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Coal Anion Structure and Chemistry
of Coal Alkylation

Final Report
for Period March 1, 1979 to February 29, 1980

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I. ABSTRACT

In accord with Task 1, some ether cleavage reactions were carried out in two different media - potassium/naphthalene/tetrahydrofuran and potassium/ammonia - so that the merits and demerits of the two methods could be compared. Preliminary results suggest that both systems yield the same products, and that the ammonia medium is more convenient to work with, because of the absence of by-products such as reduced naphthalenes and tetralin.

Dialkyl ethers were found to be least reactive compounds while the benzyl and phenyl ethers were found to be most reactive, as would be expected. Also, with respect to Task 1, the reductive alkylation of coal was carried out in ammonia at 25°C. The tetrahydrofuran solubility of the reaction product was surprisingly low.

In accord with Task 3, we have obtained additional $^{13}\text{C}\{^1\text{H}\}$ nmr data for tetrahydrofuran-soluble butylated coal and some model compounds; obtained additional Styragel(R) chromatography data of tetrahydrofuran-soluble coal labelled with 98%-enriched butyl- $1,1\text{-d}_2$ iodide; and obtained ^2D nmr spectra of all the deuterium-labelled, tetrahydrofuran-soluble coal products. The Styragel(R) chromatography data are very similar to those obtained when biphenyl instead of naphthalene serves as the electron transfer agent and suggest that electron transfer agents of similar size and reduction potential effect similar degradations of the coal, as might be expected. Reported applications of ^2D nmr spectroscopy to coal analysis are few. Our results provide evidence for C- and O-alkylation with C-alkylation predominating, as usual, in the low molecular weight fractions. Furthermore, variations in resonance linewidths are consistent with the variations in molecular weight.

In accord with Task 4, we have undertaken a review of the information now available concerning the nature of Illinois No. 6 coal. Also, the effects of organic additives on the exchange reactions between tetralin- d_{12} and diphenylmethane and on the thermal cleavage reactions of several model compounds in tetralin were investigated to probe the relationship between structure and reactivity. The exchange reaction can be accelerated by coal, asphaltene-pre-asphaltene fractions derived from coal, compounds with labile bonds, or compounds which can be reduced readily. The pyridine-insoluble coal product, acids, and bases are inactive toward the exchange reaction. The additives which are active in the exchange reaction will accelerate the thermal decomposition of 1,3-diphenylpropane but not that of 1,2-diphenylethane. For the heteroatom-containing compounds, the patterns of thermal decomposition are more complicated; even some organic acidic compounds may affect the reaction through polar interaction.

II. OBJECTIVE AND SCOPE OF WORK

A. Objective

The objective of this research is to define the structural features of coal which are important for coal conversion. Specifically, this research involves the study of new methods for coal alkylation, the use of these methods in the preparation of isotopically-labelled soluble coal compounds, the characterization of the

coal compounds by nuclear magnetic resonance spectroscopy, and the development of a satisfactory theory for the coal structure which accommodates the experimental observations.

B. Scope of Work

TASK 1 Chemistry of Coal Anion Formation and Reaction Work

This work concerns the discovery and development of efficient methods for the preparation of coal polyanions and for the alkylation of these anions. Different metals and different electron transfer agents in solution of tetrahydrofuran and other organic solvents and in solutions of ammonia and its derivatives will be considered. The utility of different alkylating agents will be studied. The work will be extended to the study of samples of different geological history.

TASK 2 Preparation of Labelled Reagents and Products

This task involves the production of soluble coal compounds with carbon-13 or deuterium isotope labels at specific positions in the alkylation reagent. The necessary synthetic work has to be accomplished and the necessary reactions have to be performed to incorporate the isotope label.

TASK 3 Determination of Reaction Sites

This task centers on the definition of the points of attachment of the alkylation reagents to establish the factors important for the achievement of a soluble material. To accomplish this objective it is necessary to develop methods for the separation of the alkylation products by chromatography and to investigate the nuclear magnetic resonance spectra of both labelled and unlabelled materials. Appropriate model compounds must be synthesized to provide reference data for a confident interpretation of the spectroscopic data.

TASK 4 Evaluation of Results

The results provided by this study are to be assessed critically for compatibility with reaction models and with coal structure models.

WORK DURING THE TWELFTH QUARTER

During this period, work has focused on the following tasks.

With respect to Task 1, certain selected ethers were cleaved using either potassium/naphthalene/tetrahydrofuran/ammonium chloride or potassium/ammonia/ammonium chloride. This makes it possible to compare the merits and demerits of these two reaction media. Furthermore, the reductive butylation of coal was carried out in ammonia at 25°C.

In accord with Task 3, we have obtained additional $^{13}\text{C}\{^1\text{H}\}$ nmr data for tetrahydrofuran-soluble butylated coal and some model compounds; obtained additional Styragel chromatography data of tetrahydrofuran-soluble coal labelled with 98%-enriched butyl-1,1-d₂ iodide; and obtained ^2D nmr spectra of all the deuterium-labelled, tetrahydrofuran-soluble coal.

The effects of organic additives on the exchange reactions between tetralin- d_{12} and diphenylmethane and on the thermal cleavage reactions of several compounds in tetralin were investigated.

III. SUMMARY OF PROGRESS TO DATE

TASK 1 Chemistry of Coal Anion Formation and Reaction Work

The reaction of Illinois No. 6 coal with potassium in tetrahydrofuran in the presence of naphthalene as an electron transfer agent has been thoroughly investigated. Replicate experiments established that the addition of coal (325 mesh) to the very dark green solution of naphthalene radical anions and naphthalene dianions gave the same results. The coal molecules rapidly acquire negative charges, but after several hours the rate of acquisition of negative charges slows. These reactions were terminated after 5 days. Control experiments established that tetrahydrofuran is not polymerized or otherwise degraded under the reaction conditions.

The success of the procedure as measured by the conversion of the insoluble coal to a product soluble in tetrahydrofuran is strongly influenced by the selection of the leaving group. We established that butyl iodide is a much superior reagent compared to butyl bromide or butyl chloride. We also established that butyl methanesulfonate may be a useful reagent in certain circumstances but that this alkylation reagent may cause the polymerization of tetrahydrofuran under other circumstances. Butyl triflate is apparently too reactive to be used as an alkylation reagent for the coal polyanion.

Methyl, butyl, and octyl iodide react with anionic coal very similarly and apparently nearly quantitatively. Butylation is the most informative procedure in terms of the chemical shift data obtained and appears to be best suited for a variety of spin-lattice relaxation and nuclear Overhauser enhancement measurements.

Potassium is superior to both sodium and lithium for the generation of anionic coal and for the conversion of the anionic coal to a product which is soluble in tetrahydrofuran. Potassium and butyl iodide are clearly the best combination of metal and alkyl iodide.

Both tetrahydrofuran and 1,2-dimethoxyethane are equally good solvents with respect to the production of soluble products.

As electron transfer agents, biphenyl appears to be better than naphthalene, which is much better than anthracene. Re-reacting the tetrahydrofuran-insoluble, butylated coal from the initial reaction of coal with potassium and biphenyl in tetrahydrofuran followed by butyl iodide proceeded in the fashion characteristic of second pass butylation reactions: (1) slow discharge of the color of the anionic biphenyl system upon addition of the tetrahydrofuran-insoluble coal, (2) gentle bubbling upon butylation, with (3) rapid formation of potassium iodide. Biphenyl seems to be a more effective electron transfer agent.

The use of a ^{13}C label in the butyl iodide is highly advantageous. In the ^1H nmr spectra, the label provides strong evidence for O-butylation. In the $^{13}\text{C}\{^1\text{H}\}$ nmr spectra, the label provides new information on the sites of butylation and even estimates on the relative amounts of butylation at various

types of oxygen. O- and C-butylation are clearly important; N-butylation is not. Butyl ethers of tertiary alcohols or butyl esters appear to be responsible for the band of resonances around 64 ppm. In contrast, butyl ethers of primary alcohols, benzyl alcohols, and 2,6-disubstituted phenols appear to be responsible for the resonances downfield of 70 ppm. Butyl ethers of other phenols and, to a much smaller extent, of secondary alcohols appear to be responsible for the large number of resonances around 68 ppm. In a high molecular weight fraction, the butyl ether α -C-13 T_1 values are similar, very short (0.04-0.12 sec), and comparable to values previously reported for model compounds. The fine structure in the carbon-13 spectra of the lower molecular weight fractions is consistent with the considerably longer α -C-13 T_1 values to be expected in these fractions.

Spectroscopic characterization of the material extracted merely by stirring the coal in tetrahydrofuran shows that the initial extract contains a very wide variety of aliphatic and aromatic resonances but that subsequent prolonged extraction yields a small amount of almost entirely paraffinic material. These extracts differ markedly from the tetrahydrofuran-soluble material obtained in the reductive alkylation reactions both with respect to their physical appearance and solubility characteristics.

In the liquid ammonia system, the coal polyanion was generated by adding ground Illinois No. 6 coal to a deep blue solution of alkali metal in liquid ammonia. In later experiments, ground coal was introduced into the reaction flask first, followed by metallic potassium and liquid ammonia. Sodium and potassium were used in these experiments. The time allowed for coal polyanion formation was varied and longer reaction times (up to 24 hours) were found to be no more effective for the formation of soluble material than short reaction times. The influence of temperature has also been studied. The coal polyanion was formed at -78°C in some experiments, and between -78° to -33°C in other experiments. The alkylation step was carried out in most instances overnight, (for approximately 16 hours), and the temperature ranged from -78°C to 25°C or from -78°C to -33°C . Reductive alkylation of the coal polyanion was accomplished using *n*-butyl iodide or methyl iodide or in one instance ^{13}C -labelled methyl iodide. Protonation of the coal polyanion was effected using solid ammonium chloride, water or 2-methyl-2-propanol as the quenching reagent.

Control reactions were carried out in the absence of both alkali metal and alkylating agent, and using wet coal instead of dry coal. The inverse quench procedure was studied. In some of the earlier reactions, anhydrous ether was used as co-solvent. In one instance dry dimethoxyethane was used. However, in later experiments no co-solvent was employed. Some second pass experiments were conducted in which the tetrahydrofuran-insoluble material was recycled and used as the substrate for a subsequent experiment.

Coal is believed to have ether linkages. The effect of potassium/liquid ammonia upon these linkages was therefore studied using model compounds such as phenyl butyl ether and benzyl butyl ether and these results were compared with results from ether cleavage reactions performed in potassium/naphthalene/tetrahydrofuran. Reductive butylation of coal was carried out at 25°C and the tetrahydrofuran solubility of the product was determined.

Elemental analysis of various molecular weight fractions of a tetrahydrofuran-soluble, butylated coal clearly indicates the importance of alkylation and again illustrates the non-uniform distribution of reactive groups.

Elemental analysis of a tetrahydrofuran-insoluble, butylated coal residue remaining after extensive degradation again indicates how successful the reactions were in dissolving organic matter in the coal.

Comparison of the $^{13}\text{C}\{^1\text{H}\}$ nmr spectra of corresponding, intermediate molecular weight fractions of tetrahydrofuran-soluble coal obtained through reductive butylation in tetrahydrofuran at room temperature and through reductive butylation in liquid ammonia reveals many similarities. Intensity differences between corresponding resonances may indicate similar reactions proceeding to somewhat different extents in these two systems. However, comparison of the $^{13}\text{C}\{^1\text{H}\}$ nmr spectra of corresponding, high molecular weight fractions of tetrahydrofuran-soluble coal obtained through reductive butylation in tetrahydrofuran at room temperature and through reductive butylation in liquid ammonia was not possible. While the former provided a useful spectrum, the latter did not. Degradation reactions may have proceeded to a smaller extent in the liquid ammonia reaction.

The use of 90%-enriched methyl- C-13 iodide is highly advantageous. The spectra very closely parallel those obtained with 90%-enriched n -butyl- 1-C-13 iodide. However, in the high molecular weight fractions, the average T_1 values for $\text{O-}^{13}\text{CH}_3$ appear to be somewhat longer than those for $\text{O-}^{13}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, which is reasonable. Insights gained from the $^{13}\text{C}\{^1\text{H}\}$ nmr spectra of the butylated coal suggest the presence of carbonyl groups and alkenes that react in the strongly basic medium to give enolates and allylic carbanions that subsequently are alkylated. IR spectroscopy provides clear evidence for a dialkyl ketone.

TASK 2 Preparation of Labelled Products

The syntheses of perdeuteriotetralin, perdeuterionaphthalene, and α,α -di-deuteriodiphenylmethane have been accomplished. The syntheses of butyl- 1-C-13 iodide and butyl- 1,1-d_2 iodide have been completed.

TASK 3 Determination of Reaction Sites

The chromatographic procedures necessary to separate the coal samples into discrete molecular weight fractions have been examined. Gel permeation chromatography on styrene-divinyl benzene copolymers (Bio-beads^R) and on Styragel(R) as well as column chromatography on silica gel have been investigated. The results obtained establish the practical value of column chromatography for the purposes of this study enabling the clean separation of the alkylated products from the electron transfer agent and its derivatives and of GPC for the separation of the alkylated products into molecular weight ranges.

The gel permeation chromatography procedure was found to yield reproducible results.

TASK 4 Evaluation of the Results

A report concerning the nmr spectra of butylated Illinois No. 6 coal has been published (1). More recent results were presented at the April 1979 meeting of the American Chemical Society in Honolulu (2). Additional work is being published (3).

The paper in Fuel indicates that the same average coal structure cannot be used for the description of the molecules both in the high and low molecular weight ranges. The high molecular weight materials have experienced extensive butylation. These fractions seem to contain fewer oxygen atoms. The prominent intermediate molecular weight fractions exhibit rich structural differences. Carbonyl and vinyl resonances are observed in the carbon and proton nmr spectra. The extent of O-butylation differs from the extent of C-butylation as the molecular weight changes. The extent of aromatic butylation compared to reductive butylation also changes as the molecular weight of the product changes. The evidence obtained from ether cleavage products suggests that aryloxy functions are much more prominent in the molecules of intermediate molecular weight than in the molecules of high or very low molecular weight.

The presentation at the American Chemical Society meeting dealt with the effect of the metal, electron transfer agent, solvent, alkyl group, and leaving group on the reductive alkylation process. The talk also demonstrated the advantages of using 90%-enriched n-butyl-1-C-13 iodide as the alkylating agent. These points are described in some detail in III. SUMMARY OF PROGRESS TO DATE and in considerable detail in previous quarterly reports and the work is being published.

The small quantity of material that had remained on the silica gel column after the first pass silica gel chromatography treatment has a molecular weight distribution similar to that of the coal-derived material that did elute. Electron transfer agents with similar reductive potentials yield coal-derived products with similar molecular weight distributions. However, whereas the first pass silica gel chromatography treatment always yields mostly high molecular weight products, the second pass silica gel chromatography treatment yields mostly low molecular weight products. The ²D nmr spectra of deuterium-labelled, tetrahydrofuran-soluble, butylated coal are profoundly affected by the molecular weight. Mostly high molecular weight material eluted in the first pass silica gel chromatography treatment yields a single broad resonance from $\approx 0-9$ ppm centered about 3.8 ppm and therefore suggesting that more O- than C-butylation occurred. The low molecular weight material obtained shows, as usual, that more C-butylation than O-butylation occurred and that butylation of resonance-stabilized anions occurred. The initial, truly hexane-soluble material eluted in the second pass silica gel chromatography treatment shows that C-butylation greatly dominates over O-butylation and therefore that most of the material reduced and butylated was naphthalene. With the Styragel elution profile of the high molecular weight material subsequently eluted skewed toward the lower molecular weight end, fairly well resolved O- and C-butylation regions are now evident; C-butylation again dominates. The lowest molecular weight material yields a spectrum similar to that obtained with the corresponding material eluted in the first pass silica gel chromatography treatment.

In the liquid ammonia system, potassium was found to be the alkali metal of choice because the alkylated coal product formed was more tetrahydrofuran soluble than that obtained in reactions using sodium. Similarly *n*-butyl iodide was observed to be more effective than methyl iodide in bringing more coal into solution in tetrahydrofuran. These findings are compatible with the results obtained for the coal/alkali metal/tetrahydrofuran/electron transfer agent/alkylating agent system.

In reactions in liquid ammonia where a longer reaction time (21 hours, 24 hours) was allowed for coal polyanion formation, the coal alkylate weight/weight of coal was higher than usual, being 1.92 and 1.91, respectively. However, the tetrahydrofuran solubility of the product was not increased. Hence a time of about 6 hours for coal anion formation was adopted for the subsequent experiments.

The protonated coal product was found to be partially water soluble at alkaline pH and correspondingly less tetrahydrofuran soluble than the alkylated coal product. Consequently, the work-up procedure had to be modified, the aqueous suspension being brought to pH 3 with dilute hydrochloric acid prior to repeated centrifugations (aqueous washes were used to remove the inorganic salts).

The control reactions carried out in the absence of alkali metal, and absence of both alkali metal and alkylating agent, confirmed that formation of the coal polyanion is a prerequisite to formation of alkylated coal product. The tetrahydrofuran solubility of the product obtained in both these reactions was the same as that of raw coal (approximately 10-20%). Using wet coal instead of dry coal for a reaction that was quenched with water appeared to make no difference to the solubility characteristics.

The inverse quench procedure, i.e., addition of the coal polyanion to the *n*-butyl iodide, instead of the usual procedure, where the alkylating agent was added slowly from a syringe to a solution of coal in alkali metal/liquid ammonia, afforded no noticeable improvement in solubilization of the coal product. However, the gel permeation chromatography of this reaction product remains to be done. This may have an elution profile slightly different from that obtained for other conventionally butylated coal samples.

Poor tetrahydrofuran solubility (only about 7%) was obtained in second pass alkylation experiments.

The results of the reactions performed on the ethers indicate that the alkali metal/liquid ammonia system probably does not disrupt the ether linkages in coal sufficiently at -78°C or -33°C to bring an appreciable amount of the coal product into solution in tetrahydrofuran. Hence, these reactions have been attempted at room temperature in a sealed tube.

It was necessary to consider another reaction process in order to characterize the reaction sites with more confidence. Accordingly, work concerning the hydrogen-deuterium exchange has been carried out. It was found that the hydrogen atoms of coal can exchange with the deuterium atoms from the α -positions of tetralin- d_{12} , toluene- d_8 , and diphenylmethane- d_2 and the 1-position of naphthalene- d_8 . The order of the exchange rate is tetralin- d_{12} > diphenylmethane- d_2 > naphthalene- d_8 > toluene- d_8 . The model compound studies show that the benzylic hydrogen atoms and

certain of the heterocyclic or polycyclic aromatic ring hydrogen atoms from the model compounds exchange with the benzylic deuterium atoms of tetralin-d₁₂. Reverse exchange from the coal products labelled with deuterium atoms to tetralin or naphthalene occurs almost exclusively on the α -position of tetralin and the 1-position of naphthalene. In separate experiments, it was established that the fraction of deuterium on the α -position of the recovered tetralin is about the same as that on the 1-position of the recovered naphthalene when the exchange was carried out with the same labelled coal product. Therefore, the availability of deuterium atoms from one labelled coal product is the same for either tetralin or naphthalene. The coal product, which was recovered from reaction between coal and tetralin, exchanges with tetralin-d₁₂ slower than the unreacted coal.

The exchange rate between tetralin-d₁₂ and one of the model compounds, diphenylmethane, is faster in the presence of coal than in the absence of coal, therefore, extensive studies on this exchange reaction with many additives have been carried out. This reaction can be catalyzed by the organic components of the Illinois No. 6 coal, the asphaltene-preasphaltene product fraction, compounds with weak bonds, some carbonyl compounds and some polynuclear aromatic hydrocarbon compounds. This reaction is not affected by the pyridine-insoluble fraction (ash), acid or base. Water and alcohol even retard the exchange reaction. It is suggested that certain molecules with fragile bonds, carbonyl functional groups and polycyclic aromatic ring may be the constituents in the coal which are responsible for the shuttle of hydrogen atoms. However, in the exchange reactions between tetralin-d₁₂ and diphenylmethane with Lewis acid type inorganic additives, the aromatic exchange, which does not occur with coal as additive, is observed. This aromatic exchange may be an acid-catalyzed electrophilic substitution reaction.

IV. DISCUSSION OF TECHNICAL PROGRESS

A. ¹³C{¹H} NMR Spectra of Additional Model Compounds

by L.B. Alemany

The alkylation of aryloxides can occur under the reaction conditions (1). Thus, nmr data for 4-butoxyphenol are useful in interpreting the spectra of deuteriochloroform-soluble, butylated coal. Data for N-butylaniline and N,N-dibutylaniline have also been obtained. The results obtained at 22.631 MHz are summarized.

4-Butoxyphenol: -OCH₂-, δ 68.7; -OCH₂CH₂-, δ 31.5; -CH₂CH₃, δ 19.3; and -CH₃, δ 13.9.

N-Butylaniline: -NHCH₂-, δ 35.1; -NHCH₂CH₂-, δ 31.5; -CH₂CH₃, δ 22.6; and -CH₃, δ 14.1.

N,N-Dibutylaniline: -N(CH₂-)(CH₂-), δ 50.9; -N(CH₂CH₂-)(CH₂CH₂-), δ 29.5; -CH₂CH₃, δ 20.5; and -CH₃, δ 14.1.

Discussion

For butyl phenyl, butyl *o*-tolyl, butyl 1-naphthyl, and butyl 2-naphthyl ether, the butyl $\underline{1-C-13}$ resonance occurs from $\delta 67.6-67.9$. However, for *p*-dibutoxybenzene, the butyl $\underline{1-C-13}$ resonance occurs at $\delta 68.4$ (4). With 4-butoxyphenol, the other oxygen atom, as remote as it is, exerts a slight deshielding effect.

B. Styragel Chromatography of Tetrahydrofuran-Soluble, Deuterium-Labelled, Butylated Coal

by L.B. Alemany

Introduction

The previous report (1) discussed the significant improvements made in the silica gel chromatography treatment of the tetrahydrofuran-soluble, alkylated coal concentrate and (2) presented Styragel(R) chromatography results for the coal-derived material that eluted in the first pass silica gel chromatography treatment (4). However, the report pointed out that a small amount (3.7%) of coal-derived material remained on the silica gel column after the first pass. While previous neglect of this relatively small quantity of material did not critically affect quantitative work (4), we wanted to determine the molecular weight distribution of this material.

The previous report also showed that the amount of coal-derived material obtained in the second pass silica gel chromatography treatment represented 24.0% of the soluble, coal-derived material, which had not been subjected to Styragel(R) chromatography in previous experiments with naphthalene as the electron transfer agent. Clearly, this amount was not small. Consequently, we particularly wanted to determine the molecular weight distribution of the coal-derived products of the second pass silica gel chromatography treatment, especially since in the experiment with biphenyl as the electron transfer agent, the first pass and second pass silica gel chromatography treatments yielded coal-derived products with substantially different molecular weight distributions.

Results

Figure 1 shows the Styragel(R) chromatography elution profile (with approximate molecular weights) of the small quantity of coal-derived material that had remained on the silica gel column after the first pass. Figure 2 shows the Styragel(R) chromatography elution profile (again with approximate molecular weights) of the much larger quantities of coal-derived materials that eluted in the first pass (upper) and second pass (lower) silica gel chromatography treatments in the experiments with naphthalene and biphenyl as electron transfer agents.

Discussion

Clearly, the small quantity of material that had remained on the silica gel column after the first pass has a molecular weight distribution similar to that of the coal-derived material that did elute. This further minimizes the importance of isolating and studying this small quantity of material.

Figure 2 clearly shows that electron transfer agents with similar reduction potentials yield coal-derived products with similar molecular weight distributions. However, whereas the first pass silica gel chromatography treatment always yields mostly high molecular weight products, the second pass silica gel chromatography treatment yields mostly low molecular weight products. As we shall see from the ^2D nmr spectra of the coal butylated with butyl- $1,1\text{-d}_2$ iodide, the molecular weight of the products profoundly influences the spectra.

C. ^2D NMR Spectra of All the Deuterium-Labelled, Tetrahydrofuran-Soluble Coal

by L.B. Alemany

Introduction

We are aware of only four reports on ^2D nmr spectra of deuterium-labelled, coal-derived liquids (5). Each of these four spectra shows aliphatic and aromatic resonance bands but very little fine structure. Figures 3-7 show 13.812 MHz ^2D nmr spectra of various samples of tetrahydrofuran-soluble coal labelled with 98%-enriched butyl- $1,1\text{-d}_2$ iodide. Each nmr sample, dissolved in chloroform- h , also contains added naphthalene- d_8 principally as a calibration standard and added chloroform- d principally as a chemical shift reference. We obtained each spectrum with a 90° pulse and a delay of 0.001 sec between the end of a pulse and the start of data acquisition (to prevent pulse feed through) over a spectral width of 500 Hz with a filter of 750 Hz. (Suspecting that some of the resonance bands might be very broad, we deliberately used this large spectral width.) An ADC with 9-bit resolution (maximum available) and 2K memory were used for conversion and storage of the data. The resulting data acquisition time of 2.048 sec clearly provided adequate resolution for these initial investigations.

The inability to obtain $^2\text{D}\{^1\text{H}\}$ spectra on our spectrometer represents a severe limitation. While quadrupolar relaxation of ^2D completely dominates and thus prevents any nuclear Overhauser enhancement, the lack of ^1H decoupling causes the $-\text{CD}_2\text{CH}_2\text{CH}_2\text{CH}_3$ signal to be split into a triplet for O-butylation and a triplet, quartet, or pentet for C-butylation. As a result, the net signal-to-noise ratio is reduced by at least a factor of 2.

Results

Figure 3. Styragel(R) fractions 18-27 (144.6 mg) of coal-derived material eluted in the first pass silica gel chromatography treatment + 0.333 mg C_{10}D_8 + 0.20 μl CDCl_3 . 26,500 pulses spaced 2.08 sec apart. $\approx 29,000$ pulses would have filled the memory.

Figure 4. Styragel(R) fractions 28 $\rightarrow$ end (18.4 mg) of coal-derived material eluted in the first pass silica gel chromatography treatment + 1.021 mg C_{10}D_8 +

0.98 μl CDCl_3 . 29,000 pulses spaced 2.08 sec apart. $\approx 33,000$ pulses would have filled the memory.

Figure 5. Initial, truly hexane-soluble material (272.9 mg undoubtedly including some hexane) eluted in the second pass silica gel chromatography treatment + 7.076 mg C_{10}D_8 + 3.53 μl CDCl_3 . 11,000 pulses spaced 5.00 sec apart. $\approx 11,700$ pulses would have filled the memory.

Figure 6. Styragel(R) fractions 20-27 (96.7 mg) of coal-derived material eluted in the second pass silica gel chromatography treatment + 0.261 mg C_{10}D_8 + 0.20 μl CDCl_3 . 17,500 pulses spaced 2.08 sec apart. $\approx 18,800$ pulses would have filled the memory.

Figure 7. Styragel(R) fractions 28 + end (39.5 mg) of coal-derived material eluted in the second pass silica gel chromatography treatment + 0.417 mg C_{10}D_8 + 0.20 μl CDCl_3 . 29,000 pulses spaced 2.08 sec apart. $\approx 31,300$ pulses would have filled the memory.

Discussion

Figure 3. Clearly, extremely short T_1 values, probably ≈ 4 -12 msec, greatly broadened the resonances (6,7). That the band is centered about 3.8 ppm suggests that more O- than C-butylation occurred. With full restoration of magnetization occurring between pulses, quantitative estimates of the extent of butylation appear possible and will be considered later.

Figure 4. Clearly, C-butylation occurred to a much greater extent than O-butylation did, which is consistent with the $^{13}\text{C}\{^1\text{H}\}$ nmr data obtained with $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$ (1), $\text{CH}_3\text{CH}_2\text{CH}_2^{13}\text{CH}_2\text{I}$ (7,8,9), and $^{13}\text{CH}_3\text{I}$ (4,10) as alkylating agents. As the T_1 values for O- CD_2 and C- CD_2 are probably $< \approx 0.5$ sec while T_1 values of naphthalene- d_8 are probably ≈ 0.5 sec (11), nearly complete restoration of magnetization should have occurred between pulses, and, therefore, relative signal intensities should be significant and will be considered in more detail later.

That the T_1 values are substantially longer and therefore the resonances are much narrower than in the spectrum of the higher molecular weight material is consistent with the much lower molecular weight of the material in the terminal Styragel(R) fractions. That appreciable signal intensity is present upfield of 1.7 ppm again suggests that butylation of resonance-stabilized (benzylic, allylic, or enolic) anions has occurred (4,10). Finally, the ratio of C- to O-butylation is $\approx 3.7 \pm 0.6$; the uncertainty principally arises from certain arylbutanes and certain butyl ethers both having $-\text{CD}_2\text{CH}_2\text{CH}_2\text{CH}_3$ resonances from δ_{D} 3.05-3.30.

Figure 5. Clearly, C-butylation greatly dominated over O-butylation. Thus, most of the material reduced and butylated almost certainly was naphthalene (the electron transfer agent), not coal, which is consistent with Larsen's recent work (12). With a longer delay between pulses to allow for more restoration of magnetization in these very low molecular weight molecules, the signal intensities of these relatively narrow resonances probably are meaningful. Since the band of $-\text{CD}_2\text{CH}_2\text{CH}_2\text{CH}_3$ resonances at $\delta 3.15$ falls within the region within which certain C- $\text{CD}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and certain O- $\text{CD}_2\text{CH}_2\text{CH}_2\text{CH}_3$ resonances occur,

accurately estimating the ratio of C- to O-butylation is not possible, as it is $\approx 10.4 \pm 4.8$.

Figure 6. Clearly, C-butylation again dominated, and much less signal broadening occurred in the spectrum of the higher molecular weight material obtained from the second pass silica gel chromatography treatment than in the spectrum of the corresponding material obtained from the first pass silica gel chromatography treatment. Fairly well resolved O- and C-butylation regions are now evident; again, the T_1 values for $-\text{CD}_2\text{CH}_2\text{CH}_2\text{CH}_3$ must now be appreciably longer. These results are consistent with the Styragel(R) elution profile of this material being skewed toward the lower molecular weight end. Again, nearly complete restoration of magnetization should have occurred between pulses, and, therefore, relative signal intensities should be significant and will be considered in more detail later.

Figure 7. Just as in the higher molecular weight fractions, C-butylation again clearly occurred to a greater extent than O-butylation did (ratio of $\approx 3.0 \pm 0.4$). However, the resonance from $\delta 3.3$ - 3.5 suggests that a greater concentration of 1° , 2° , or 3° alkyl butyl ethers, benzyl butyl ethers, or *peri*-substituted arylbutanes are present. Just as in the spectrum of the lower molecular weight material obtained from the first pass silica gel chromatography treatment (Fig. 4), appreciable signal intensity is present upfield of 1.7 ppm. Since excessive line broadening is not occurring, butylation of resonance-stabilized anions apparently again occurred. Fig. 7 probably exhibits substantially better signal-to-noise than Fig. 4 does because more than twice as much coal-derived material yielded Fig. 7. Nevertheless, the similarity of these two spectra (e.g., their very nearly equal C- to O-butylation ratios) strongly suggests that the materials yielding Figs. 4 and 7 are similar.

Finally, we obtained the spectrum of the small quantity of coal-derived material that had remained on the column after the first pass silica gel chromatography treatment. However, after 48,300 pulses spaced 2.08 sec apart ($\approx 64,000$ pulses would have filled the memory), we could detect only the added C_{10}D_8 and CDCl_3 .

Each nmr sample contained added naphthalene- d_8 as a calibration standard and added chloroform- d as a chemical shift reference. The linewidths at half-height of these resonances also provide a means of estimating the field homogeneity. We are able to achieve $\nu_{1/2}$ for CDCl_3 of 0.6 Hz; a literature report gives 0.5 Hz (11). The acquisition time of 2.048 sec limits the resolution to 0.49 Hz.

The results obtained with naphthalene- d_8 as a calibration standard are not satisfactory. More work will be necessary to obtain quantitative results using D nmr spectroscopy.

The resonances from about δ_D 3.05-3.30 in all the samples presumably arise from certain C-butylated and O-butylated products. The alkyl butyl ethers $R-O-CD_2CH_2CH_2CH_3$ that have chemical shifts in this region apparently must have bulky, fully substituted alkyl groups, e.g., $-C(CH_3)_2(C_6H_5)$ or $-C(C_6H_5)_3$ (9). Previous work with tetrahydrofuran-soluble coal alkylated with 90%-enriched butyl-1-C-13 iodide or with 90%-enriched methyl-C-13 iodide has shown that butylation of $CR^1R^2R^3-O^-$ ($R^1, R^2, R^3 \neq H$) is far less important than butylation of aryloxides (4,7-10). Accordingly, most of the resonances from δ 3.05-3.30 probably result from the benzylic resonances of arylbutanes, e.g., 1-butyl-naphthalene,¹³ δ 3.05 and 1-butylpyrene,¹⁴ δ 3.28.

D. Summary and Review

To put this work on the reductive alkylation of Illinois No. 6 coal in perspective, we have undertaken the preparation of a written summary of the available information about the structure and chemistry of this coal. This summary will be presented together with an analysis of all the new data developed in this work and conclusions based upon this work.

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E. Reduction and Alkylation in Liquid Ammonia

by C.I. Handy

Introduction

The research undertaken during this quarter can be divided into three parts. First, the study of the cleavage reactions of selected diaryl, dialkyl, aryl alkyl and benzyl alkyl ethers with potassium/ammonia at -78° , -33° and 25°C , for comparison with cleavage reactions of the same ethers with potassium/naphthalene/tetrahydrofuran at 25°C . Second, reductive alkylations of coal performed at 25°C in a sealed stainless steel reactor. Third, examination by 22.631 MHz $^{13}\text{C}\{^1\text{H}\}$ nmr spectroscopy of butylated (coal/liquid $\text{NH}_3/\text{K}/n\text{-BuI}$) Illinois No. 6 coal, fractions 17-20, which had been fractionated previously using gel permeation chromatography (1).

Results

The results of the ether cleavage reactions using either potassium/ammonia or potassium/naphthalene/tetrahydrofuran to generate the anions and ammonium chloride to quench the reactions, are summarized in Table 1. In all the ammonia reactions unreacted starting material was found to be present. The results of duplicate alkylation experiments conducted at 25° in potassium/ammonia are summarized in Table 2.

The 22.631 MHz $^{13}\text{C}\{^1\text{H}\}$ nmr spectrum of fractions 17-20, of the tetrahydrofuran-soluble material ($600 < \text{MW} \leq 2900$), obtained from the reductive butylation of coal at -78°C with unenriched n -butyl iodide, was examined. This spectrum was found to resemble previously discussed spectra very closely (2). The resonance at $\delta 13.83$ ppm due to C_β of the butyl group is prominent. The resonances due to C_γ of butyl are split into two regions, due to $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-O-}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-C-}$, which appear at $\delta 20.06$ and $\delta 22.84$ respectively. The resonances of C_β of butyl bonded to quaternary carbon and tertiary carbon are centered around $\delta 26.40$ and $\delta 29.65$ respectively, while the resonance due to C_β of butyl bonded to aryloxy oxygen is observed at $\delta 31.49$. The weak resonances due to C_α of butyl bonded to unhindered aryloxy oxygen are seen at $\delta 68.02$ and $\delta 67.63$. A fairly well defined signal at $\delta 59.36$ may possibly be attributed to C_α of butyl bonded to aromatic nitrogen.

Figure 1. Approximate Molecular Weight Distribution of Tetrahydrofuran-Soluble, Butylated Coal
(Potassium/Naphthalene/Butyl- $1,1-d_2$ Iodide First Pass Reaction):

Residuals after First Pass Silica Gel Chromatography Treatment

Figure 2. Approximate Molecular Weight Distribution of Tetrahydrofuran-Soluble, Butylated Coal (Potassium/Electron Transfer Agent/Butyl Iodide First Pass Reaction) obtained from First Pass (upper) and Second Pass (lower) Silica Gel Chromatography Treatments

Figure 3. ^2D nmr spectrum of Styragel fractions 18-27 (144.6 mg) of coal-derived material eluted in the first pass silica gel chromatography treatment + 0.333 mg C_{10}D_8 + 0.20 μl CDCl_3

Figure 4. ^2D nmr spectrum of Styragel fractions 28 $\rightarrow$ end (18.4 mg) of coal-derived material eluted in the first pass silica gel chromatography treatment + 1.021 mg C_{10}D_8 + 0.98 μl CDCl_3 (8-fold expansion)

Figure 5. ^2D nmr spectrum of initial, truly hexane-soluble material (272.9 mg) eluted in the second pass silica gel chromatography treatment + 7.076 mg C_{10}D_8 + 3.53 μl CDCl_3

Figure 6. ^2D nmr spectrum of Styragel fractions 20-27 (96.7 mg) of coal-derived material eluted in the second pass silica gel chromatography treatment + 0.261 mg C_{10}D_8 + 0.20 μl CDCl_3

Figure 7. ^2D nmr spectrum of Styragel fractions 28 + end (39.5 mg) of coal-derived material eluted in the second pass silica gel chromatography treatment + 0.417 mg C_{10}D_8 + 0.20 μl CDCl_3

22.631 MHz $^{13}\text{C}\{^1\text{H}\}$ Spectrum of Butylated Coal, Fractions 17-20, 600 < MW < 2900

NAME: _____
 DATE: _____
 TIME: _____
 OPERATOR: _____
 INSTRUMENT: _____
 SAMPLE: _____

22

NAME: _____
 DATE: _____
 TIME: _____
 OPERATOR: _____
 INSTRUMENT: _____
 SAMPLE: _____
 COMMENTS: _____

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Table 1. Results for the Cleavage of Ethers by Potassium in Liquid Ammonia and by Potassium Naphthalide in Tetrahydrofuran.

Ether	Conversion, %, and Principal Products	
	Potassium in Ammonia 6 hrs at -33°C	Potassium, Naphthalene in Tetrahydrofuran 5 days at 25°C
PhOPh	100% Phenol, ^a Benzene	100% Phenol, ^a Benzene
PhCH ₂ OPh	90% Phenol, ^a Bibenzyl	-
PhCH ₂ OBu	20% Butyl alcohol, Bibenzyl	-
PhOBu	0%	100% Phenol ^b
BuOBu	0%	0%

^aPhenol is not reduced under the experimental conditions.

^bIn this instance, phenol was produced in 76% yield.

TABLE 2

Wt. of reac- tive coal in g	No. of moles of K/g coal	Time allowed for coal anion form ⁿ in hours	No. of moles of n-BuI/g coal	Time allowed for alkyla- tion in hours	Wt. of water- insol. resi- due in g	Wt. of THF- soluble mate- rial in g	% THF solu- bility	Wt. of coal <u>alkylate</u> Wt. of coal
0.2277	0.031	20	0.044	20	0.3172	0.0661	20.84	1.39
0.4753	0.029	20	0.043	20	0.6094	0.1298	21.30	1.28

The downfield resonances for the aromatic carbon atoms in the coal are weak, broad and centered about $\delta 128.79$ and $\delta 130.89$. Sharp signals at $\delta 47.88$ and $\delta 0.98$ have not been assigned as yet.

Discussion

a) It is known that Illinois No. 6 coal has many C-O-C etheral linkages which are diaryl, dialkyl, aryl alkyl, benzyl aryl or benzyl alkyl in nature. The study of the cleavage reactions of certain selected ethers belonging to the above categories was therefore undertaken to determine which ethers cleave more readily under the two sets of reaction conditions employed in this laboratory to reductively alkylate coal.

The products from a control reaction carried out with potassium and naphthalene in tetrahydrofuran contained 21% unreacted naphthalene, 69% 1,4-dihydronaphthalene and 10% tetralin with a trace of 1,2-dihydronaphthalene. The presence of these compounds and their dimeric by-products (3) which are formed in trace amounts complicate the quantitative identification of the reaction products in the reactions of the ethers with potassium naphthalide in tetrahydrofuran. In addition, control experiments performed with phenol in the potassium naphthalene system in tetrahydrofuran and with potassium in liquid ammonia established that phenol was not reduced under the experimental conditions and that phenol could be recovered quantitatively from the complex mixture of products formed in the presence of naphthalene.

The reactions of both aryl ethers and aralkyl ethers with potassium naphthalide in tetrahydrofuran result in the ether cleavage with phenol formed in high yield as shown in Table I. On the other hand, dibutyl ether and tetrahydrofuran, the solvent, are cleaved only very slowly under these experimental conditions.

The reactions of aryl ethers with potassium in liquid ammonia also result in ether cleavage with phenol formed in high yield. The benzylic ethers, benzyl phenyl ether and benzyl butyl ether, are not rapidly cleaved by potassium in liquid ammonia. Indeed, only 20% of benzyl butyl ether is converted to butyl alcohol and bibenzyl under the mild experimental conditions. In addition, phenyl butyl ether is recovered unchanged from the reaction with potassium in liquid ammonia. The reactivity established in this study indicates that only reactive ethers are cleaved in the reactions in liquid ammonia, whereas some quite unreactive aralkyl ethers, e.g. phenyl butyl ether, are cleaved in the etheral solution.

For ammonia

For tetrahydrofuran

Consequently, the success of a reductive alkylation reaction depends upon the selection of the proper kinds of reaction conditions. For coals with significant quantities of ether linkages, it is desirable to use potassium with naphthalene in an ethereal solvent to insure the complete conversion of the less reactive ethers to cleavage products suitable for alkylation.

b) The tetrahydrofuran solubility of the coal product obtained from reductive butylation of coal at 25°C was a surprisingly low 21%. This may be due to the fact that during the transfer of potassium/liquid ammonia to the stainless steel reactor, the latter is surrounded by an atmosphere of carbon dioxide (from the dry ice/acetone bath) and is also exposed to atmospheric moisture. This could lead to the formation of carbamate, which could subsequently hydrolyze to form ammonium carbonate. The ammonium carbonate would then serve to protonate the coal, leaving it less susceptible to alkylation. In support of this hypothesis, a white solid was indeed observed on the inner walls of the reactor. The reduced or protonated coal product is less soluble in tetrahydrofuran, as we have seen in an earlier report where water, 2-methyl-2-propanol or ammonium chloride was used to quench the reaction (4). This problem can probably be overcome by cooling the reactor in liquid nitrogen, so that it will be enveloped in an inert atmosphere of nitrogen and, if possible, by transferring the potassium/liquid ammonia into the reactor in a glove bag, so that no moisture can condense on the walls of the reactor.

c) The 22.631 MHz $^{13}\text{C}\{^1\text{H}\}$ nmr spectrum of comparable low molecular weight fractions (17-20), of butylated coal from a coal/potassium/naphthalene/tetrahydrofuran reaction will be obtained in the near future, so as to study the similarities and dissimilarities of the coal alkylates obtained from the electron transfer agent system and the liquid ammonia system.

Experimental

Equipment

A cylindrical stainless steel tube, approximately 18 cm. long and 1.6 cm. in internal diameter, was equipped with a Swagelok^R threaded fitting at either end. This stainless steel reactor was used to carry out the room temperature reactions in the potassium/ammonia medium.

Procedure

Benzyl n-butyl ether was synthesized according to the method described by Van Duzee and Adkins (5). The ether cleavage reactions performed at -78°C and -33°C were carried out in the same way as the coal reactions described in previous quarterly progress reports.

The ether cleavage and coal alkylation reactions conducted at 25°C however, were performed in a stainless steel reactor and the procedure adopted warrants a more detailed description.

In a typical experiment, benzyl n-butyl ether (0.5257 g, 3.2×10^{-3} moles) was introduced into the reactor which was closed at one end. Metallic potassium (0.6 g, 2.9×10^{-2} moles/g ether) was dissolved in ammonia (25-30 ml) which was condensed in a flask maintained at -78°C . The deep blue solution of solvated electrons was transferred as quickly as possible into the reactor which was also cooled in a dry ice/acetone bath at -78°C . The reactor was sealed with the Swagelok^R fittings, clamped to a shaker and allowed to shake for approximately 20 hours at room temperature. Before the reactor was opened to quench the reaction, the precaution of cooling it to -78°C was taken, so as to prevent the sudden escape of ammonia gas. More liquid ammonia (~ 5 ml) was added if necessary, and the reaction quenched with solid ammonium chloride (1.1 g, 3.9×10^{-2} moles/g ether). The tube was sealed once again and the contents agitated for a further 20 hours approximately, at 25°C . The reactor was cooled to -78°C , opened cautiously and the contents poured into a flask. After the ammonia had boiled off, the reactor was rinsed with diethyl ether and water, the crude reaction product was extracted into diethyl ether, washed with water, dried over anhydrous magnesium sulfate, filtered and the solvent (diethyl ether) removed on a rotary evaporator at room temperature. The resulting pale yellow liquid was analyzed by 270 MHz proton magnetic resonance spectroscopy and gas chromatography.

The phenyl ether reactions were worked-up slightly differently. Phenyl n-butyl ether (0.5270 g, 3.5×10^{-3} moles) was reacted in a similar manner with potassium (0.57 g, 2.8×10^{-2} moles/g ether), ammonia (~ 25 ml) and ammonium chloride (1.34 g, 4.8×10^{-2} moles/g ether). However, the crude reaction product was partitioned between a 5% (w/v) aqueous sodium hydroxide solution and diethyl ether (ether extract 1). The sodium hydroxide solution was acidified with dilute hydrochloric acid and extracted into diethyl ether (ether extract 2). Both ether solutions (1 and 2) were individually washed with water, dried, filtered and concentrated. The products were then analyzed by 270 MHz. nmr spectroscopy and gas chromatography on OV 101 and/or carbowax columns.

The ether cleavage reactions performed at 25°C in potassium/naphthalene/tetrahydrofuran, were executed as described in previous progress reports, with the ether being substituted for the Illinois No. 6 coal.

In a typical reaction the ether (6.09×10^{-3} moles), naphthalene (3.12×10^{-3} moles) and potassium (2.56×10^{-2} moles) were added to dry tetrahydrofuran (~ 55 ml) and stirred at 25°C under an atmosphere of argon. Approximately 25 hours later each reaction was quenched with ammonium chloride (~ 2 g) dissolved in tetrahydrofuran (10 ml) followed by dry methanol (5 ml) to bring all the ammonium chloride into solution. The reactions were worked-up approximately 23 hours after quenching.

The reactions in which phenyl ethers were used as starting materials were worked-up as follows. Potassium chloride was removed by filtration, and tetrahydrofuran and methanol were distilled off. The residual liquid was partitioned between a 10% (w/v) aqueous sodium hydroxide solution and diethyl ether. The ether extract was washed with water, dried over anhydrous magnesium sulfate and concentrated by distillation. The aqueous layer was acidified with dilute hydrochloric acid, extracted into diethyl ether, washed, dried and concentrated in the usual way.

In the cleavage reactions of ethers not containing a phenyl moiety, the work-up procedure was simpler because the extraction into aqueous sodium hydroxide was eliminated. The crude reaction product after filtration (to remove potassium chloride) and distillation (to remove tetrahydrofuran and methanol), was extracted

into diethyl ether. The ether solution was washed with water, dried and concentrated by distillation. The products were then analyzed by nmr spectroscopy and gas chromatography.

The alkylation of coal at 25°C was performed in the stainless steel reactor in much the same way as the ether cleavage reactions. The quenching reagent however was n-butyl iodide. The crude reaction product was washed with water on a 4-5.5μ fritted funnel until the washings were neutral (pH 6-7). The water-insoluble residue was dried, weighed and washed with distilled tetrahydrofuran, until this solvent ceased to extract any appreciable amount of colored material from the coal residue. The tetrahydrofuran-insoluble residue was dried and weighed, while the tetrahydrofuran-soluble material was weighed after removal of the solvent from the orange-brown solution.

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F. Exchange and Cleavage Reactions in Tetralin

by H.-H. King

Introduction

The effects of organic additives on the exchange reactions between tetralin-d₁₂ and diphenylmethane and on the thermal cleavage reactions of several model compounds in tetralin were investigated.

Experimental

Equipment.--The equipment used in these experiments was described in a previous report (1).

Materials.--Many of the compounds used in this quarter's work were described in previous report (1). In addition, benzyl ether, dibenzylamine, 1-naphthol, 1-naphthoic acid, p-toluenesulfonic acid monohydrate, 2-hydroxypyridine, 3-hydroxypyridine, and di-n-butylamine were obtained from Aldrich Chemical Co., Potassium tert-butoxide (K & K Lab.), piperidine (Eastman Kodak Co.), cyclohexylamine (Baker Chemical Co.), 2-naphthol (Matheson, Coleman & Bell Co.) were obtained from commercial sources.

Procedure.--The procedures used in these experiments were also described in the previous report (1). The experimental conditions are summarized in the tables.

Table 1. The Influence of Some Representative Compounds on the Exchange Reaction at 400°C^a

Reaction	Time, hr.	Additive
213	1	1-naphthol
214	1	2-naphthol
215	1	1-naphthoic acid
216	1	p-toluenesulfonic acid monohydrate
217	1	acetic acid
218	1	3-hydroxypyridine
219	1	2-hydroxypyridine
220	1	cyclohexylamine
221	1	piperidine
222	1	di-n-butylamine
223	1	potassium tert-butoxide

^aTetralin-d₁₂ (0.376 mmole), diphenylmethane (0.377 mmole), and additive (0.045 mmole) were sealed in a 10 cm-long glass tube reactor. More than 95% of the materials were recovered for analysis.

Table 2. The Influence of Illinois No. 6 Coal and Other Representative Compounds on the Cleavage Reaction of Benzyl Phenyl Ether in Tetralin at 350°C^a

Reaction	Time, min.	Additive
224	10	none
225	10	coal (50.4 mg)
226	10	benzyl phenyl sulfide (0.090 mmole)
227	10	9,10-anthraquinone (0.089 mmole)
228	10	tetracene (0.090 mmole)
229	10	thiophenol (0.091 mmole)
230	10	none ^b

Table 2--Continued

Reaction	Time, min.	Additive
231	10	phenol (0.229 mmole)
232	10	phenol (0.755 mmole)
233	10	1-naphthol (0.228 mmole)
234	10	1-naphthol (0.758 mmole)
235	10	benzoic acid (0.229 mmole)
236	10	benzoic acid (0.758 mmole)

^aTetralin (0.758 mmole), benzyl phenyl ether (0.761 mmole), and additive were sealed in a 20 cm-long glass tube reactor. More than 95% of the materials were recovered for analysis.

^bTetralin (1.516 mmole) and benzyl phenyl ether (0.761 mmole) were used.

Table 3. The Influence of Illinois No. 6 Coal and Other Representative Compounds on the Cleavage Reaction of Benzyl Ether in Tetralin at 400°C^a

Reaction	Time, min.	Additive
237	10	none
238	10	coal (50.8 mg)
239	10	benzyl phenyl sulfide (0.090 mmole)
240	10	9,10-anthraquinone (0.090 mmole)
241	10	tetracene (0.090 mmole)
242	10	thiophenol (0.091 mmole)
243	10	none ^b
244	10	phenol (0.228 mmole)
245	10	phenol (0.763 mmole)
246	10	1-naphthol (0.227 mmole)
247	10	1-naphthol (0.761 mmole)
248	10	benzoic acid (0.228 mmole)
249	10	benzoic acid (0.758 mmole)

^aTetralin (0.758 mmole), benzyl ether (0.758 mmole), and additive were sealed in a 20 cm-long glass tube reactor. More than 95% of the materials were recovered for analysis. ^bTetralin (1.516 mmole) and benzyl ether (0.758 mmole) were used.

Table 4. The Influence of Illinois No. 6 Coal and Other Representative Compounds on the Cleavage Reaction of N-Benzylaniline in Tetralin at 400°C^a

Reaction	Time, min.	Additive
250	20	none
251	20	coal (50.4 mg)
252	20	benzyl phenyl sulfide (0.091 mmole)
253	20	9,10-anthraquinone (0.090 mmole)
254	20	tetracene (0.090 mmole)
255	20	thiophenol (0.091 mmole)
256	20	none ^b
257	20	phenol (0.226 mmole)
258	20	phenol (0.760 mmole)
259	20	1-naphthol (0.226 mmole)
260	20	1-naphthol (0.758 mmole)
261	20	benzoic acid (0.228 mmole)
262	20	benzoic acid (0.758 mmole)

^aTetralin (0.758 mmole), N-benzylaniline (0.758 mmole), and additive were sealed in a 20 cm-long glass tube reactor. More than 95% of the materials were recovered for analysis.

^bTetralin (1.516 mmole) and N-benzylaniline (0.758 mmole) were used.

Table 5. The Influence of Illinois No. 6 Coal and Other Representative Compounds on the Cleavage Reaction of Dibenzylamine in Tetralin at 350°C^a

Reaction	Time, min.	Additive
263	10	none
264	10	coal (50.1 mg)
265	10	benzyl phenyl sulfide (0.091 mmole)
266	10	9,10-anthraquinone (0.090 mmole)
267	10	tetracene (0.089 mmole)
268	10	thiophenol (0.091 mmole)
269	10	phenol (0.226 mmole)
270	10	phenol (0.761 mmole)

Table 5--Continued

Reaction	Time, min.	Additive
271	10	1-naphthol (0.228 mmole)
272	10	1-naphthol (0.761 mmole)
273	10	benzoic acid (0.228 mmole)
274	10	benzoic acid (0.757 mmole)

^aTetralin (0.758 mmole), dibenzylamine (0.760 mmole), and additive were sealed in a 20 cm-long glass tube reactor. More than 95% of the materials were recovered for analysis.

Table 6. The Influence of Illinois No. 6 Coal and Other Representative Compounds on the Cleavage Reaction of 1,2-Diphenylethane in Tetralin at 400°C^a

Reaction	Time, hr.	Additive
275	4	none
276	4	coal (50.4 mg)
277	4	benzyl phenyl sulfide (0.091 mmole)
278	4	9,10-anthraquinone (0.090 mmole)
279	4	tetracene (0.090 mmole)
280	4	thiophenol (0.091 mmole)
281	4	none ^b
282	4	phenol (0.230 mmole)
283	4	phenol (0.760 mmole)
284	4	1-naphthol (0.227 mmole)
285	4	1-naphthol (0.759 mmole)
286	4	benzoic acid (0.228 mmole)
287	4	benzoic acid (0.758 mmole)

^aTetralin (0.758 mmole), 1,2-diphenylethane (0.758 mmole), and additive were sealed in a 20 cm-long glass tube reactor. More than 95% of the materials were recovered for analysis.

^bTetralin (1.516 mmole) and 1,2-diphenylethane (0.758 mmole) were used.

Table 7. The Influence of Some Representative Compounds on the Cleavage Reaction of 1,3-Diphenylpropane in Tetralin at 400°C^a

Reaction	Time, min.	Additive
288	30	none
289	30	none ^b
290	30	phenol (0.228 mmole)
291	30	phenol (0.762 mmole)
292	30	1-naphthol (0.229 mmole)
293	30	1-naphthol (0.758 mmole)
294	30	benzoic acid (0.226 mmole)
295	30	benzoic acid (0.757 mmole)

^aTetralin (0.758 mmole), 1,3-diphenylpropane (0.757 mmole), and additive were sealed in a 20 cm-long glass tube reactor. More than 95% of the materials were recovered for analysis.

^bTetralin (1.516 mmole) and 1,3-diphenylpropane (0.757 mmole) were used.

Table 8. The Influence of Organic Additives on the Coal Liquefaction Conversion at 400°C^a

Reaction	Time, min.	Additive
296	4	none
297	4	benzyl phenyl sulfide (1.345 mmole)
298	4	thiophenol (1.364 mmole)

^aCoal (0.75 g), tetralin (1.5 g), and additive were sealed in a stainless steel reactor.

Results and Discussion

Reactions 213-223 were performed to determine the influence of several acids and bases on the exchange reaction between tetralin-d₁₂ and diphenylmethane. The results are presented in Table 9.

Table 9. The Influence of Some Representative Compounds on the Exchange Reaction at 400°C

Reaction	Additive	%D on Recovered Diphenylmethane	
		Aromatic	Benzylic
95	none	0	28
213	1-naphthol	0	21
214	2-naphthol	0	26
215	1-naphthoic acid	0	21
216	p-toluenesulfonic acid monohydrate	6	64
217	acetic acid	0	2
218	3-hydroxypyridine	0	24
219	2-hydroxypyridine	0	27
220	cyclohexylamine	0	25
221	piperidine	0	15
222	di-n-butylamine	0	23
223	potassium tert-butoxide	0	12

The results indicate that all the additives except p-toluenesulfonic acid are inactive. Control experiment shows that black insoluble solid is formed from p-toluenesulfonic acid. The acceleration produced by p-toluenesulfonic acid is apparently the consequence of its decomposition rather than its acidity. On the other hand, its acidity does initiate some aromatic exchange.

As the continuation of last quarter's work, the cleavage reactions of benzyl phenyl ether, benzyl ether, N-benzyl aniline, and dibenzylamine were studied. The results are presented in Tables 10-13.

The products derived from benzyl phenyl ether are mainly toluene and phenol together with small amount of diphenylmethane and benzyl phenols. Just like 1,2-diphenylethane, the rates of decomposition are not influenced by benzyl phenyl sulfide, 9,10-anthraquinone, tetracene, and thiophenol. On the other hand, phenol,

Table 10. The Influence of Illinois No. 6 Coal and Other Representative Compounds on the Cleavage Reaction of Benzyl Phenyl Ether in Tetralin at 350°C

Reaction	Time, min.	Additive	% Conversion
224	10	none	33
225	10	coal	91
226	10	benzyl phenyl sulfide	34
227	10	9,10-anthraquinone	36
228	10	tetracene	40
229	10	thiophenol	35
230	10	none	33
231	10	phenol	38
232	10	phenol	51
233	10	1-naphthol	39
234	10	1-naphthol	54
235	10	benzoic acid	41
236	10	benzoic acid	54

Table 11. The Influence of Illinois No. 6 Coal and Other Representative Compounds on the Cleavage Reaction of Benzyl Ether in Tetralin at 400°C

Reaction	Time, min.	Additive	% Conversion
237	10	none	22
238	10	coal	100
239	10	benzyl phenyl sulfide	100
240	10	9,10-anthraquinone	61
241	10	tetracene	80
242	10	thiophenol	100
243	10	none	21
244	10	phenol	47
245	10	phenol	71
246	10	1-naphthol	58
247	10	1-naphthol	75
248	10	benzoic acid	30
249	10	benzoic acid	45

Table 12. The Influence of Illinois No. 6 Coal and Other Representative Compounds on the Cleavage Reaction of N-Benzylaniline in Tetralin at 400°C

Reaction	Time, min.	Additive	% Conversion
250	20	none	14
251	20	coal	100
252	20	benzyl phenyl sulfide	65
253	20	9,10-anthraquinone	53
254	20	tetracene	37
255	20	thiophenol	65
256	20	none	18
257	20	phenol	55
258	20	phenol	84
259	20	1-naphthol	79
260	20	1-naphthol	88
261	20	benzoic acid	60
262	20	benzoic acid	78

Table 13. The Influence of Illinois No. 6 Coal and Other Representative Compounds on the Cleavage Reaction of Dibenzylamine in Tetralin at 350°C

Reaction	Time, min.	Additive	% Conversion
263	10	none	60
264	10	coal	100
265	10	benzyl phenyl sulfide	100
266	10	9,10-anthraquinone	93
267	10	tetracene	91
268	10	thiophenol	100
269	10	phenol	85
270	10	phenol	81
271	10	1-naphthol	100
272	10	1-naphthol	99
273	10	benzoic acid	60
274	10	benzoic acid	100

1-naphthol, and benzoic acid accelerate the decomposition probably with the assistance of polar interaction between benzyl phenyl ether and additive (2). The acceleration produced by coal may be caused by the structural elements of phenol type.

The main products derived from benzyl ether are toluene and benzaldehyde. The results in Table 11 show that the decomposition of benzyl ether is accelerated not only by the free radical promoters, benzyl phenyl sulfide, 9,10-anthraquinone, tetracene, and thiophenol, but also by phenol, 1-naphthol, and benzoic acid probably via polar interaction. Coal may accelerate the reaction by either way.

The main products derived from N-benzylaniline are toluene and aniline. The results in Table 12 show that the reaction is accelerated by all the additives. The reason why benzyl phenyl sulfide, 9,10-anthraquinone, tetracene, and thiophenol are active is not clear.

The main products derived from dibenzylamine are toluene and 1,2-diphenylethane. Gaseous products which may contain nitrogen is also formed. Control experiment shows that benzylamine, which is the possible intermediate, converts to toluene and 1,2-diphenylethane under the reaction conditions. The results in Table 13 show that all the additives are active either by promoting the free radical generation or by polar interaction.

Since phenol, 1-naphthol, and benzoic acid accelerate the cleavage reactions of the heteroatom containing compounds mentioned above, their effects on the cleavage reactions of 1,2-diphenylethane and 1,3-diphenylpropane are studied. The results are presented in Tables 14 and 15.

The reactions 275-280 are the repeated reactions which were reported in the last quarterly report. The decomposition rate of 1,2-diphenylethane is not affected by any additive.

Table 14. The Influence of Illinois No. 6 Coal and Other Representative Compounds on the Cleavage Reaction of 1,2-Diphenylethane in Tetralin at 400°C

Reaction	Time, hr.	Additive	% Decomposed
275	4	none	8
276	4	coal	8
277	4	benzyl phenyl sulfide	8
278	4	9,10-anthraquinone	7
279	4	tetracene	7
280	4	thiophenol	7
281	4	none	8
282	4	phenol	9
283	4	phenol	8
284	4	1-naphthol	6
285	4	1-naphthol	8
286	4	benzoic acid	6
287	4	benzoic acid	6

Table 15. The Influence of Illinois No. 6 Coal and Other Representative Compounds on the Cleavage Reaction of 1,3-Diphenylpropane in Tetralin at 400°C

Reaction	Time, min.	Additive	Product Distribution (%)			% Decomposed ^a
			Toluene	Ethyl- benzene	Diphenyl- propane	
288	30	none	29	10	61	24
289	30	none	29	9	62	24
290	30	phenol	28	11	61	24
291	30	phenol	30	12	58	27
292	30	1-naphthol	33	22	45	38
293	30	1-naphthol	30	23	47	36
294	30	benzoic acid	23	10	67	20
295	30	benzoic acid	27	9	64	22

$$^a\% \text{ decomposed} = \frac{(\% \text{ toluene} + \% \text{ ethylbenzene})/2}{(\% \text{ toluene} + \% \text{ ethylbenzene})/2 + \% \text{ 1,3-diphenylpropane}}$$

The cleavage reaction of 1,3-diphenylpropane is accelerated by 1-naphthol which is an inactive additive on the exchange reaction between tetralin-d₁₂ and diphenylmethane. Phenol and benzoic acid do not accelerate this reaction. Since more ethylbenzene is formed in the cases with 1-naphthol than in the cases with phenol or benzoic acid, the acceleration produced by 1-naphthol might be the result of its being a better hydrogen donor kinetically. More experiments are necessary to prove this point.

Table 16. The Influence of Organic Additives on the Coal Liquefaction Conversion at 400°C

Reaction	Time, min.	Additive	% Soluble in Pyridine (d.a.f)
296	4	none	59
297	4	benzyl phenyl sulfide	87
298	4	thiophenol	88

These results in Table 16 indicate that more soluble products are obtained with the assistance of benzyl phenyl sulfide or thiophenol. This suggests that the free radical generation and the subsequent β -scission are very important reactions in the coal liquefaction process.

References

1. Sixth Quarterly Progress Report.
2. Kamiya, Y.; Sato, H.; Yao, T. Fuel 1978, 57, 681.