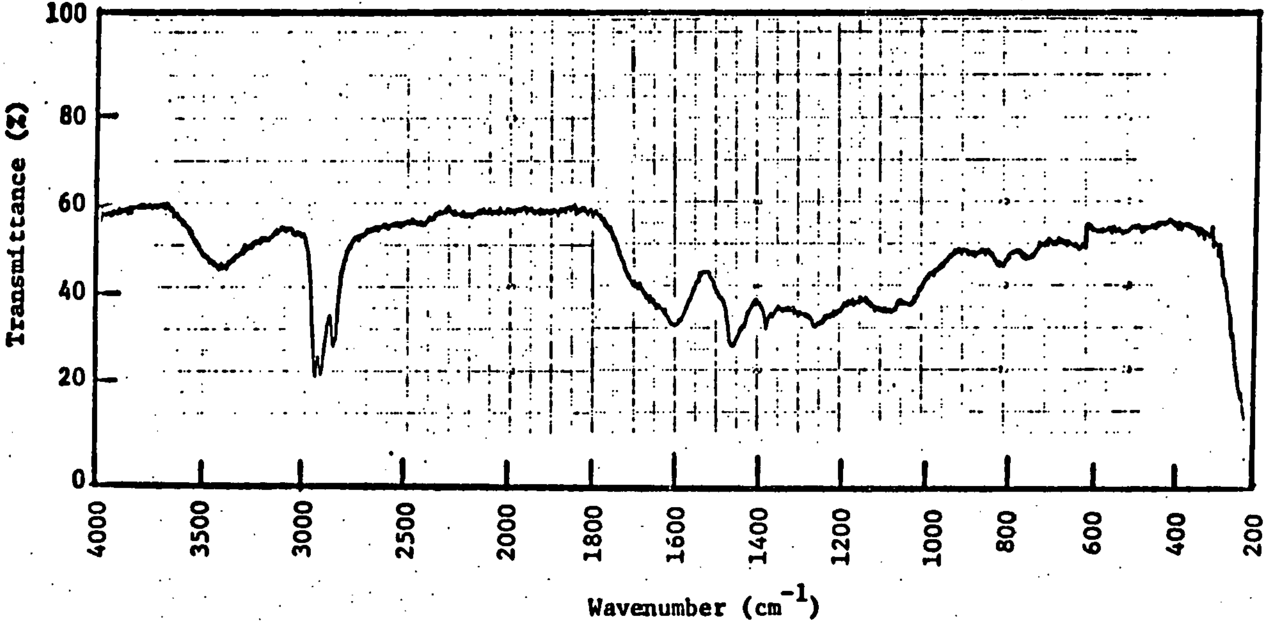


Figure D2a.--The infrared spectrum of THF-insoluble reductively butylated (K/NH_3/BuI) Illinois No. 6 coal.

Figure D2b.--The infrared spectrum of THF-soluble reductively butylated (K/NH_3/BuI) Illinois No. 6 coal.

Figure D3a

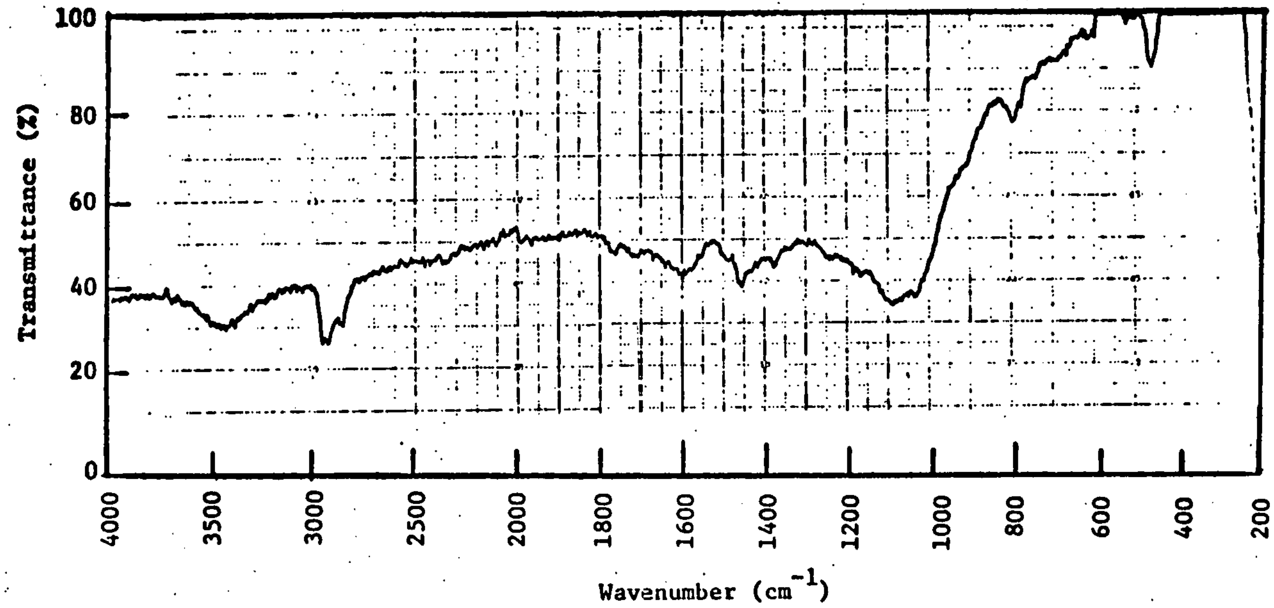


Figure D3b

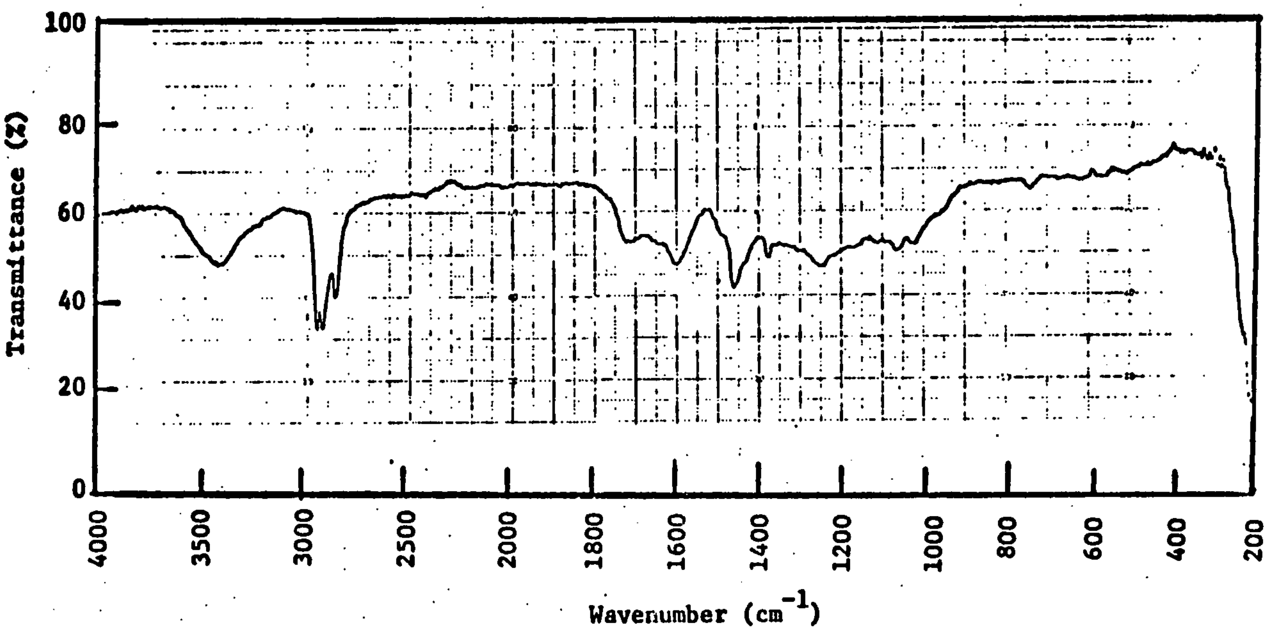


Figure D3a.--The infrared spectrum of THF-insoluble reductively butylated (K/naphthalene/THF/BuI) Illinois No. 6 coal.

Figure D3b.--The infrared spectrum of THF-soluble reductively butylated (K/naphthalene/THF/BuI) Illinois No. 6 coal.

Figure D4a

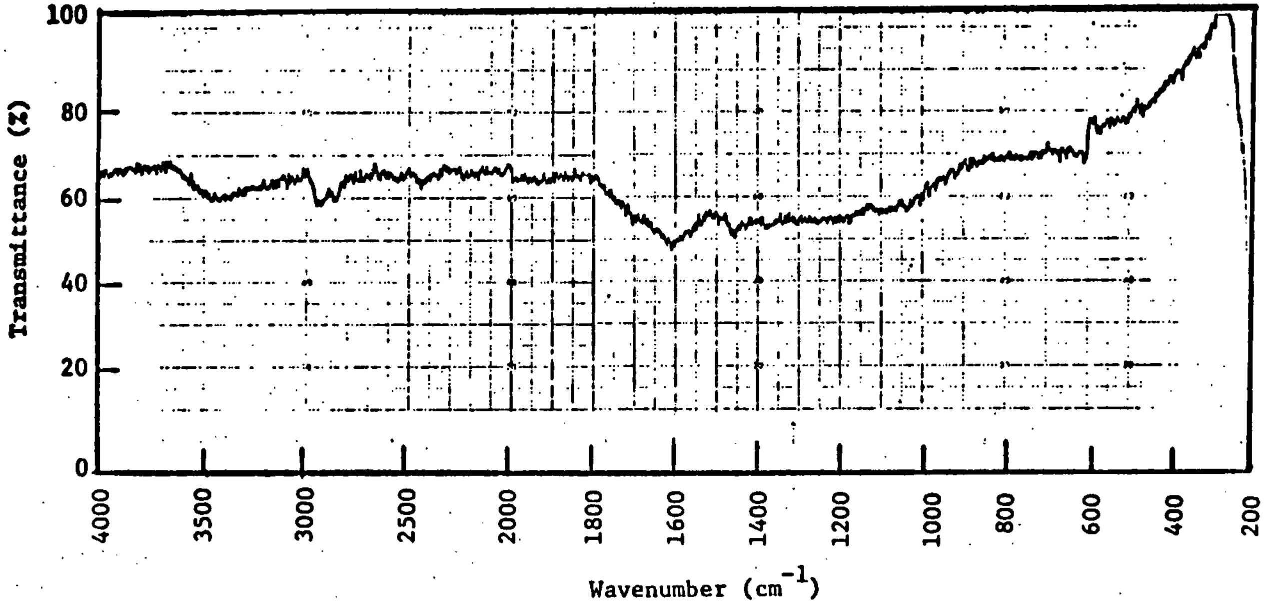


Figure D4b

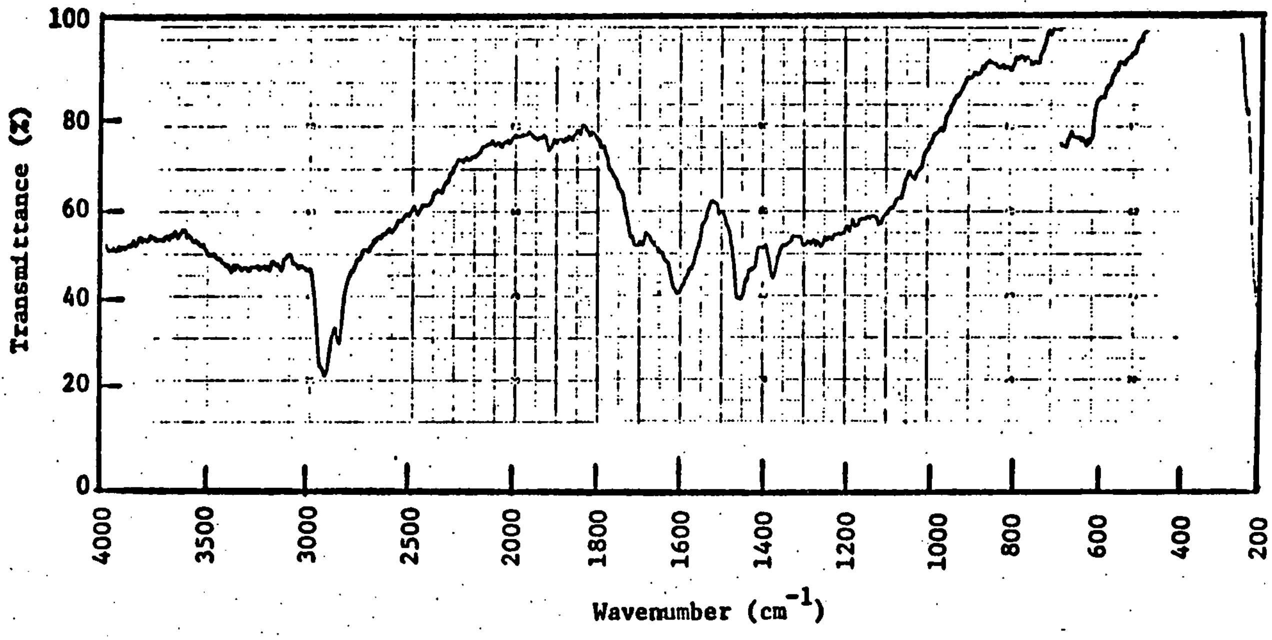


Figure D4a.--The infrared spectrum of THF-insoluble reductively butylated (K/NH_3/BuI) Colorado coal.

Figure D4b.--The infrared spectrum of THF-soluble reductively butylated (K/NH_3/BuI) Colorado coal.

Figure D5a

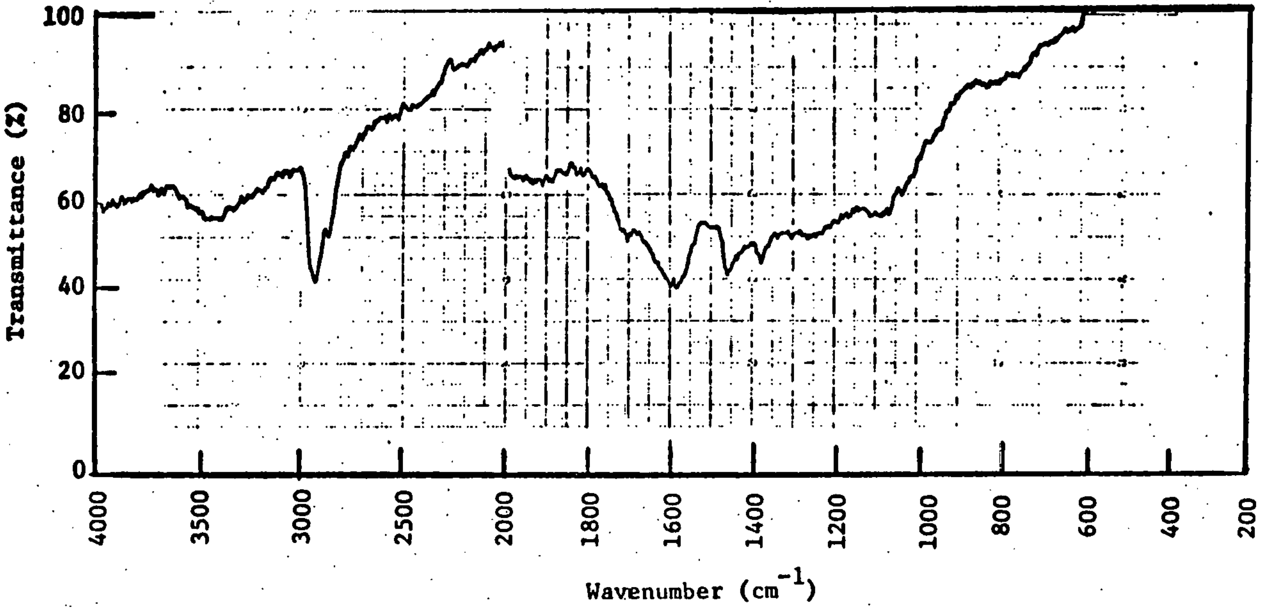


Figure D5b

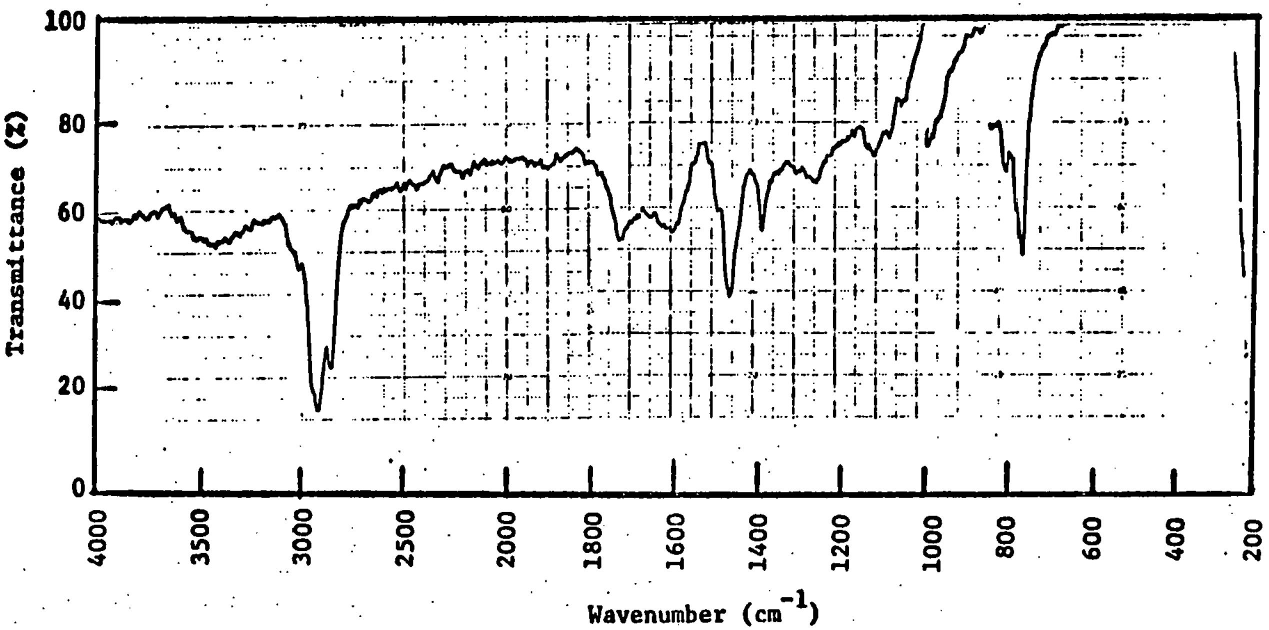


Figure D5a.--The infrared spectrum of THF-insoluble reductively butylated (K/naphthalene/THF/BuI) Colorado coal.

Figure D5b.--The infrared spectrum of THF-soluble reductively butylated (K/naphthalene/THF/BuI) Colorado coal.

Figure D6a

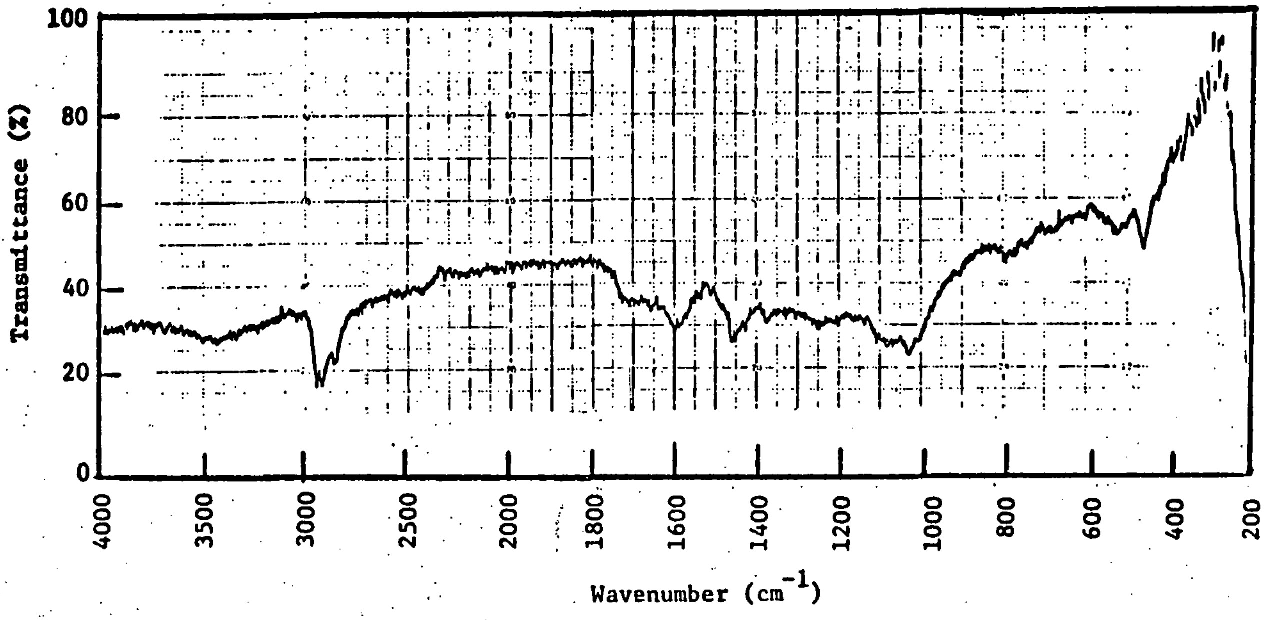


Figure D6b

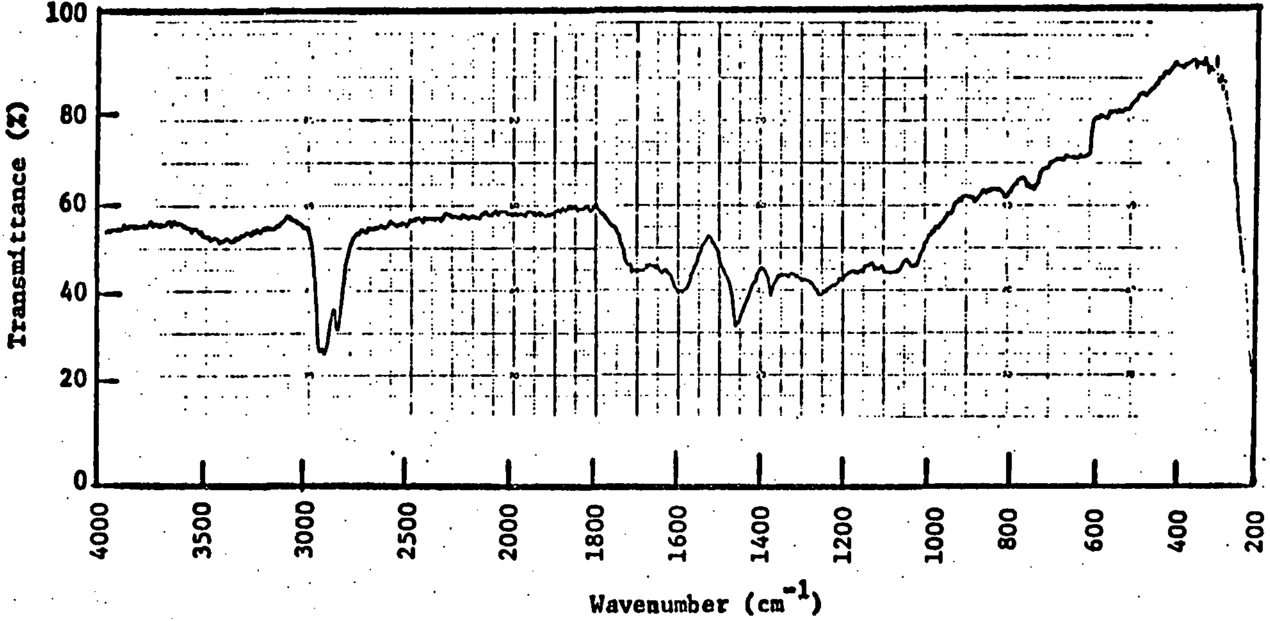


Figure D6a.--The infrared spectrum of THF-insoluble Illinois No. 6 coal after $K/NH_3/BuI$ treatment and methylation.

Figure D6b.--The infrared spectrum of THF-soluble Illinois No. 6 coal after $K/NH_3/BuI$ treatment and methylation.

Figure D7a

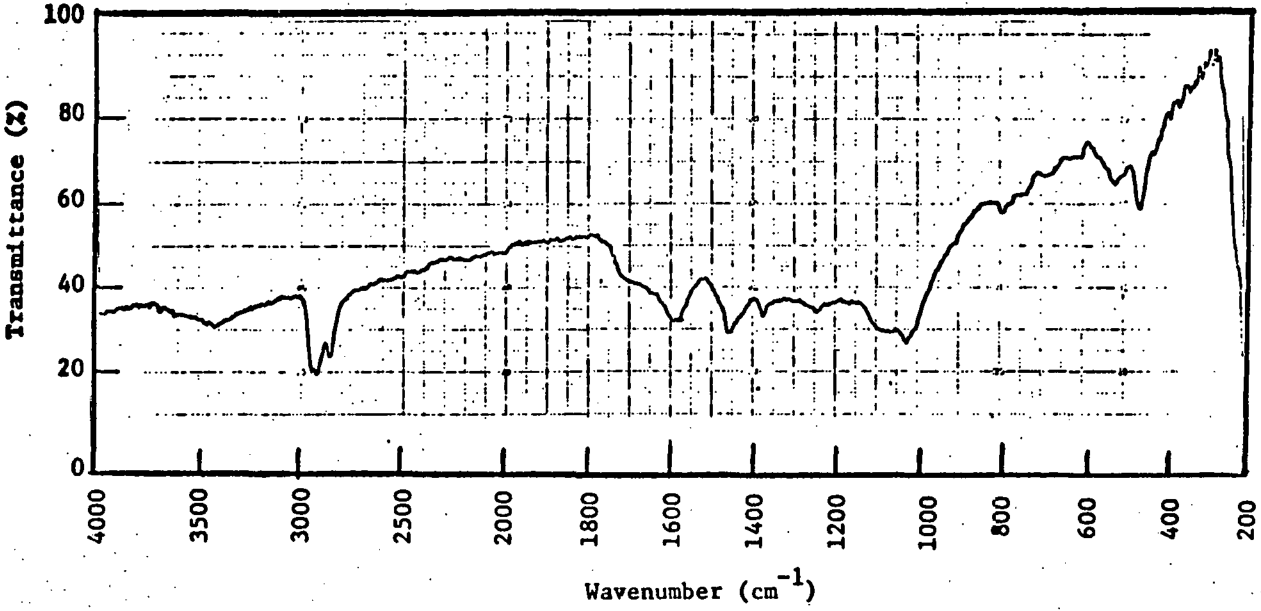


Figure D7b

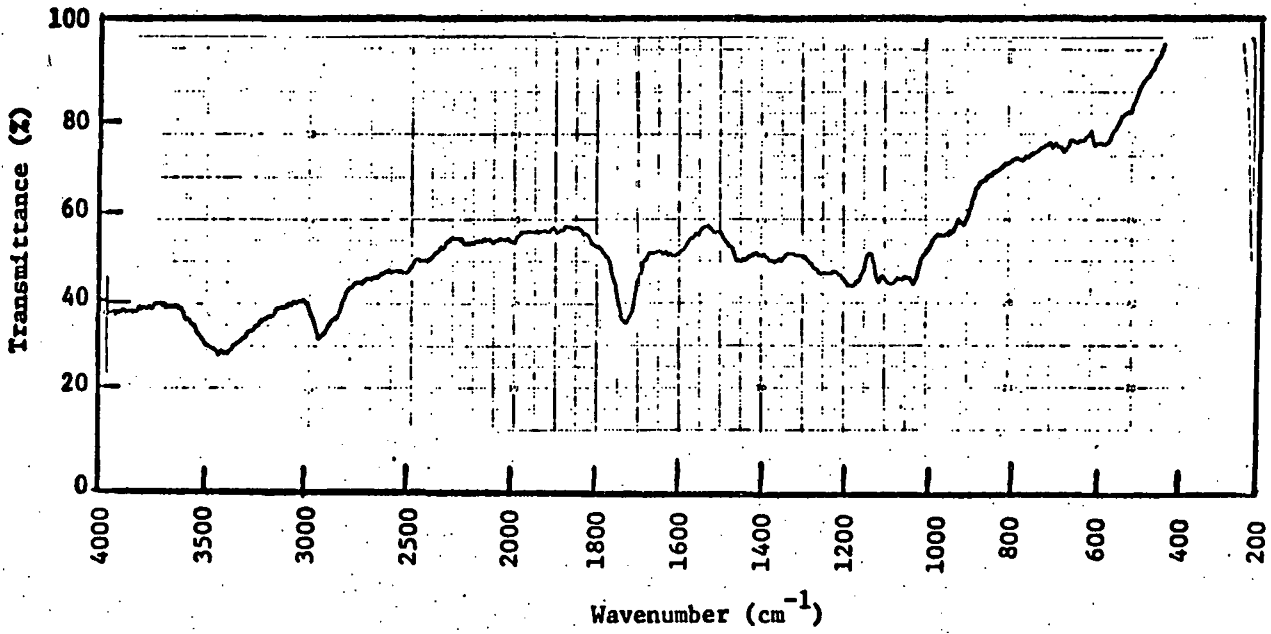


Figure D7a.--The infrared spectrum of THF-insoluble Illinois No. 6 coal obtained from the butylation of a THF-insoluble residue from $K/NH_3/BuI$ reaction.

Figure D7b.--The infrared spectrum of THF-soluble Illinois No. 6 coal obtained from the butylation of a THF-insoluble residue from $K/NH_3/BuI$ reaction.

soluble Illinois No. 6 coal reductive alkylate does show a weak absorption or shoulder in the region of 1730 cm^{-1} (Figures D2b and D3b). As one would expect, this characteristic absorption near 1730 cm^{-1} is stronger in the tetrahydrofuran-soluble product obtained from experiment 5, Table D1 (see Figure D7b), where the tetrahydrofuran-insoluble residue from reductively butylated Illinois No. 6 coal was subjected to a second butylation using tetrabutylammonium hydroxide and 1-iodobutane. Similarly, this stretching frequency is observed in the tetrahydrofuran-soluble product of experiment 2, Table D1 (Figure D6b). These observations are in good agreement with those of Liotta (D2) and Niemann (D3).

Experimental

Reductive alkylation reactions in liquid ammonia were conducted as outlined in previous Quarterly Reports. The selective alkylation of acidic hydroxylic groups was carried out in tetrahydrofuran under mild conditions at ambient temperature, as described by Liotta (D1) using tetrabutylammonium hydroxide and methyl or n-butyl iodide as reagents. When the selective alkylation reaction was carried out immediately after a reductive alkylation, without isolating the product from the first experiment, a large excess of tetrabutylammonium hydroxide and an even larger excess of alkyl halide were used in the second experiment (Table D1, experiments 2, 3 and 4). Infrared spectra were recorded on a Perkin-Elmer model 283 grating spectrophotometer. The samples were suspended in a matrix of potassium bromide.

References

D1. R. Liotta, Fuel, 58, 724 (1979).

D2. R. Liotta, K. Rose and E. Hippo, J. Org. Chem., 46, 277 (1981).

D3. K. Niemann and U.-B. Richter, Fuel, 58, 838 (1979).

D4. The infrared spectrum shown in Figure D3b was recorded by R.S. Willis.

D5. Samples for infrared spectra Figures D5a and D5b were supplied by D. Blain.

PART E

Reaction of Phenol with Inorganic Sulfide and Reactions of Perdeutetralin

by C.B. Huang

Introduction

The study of the reactions between phenol and sodium sulfide at 400°C has continued. In this quarter, the effects of Illinois No. 6 coal and tetralin on the course of the reaction were investigated. In addition, the deuterium hydrogen exchange reactions between diphenylmethane and tetralin-d_{12} in the presence of inorganic compounds and minerals as well as in the presence of phenols, naphthols, and the related thiols has been undertaken to define the impact of sulfur compounds on the liquefaction reaction.

Experimental

Equipment.--The equipment used in these experiments has been described in previous reports.

Material.--Many of the chemicals used in this quarter's work were described in previous reports. In addition, 2-mercaptonaphthalene (ICN), 1-naphthol (Aldrich), 2-naphthol (Aldrich), benzoic acid (B&A), and chars (E1).

Procedure.--The procedures used in these experiments has been described previously (E2). The experimental conditions are summarized in the tables.

Results and Discussion

The formation of thiophenol and other organic products has been detected in the reaction of phenol with anhydrous sodium sulfide as shown in Table E1. Coal and tetralin do not appear to affect the rate of formation of thiophenol in those reactions. It is pertinent that 75% to 80% of the thiophenol used in control experiments decomposes at 400°C to form diphenylsulfide as shown in Table E2.

Previous work in this laboratory and the new results reported in Table E3 and E4 indicate that mercaptans accelerate the deuterium-hydrogen exchange reaction of diphenylmethane and tetralin-d_{12}. Sodium sulfide (E3), phenol (E3), 1-naphthol, 2-naphthol do not accelerate the exchange reaction; but the combination of sodium sulfide with 1-naphthol or with 2-naphthol yields an important increase in the rate of the exchange reactions. We postulate that the related mercaptans form at 400°C from the reactions of sodium sulfide with the naphthols as observed in the reactions of this sulfide with phenol. We also postulate that the rate of formation of thiophenol from the reactions of sodium sulfide and phenol may be too slow to accelerate the exchange reaction between tetralin-d_{12} and diphenylmethane. Because our research on the influences of inorganic sulfides on the hydrogen-deuterium exchange reactions is continuing we defer further commentary on the meaning of these results. However, it is very pertinent that a probable pathway for the description of the influence of inorganic sulfur compounds on the liquefaction reaction has been uncovered.

References

E1. Chars (CF 146, CF 146-AC-36) CF 147, and CF 152) are from Illinois Institute of Natural Resources.

E2. Third Quarterly Progress Report, 1980.

E3. Eleventh Quarterly Progress Report, 1979.

Table El. Reaction of Phenol with Sodium Sulfide.[a]

Reaction	T°C	Time	Additive	PhSH	PhOH	$(Ph)_2S$	Dibenzofuran
15	400°C	4 hrs	None	6%	35%	0.2%	0.5%
16	400°C	4 hrs	Coal[b]	5%	21%	0.5%	0.3%
17	400°C	4 hrs	Tetralin[c]	4%	55%	0.3%	0.5%

[a] The mole ratio between phenol and sodium sulfide was 1:1 in each reaction.

[b] Coal (0.0190 g) was added to the mixture of phenol and sodium sulfide (0.1939 g, mole ratio 1:1).

[c] The mole ratio between phenol, sodium sulfide and tetralin was 1:1:1.

Table E2. The Reactions of Thiophenol

Reaction	Reactants	T°C	Time	PhSH	$(Ph)_2S$	PhOH	$(Ph)_2O$
18	PhSH + PhOH[a]	400°C	1 hr	20%	21%	100	-
19	PhSH + PhOH[a]	400°C	4 hrs	17%	33%	100	-
20	PhSH + $(Ph)_2O$[b]	400°C	4 hrs	17%	48%	1	92%
21	PhSH	400°C	1 hr	25%	29%	-	-
22	PhSH	400°C	4 hrs	25%	34%	-	-
23	PhSH + Na_2S[c]	400°C	1 hr	22%	28%	-	-

[a] The mole ratio between phenol and thiophenol was 10:1.

[b] The mole ratio between diphenylether and thiophenol was 10:1.

[c] The mole ratio between sodium sulfide and thiophenol was 4.5:1.

Table E3. Deuterium-Hydrogen Exchange Reaction at 400°C[a]

			Diphenylmethane, D%	Tetralin-d_{12}, D%		
Reaction	Time	Additive	αH	α	β	Ar
24	30 min	None	15.5	91.1	91.4	91.4
25	30 min	PhOH + Na_2S	13.6	90.1	91.0	91.0
26	30 min	$PhCO_2H$ + Na_2S	25.1	81.0	92.2	92.2
27	30 min	1-naphthol	11.7	90.1	90.1	91.7
28	30 min	1-naphthol + Na_2S	41.1	67.9	90.0	92.0
29	30 min	2-naphthol	19.5	91.8	93.2	91.8
30	30 min	2-naphthol + Na_2S	46.7	73.5	90.0	90.0
31	30 min	2-mercaptonaphthalene	70.7	66.1	89.2	90.8
32	30 min	Char (CF 146)	12.2	92.2	93.5	89.6
33	30 min	Char (CF 146-AL-36)	13.8	89.4	90.7	81.5
34	30 min	Char (CF 147)	15.7	91.2	91.2	92.7
35	30 min	Char (CF 152)	16.0	91.3	91.3	92.8

[a] Tetralin-d_{12} (0.376 mmole), diphenylmethane (0.377 mmole), and the additive (0.045 mmole) were used in each reaction. The length of the glass reactor is 10 cm.

Table E4. Deuterium-Hydrogen Exchange Reaction at 400°C[a]

			Diphenylmethane, D%	Tetralin-d_{12}, D%		
Reaction	Time	Additive	α	α	β	Ar
36	1 hr	None	14.6	90.8	92.7	89.0
37	1 hr	PhOH + Na_2S	16.2	80.5	91.3	88.3
38	1 hr	$PhCO_2H$ + Na_2S	37.6	72.0	90.7	89.5
39	1 hr	1-naphthol	9.4	88.9	91.4	87.7
40	1 hr	1-naphthol + Na_2S	49.6	60.5	92.1	88.9
41	1 hr	2-naphthol	11.6	89.9	91.9	88.9
42	1 hr	2-naphthol + Na_2S	61.7	63.9	92.8	89.2
43	1 hr	2-Mercaptonaphthalene	67.2	60.1	88.6	88.6
44	1 hr	Char (CF 146)	12.3	90.7	90.9	90.0
45	1 hr	Char (CF 146-AL-36)	8.3	92.3	92.3	80.5
46	1 hr	Char (CF 147)	11.5	88.8	88.8	87.5
47		Char (CF 152)	14.1	90.1	91.0	91.0

[a] Tetralin-d_{12} (0.376 mmole), diphenylmethane (0.376 mmole), and additive (0.045 mmole) were used in each reaction. The length of the glass reactor is 10 cm.