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Coal Transformation Chemistry

Third Quarterly Progress Report

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I. ABSTRACT

A Colorado subbituminous coal was reacted with potassium and naphthalene in tetrahydrofuran. This was then alkylated with n-butyl iodide and the solubility in tetrahydrofuran was determined. The solubility was found to be less than in a corresponding reaction with Illinois No. 6 coal. This work is discussed in Part A.

The solubilization of a Colorado subbituminous coal by reacting it with potassium in liquid ammonia, followed by alkylation is discussed. The preliminary results from a reaction of Illinois No. 6 coal with tetrabutylammonium hydroxide and methyl iodide are reported. This work is discussed in Part B.

Reductive acylation of coal is being studied at the present time using trifluoroacetic anhydride as a quenching reagent. ^{19}F is a candidate for nmr studies and chemical shifts for trifluoroacetyl derivatives of phenols, thiols, and amides indicate that fluorine may be useful as a sensitive probe for reactive speices in coal. This work is described in Part C.

The effort on donor solvent coal chemistry during this quarter was directed to the role played by pericyclic reactions in the liquefaction process. The acceptors were reduced by the deuterated donors. The isotopic distribution of the reduction product indicates that free radical processes occur preferentially. Thus, the pericyclic reactions appear to be unimportant at the threshold reaction temperatures of 350-425°C. This work is described in Part D.

The reactions of aromatic ethers with inorganic sulfide at 400°C produces thiophenols. This work is discussed 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

A Colorado subbituminous coal was reductively alkylated in both first and second pass reactions to determine tetrahydrofuran solubility. The coal was stirred in tetrahydrofuran for 168 hours to determine the tetrahydrofuran solubility. Each reaction was repeated to insure consistency. This work is described in Section IV A.

A comparative study of the optimum conditions for rendering Illinois No. 6 and Colorado coals soluble in tetrahydrofuran is in progress. The alkylation of acidic hydroxyl groups in Illinois No. 6 coal has been attempted using Liotta's[1B] method. The work is described in Section IV B.

The synthesis of model compounds for the purposes of acquiring chemical shift data for butylated dihydroaromatics has been pursued. Experimental procedures and chemical shift information have been obtained. Reductive trifluoroacylation of coal has been performed and a lower limit of solubility in tetrahydrofuran of the coal product has been calculated. This work is described in Section IV C.

The role of pericyclic reactions in the liquefaction reactions of Illinois No. 6 coal has been considered via the study of deuterated donors with selected acceptors. The results suggest that free radical processes are much more important than pericyclic processes. The results are discussed in Section IV D.

The formation of thiophenol in the reactions of phenol or phenyl ether with anhydrous sodium sulfide or iron(II) sulfide were investigated at 400°C. Additives, such as Illinois No. 6 coal or tetralin, did not affect the rate of formation of thiophenol. The results are discussed in Section IV E.

C. Summary of Progress to Date

TASK 1 Solublization Reactions

In the past we have worked with Illinois No. 6 coal as described in previous Quarterly Progress Reports. This quarter we began studying a Colorado subbituminous

B coal. We reacted the Colorado coal by our usual procedure with $K/C_{10}H_8/THF/$ n-BuI. In the reactions with fresh Colorado coal there was much less solubilization than in a comparable reaction with Illinois No. 6 coal. When the insoluble Colorado coal residue was rereacted in our system, significantly more solubilization occurred.

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. From preliminary data available at this stage, it appears that the tetrahydrofuran solubility of Illinois No. 6 coal alkylated by the method of Liotta, is little or no different from that of raw Illinois No. 6 coal. This observation however, needs to be confirmed by further experiments.

The feasibility of reductive acylation is being studied at the present time for two reasons. First, it is instructive to compare the solubilities of coal products in tetrahydrofuran for reductive alkylation and acylation and secondly, it is possible that information regarding the reactive entities in coal (i.e. entities which accept electrons) can be established. To this end, trifluoroacetic anhydride has been used as a quenching reagent. Preliminary results show that it is effective in the solubilization of coal, although not as good as butyl iodide Furthermore, resonances in ^{19}F nmr spectra are seen. The assignment of these resonances will almost certainly provide new structural information.

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 $d_0:d_1:d_2:d_3:d_4 = 62:29:7:1:0$.

Anhydrous sodium sulfide reacted with phenol to form the thiophenol (2%) at 400°C in 1 hr. Thiophenol was not detected in the reactions of anhydrous sodium sulfide with phenyl ether or iron(II) sulfide with phenol or with phenyl ether at 400°C. Neither Illinois coal nor tetralin appeared to alter the rate of formation of thiophenol

IV. DISCUSSION OF TECHNICAL PROGRESS

PART A

Reductive Alkylation of Colorado Subbituminous B Coal

by David A. Blain and William Landschulz

Introduction

Sternberg and Delle Donne showed that the solubility in pyridine or benzene of an alkylated Colorado subbituminous coal was less than the solubility of a bituminous coal alkylated under the same conditions.[1A] We obtained a sample of Colorado subbituminous B coal and reacted it under our conditions to find how its solubility compared to that of alkylated Illinois No. 6 bituminous coal.

Experimental Procedure

A control reaction was run in which 1 gram of Colorado subbituminous coal (< 325 mesh) was added to tetrahydrofuran (55 ml) under argon. This was stirred for 168 hours. When the stirring was stopped there was a brown coal suspension. This was extracted several times with distilled tetrahydrofuran until the tetrahydrofuran extracts were very light yellow. The light orange tetrahydrofuran soluble material was concentrated on a rotary evaporator. The dark brown insoluble material was dried under a gentle stream of nitrogen. This reaction was done twice and the results are summarized in Table A1, experiments 1 and 2.

In the next two reactions the Colorado subbituminous coal was reacted under our usual reaction conditions of coal/$C_{10}H_8$/K/THF/*n*-BuI. These reactions were carried out and worked up as described in previous progress reports. The results of these two reactions are given in Table A1, experiments 3 and 4. The insoluble residue from experiment 4 was rereacted under the same conditions. This reaction is presently being worked up. The initial data are given in the fifth line of Table A1. For comparison, the bottom row of Table A1 gives relevant data for the reaction of Illinois No. 6 coal under the same conditions.

Results and Discussion

The Colorado subbituminous B coal is from Seam No. 3 of the Laramie formation in Weld County, Colorado.[2A]

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.

Sternberg and Delle Donne reported that in their reactions with Colorado subbituminous coal [% carbon (daf) = 71], much less solubility was achieved in pyridine or benzene compared to comparable reactions with a bituminous coal.[1A] Our results closely parallel theirs. This was first apparent from direct observations

Table A1. Results for the Coal/K/$C_{10}H_8$/THF/n-BuI Reactions.

Expt.	Weight coal (daf) (g)	Weight THF insoluble coal (daf) (g)	Weight THF insoluble coal (daf) (g)	$\frac{\text{Mass K consumed}}{\text{gram coal (daf)}}$ (g)	$\frac{\theta\text{ charges}}{\text{100 C atoms (daf)}}$
1	1.0084[a]	1.0487	0.1319[c]	-	-
2	0.9797[a]	1.0340	0.1669[c]	-	-
3	0.9800[a]	1.1164	0.7671[d]	0.8381	21.90
4	0.9789[a]	1.0556	0.6856[d]	0.8520	22.21
5	0.9171[a,e]	-	-	0.9405	
6	0.9218[b]	0.551	1.633[d]	0.9796	20.9

[a] Colorado Subbituminous coal. [b] Illinois No. 6 coal. [c] Weight determined after concentration on a rotary evaporator. [d] Includes naphthalene and naphthalene derivatives; weight determined after concentration on a rotary evaporator and ≃ 72 hours vacuum pumping. [e] Workup of this reaction in progress.

of the reaction progress. After a reaction with Illinois No. 6 coal is quenched with n-butyl iodide, potassium iodide can be seen precipitating out of the solution within about 0.5 hour. When the stirring is stopped after 48 hours, there is a dark brown liquid over the precipitated potassium iodide. The observations from the Colorado coal sharply contrast this. After quenching, the potassium iodide cannot be directly observed for several hours. When the stirring is stopped, the solution over the potassium iodide is light brown in color. The observations from the second pass reaction of the Colorado coal are intermediate. The solution was medium brown and more potassium was consumed per gram of coal in the second pass than in the first.

The solubility of the alkylated Colorado subbituminous coal was markedly lower than the solubility of alkylated Illinois No. 6 coal. Comparison of the results obtained in experiments 3, 4 and 6 in Table A1 clearly shows this trend; both in the amounts of soluble and insoluble coal found. In each case the weight of soluble coal also includes naphthalene and its derivatives. Work in this laboratory[3A] and also studies by Franz and Skiens[4A] show that many naphthalene by-products are formed. These include reduced, alkylated, and/or dimerized naphthalenes. These must be removed from the soluble material before absolute weights of soluble coal can be given.

Sternberg attributes the low solubility of the alkylated subbituminous coal to the observation that most of the oxygen atoms are in ether linkages that are not readily cleaved under these reaction conditions.[1A] Our preliminary results of the second pass reaction show that some of these ethers may be cleaved in further reactions of the once alkylated coal.

The entries in Table A1 show that in reactions with Colorado subbituminous coal the weight of the tetrahydrofuran insoluble material is greater than the original mass of coal added to the system. This suggests that some tetrahydrofuran is being incorporated into the coal matrix. Ignasiak and his coworkers suggest that as the rank of the coal decreases, there is a larger amount of solvent incorporation.[5A]

Up to now there have been very few studies of reductive alkylation of subbituminous coals. However, from the work that has been done previously and from our work a trend can be seen. As the percentage of carbon in the coal decreases, the solubility of the coal after it has been reductively alkylated also decreases.

References

1A. H.W. Sternberg and C.L. Delle Donne, Fuel, 53, 172 (1974).

2A. Coal and ultimate analysis furnished by The Institute of Gas Technology, Chicago, Illinois.

3A. Twelfth (Final) Quarterly Progress Report.

4A. J.A. Franz and W.E. Skiens, Fuel, 57, 502 (1978).

5A. B.S. Ignasiak, S.K. Chakrabatty, and N. Berkowitz, Fuel, 57, 507 (1978).

PART B

by Indira Handy

Reductive Alkylation of Coal in Liquid Ammonia

Introduction

During this quarter attention has been directed toward the solubilization of a Colorado subbituminous B coal, by reacting it with potassium in liquid ammonia at -33° and alkylating with n-butyl iodide in tetrahydrofuran. The amount of metallic potassium used and the time allowed for alkylation were varied to achieve greater tetrahydrofuran solubility of the product. A methylation reaction following the procedure of Liotta[1B] was carried out on Illinois No. 6 coal and preliminary results from this experiment are available. Also reported in this Quarterly Report is a second pass butylation reaction conducted in liquid ammonia medium, on a sample of tetrahydrofuran-insoluble Illinois No. 6 coal that had already been treated (in the first pass experiment) with potassium, naphthalene and tetrahydrofuran followed by n-butyl iodide at room temperature.

Results

The results obtained for the experiments in which Colorado subbituminous B and Illinois No. 6 coals were reductively alkylated are summarized in Table B1.

Discussion

The solubility of reductively alkylated coal in an organic solvent such as tetrahydrofuran seems to depend upon two factors.

1. The number of alkyl groups added to the coal.
2. The number of bonds that are cleaved or broken.

The number of alkyl groups added to the coal is reflected by the ratio of the weight of coal alkylate to the weight of raw coal. One might expect that as this ratio increases, the solubility of the coal increases. However, the results from experiments 1 and 2 (Table B1) serve to illustrate the point that this is not necessarily true in all cases. This phenomenon can be explained by the fact that alkyl groups are added to both the tetrahydrofuran-soluble and tetrahydrofuran-insoluble fractions of the coal. It is believed that in order to enhance the solubility, one must not only add alkyl groups, but also break covalent bonds and disrupt intermolecular and intramolecular hydrogen bonds in the coal matrix, thus causing it to fragment into smaller units of lower molecular weight.

Colorado subbituminous B coal has an oxygen content of about 20%.[2B] Illinois No. 6 coal, on the other hand, has an oxygen content of about 12%. Colorado coal may therefore be assumed to contain more etheral C-O-C linkages and more free phenolic and carboxylic groups, as compared to Illinois No. 6 coal. Consequently, one would expect Colorado coal to consume more metallic potassium during the formation of coal polyanions, by the interaction of coal molecules with solvated electrons. This is indeed found to be the case in the liquid ammonia system where

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

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

Table B1. Reaction Parameters for Butylation of Coal in Liquid Ammonia

Expt. No.	Wt. of Coal in g	Moles K / g. coal	Coal anion formation time, hr.	Coal anion formation temp., °C	Moles n-BuI / g. coal	Alkylation time, hr.	Alkylation temp., °C	Wt. of coal alkylate g	THF-soluble material, g.	% THF solubility	Wt. of coal alkylate/ Wt. of coal
1[a]	1.2514	0.029	6	-33	0.041	40	-33 to 25	1.6999	0.2778	16	1.36
2[a]	1.2679	0.060	6	-33	0.061	64	-33 to 25	1.7495	0.5624	32	1.38
3[a]	1.4626	0.087	6	-33	0.090	88	-33 to 25	2.1830	1.3559	62	1.49
4[a]	1.1097	0.117	6	-33	0.120	43	-33 to 25	1.5987	0.6911	43	1.44
5[b]	0.8345	0.029	6	-33	0.040	46	-33 to 25	1.2444	0.6515	52	1.49
6[b,c]	1.1042	0.029	6	-33	0.040	40	-33 to 25	1.3309	0.6421	48	1.21

[a] Experiments done with Colorado, subbituminous B coal. [b] Experiments done with Illinois No. 6 bituminous coal. [c] Second pass experiment on THF-insoluble material from a coal/K/naphthalene/THF/n-BuI reaction.

Table B2. Reaction Parameters for Selective Methylation of Acidic Hydroxyl Groups in Illinois No. 6 Coal by Liotta's[1B] Method

Wt. of coal in g.	Volume of 40% aq.(w/v)NBu_4OH in ml	No. of moles NBu_4OH	Vol. of MeI in ml	No. of moles MeI	Wt. of coal alkylate, g.	THF-soluble material, g.	% THF solubility	Wt. of coal alkylate/Wt of coal
1.0915	2	3.1×10^{-3}	0.5	8.0×10^{-3}	1.3003	0.1169	8.99	1.19

as the number of moles of potassium per gram of Colorado coal was increased from 0.029 to 0.060 to 0.087 (Experiments 1,2 and 3, Table B1) the tetrahydrofuran solubility of the product increased from 16 to 32 to 62%. Alkylation time was also a variable factor in these experiments, varying from 40 to 64 to 88 hours, in experiments 1,2 and 3 respectively. Experiments 1 and 4 (Table B1) however, differ mainly[3B] in the number of moles of potassium used per gram of coal, the alkylation times being comparable (40 and 43 hr., respectively). The tetrahydrofuran solubilities of the products were 16% and 43%, when 0.029 and 0.117 moles of potassium were used per gram of Colorado coal. In contrast, experiments carried out previously in this laboratory on Illinois No. 6 coal, with varying amounts of potassium metal in liquid ammonia, indicate that 0.029 moles of potassium per gram of coal is the optimum amount for this particular coal. When Colorado and Illinois coals were alkylated under similar conditions, using 0.029 moles of potassium per gram of coal (Experiments 1 and 5, Table B1), the Colorado coal was only soluble in tetrahydrofuran to the extent of 16%, whereas the Illinois coal yielded much more tetrahydrofuran-soluble material (52%).

Examination of the results from Experiments 3 and 4 (Table B1) shows that the time allotted for alkylation does play an important part in the solubilization of the product. Longer alkylation times seem to favor greater product solubility.

The results from Experiment 6 (Table B1) proved to be interesting. The tetrahydrofuran-insoluble fraction of Illinois No. 6 coal that had been reductively butylated according to the procedure of Sternberg[4Ba-c] using potassium, naphthalene (as electron transfer reagent), tetrahydrofuran and n-butyl iodide, was reacted in a second pass experiment with potassium in liquid ammonia, and alkylated with n-butyl iodide dissolved in tetrahydrofuran. The product was soluble in tetrahydrofuran to the extent of 48%. In another experiment conducted in this laboratory, the reaction sequence was reversed. The first alkylation was done in liquid ammonia medium, and the second pass experiment was executed in the manner originally outlined by Sternberg[4Ba-c] et al., and adopted in this laboratory by Alemany.[5B] The tetrahydrofuran solubility of the material was 64%.[6B] These results suggest that the two methods employed in this laboratory to effect reductive alkylation of coal complement one another, or in other words, that different kinds of bonds in the coal macrostructure are cleaved to varying degrees by the two types of reactions.

A selective methylation of coal following the procedure of Liotta,[1B] which may be represented by the following equations, was carried out on a sample of Illinois No. 6 coal in this laboratory. Preliminary results (Table B2) indicate

$$\text{Coal-OH} + \overset{+}{\text{N}}\text{Bu}_4\overset{-}{\text{OH}} \rightarrow \text{Coal-}\overset{-}{\text{O}}\overset{+}{\text{N}}\text{Bu}_4 + \text{H}_2\text{O} \tag{1}$$

$$\text{Coal-}\overset{-}{\text{O}}\overset{+}{\text{N}}\text{Bu}_4 + \text{MeI} \rightarrow \text{Coal-OMe} + \overset{+}{\text{N}}\text{Bu}_4\text{I}^- \tag{2}$$

$$\text{Coal-COOH} + \overset{+}{\text{N}}\text{Bu}_4\overset{-}{\text{OH}} \rightarrow \text{Coal-CO}\overset{-}{\text{O}}\overset{+}{\text{N}}\text{Bu}_4 + \text{H}_2\text{O} \tag{3}$$

$$\text{Coal-CO}\overset{-}{\text{O}}\overset{+}{\text{N}}\text{Bu}_4 + \text{MeI} \rightarrow \text{Coal-COOMe} + \overset{+}{\text{N}}\text{Bu}_4\text{I}^- \tag{4}$$

a weight gain of approximately 19%, with no enhanced tetrahydrofuran solubility of the product, as compared to that of raw Illinois No. 6 coal. We hope to obtain further information such as an elemental analysis, infrared and nuclear magnetic resonance data on the product, so that we may be able to make more definitive conclusions and compare our results with those of Liotta. We also intend to repeat this reaction using the Colorado subbituminous B coal, in order to learn whether this coal has a greater number of free hydroxylic and carboxylic groups than Illinois No. 6 high volatile, bituminous coal, with which we are more familiar.

Experimental

Reductive alkylations in liquid ammonia were conducted as outlined in previous Quarterly Reports.

The selective methylation of acidic hydroxylic groups was carried out under mild conditions at ambient temperature, as described by Liotta,[1B] using tetrabutylammonium hydroxide and methyl iodide in tetrahydrofuran solvent.

References

1B. R. Liotta, Fuel, 58, 724 (1979).

2B. Personal communication from Institute of Gas Technology, Chicago, Illinois.

3B. Whenever a large excess of potassium metal was used, a correspondingly large amount of n-butyl iodide was added to ensure safety, because the first step of the work-up procedure involves the addition of water to the solvent-free crude reaction product.

4B. (a) H.W. Sternberg and C.L. Delle Donne, "Solvation and Reductive Alkylation of Coal via a Coal Anion Intermediate," in American Chemical Society, Division of Fuel Chemistry, Preprints of Papers, 12 (4), 13-18, Sept. 8-13, 1968; (b) H.W. Sternberg, C.L. Delle Donne and P. Pantages, "On the Solubilization of Coal via Reductive Alkylation," in American Chemical Society, Division of Fuel Chemistry, Preprints of Papers, 14 (1), 87-94, May 24-29, 1970; (c) H.W. Sternberg, C.L. Delle Donne, P. Pantages, E.C. Moroni and R.E. Markby, Fuel, 50, 432 (1971).

5B. L. Alemany, Ph.D. thesis, University of Chicago, 1980.

6B. Personal communication from D. Blain, this laboratory.

PART C

The Synthesis of Model Compounds and the Reductive Acylation of Coal

by R. Willis

Introduction

In the last quarter, attention has been focused on the synthesis of model compounds for the purposes of compiling ^{13}C nmr chemical shift information and the study of ^{19}F nmr for the purpose of structural elucidation of coal.

Very little attention has been given to those model compounds which are reductive butylation products of polycyclic aromatic compounds.[1C] Accordingly, the synthesis of several butyldihydronaphthalenes and phenanthrenes has been undertaken to obtain their ^{13}C nmr spectra. The chemical shifts are of interest to determine whether or not the β carbon resonances overlap. The ^{13}C chemical shift for the β carbon of the butyl group can be studied directly to define the nature of the carbon alkylation products. The nmr chemical shifts for the butylated phenanthrenes are given in Table C1. At this time, chemical shift information on the butylated dihydrophenanthrenes and the dihydronaphthalenes has not been obtained.

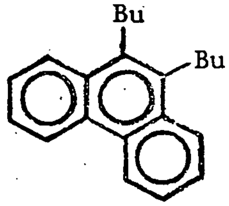
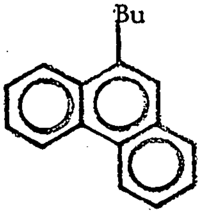
Other reagents which lead themselves to the issue of the structural elucidation of coal are also under study. One interesting possibility is trifluoroacetic anhydride. There is no fluorine in coal and ^{19}F has a natural abundance of 100%. Furthermore, it has been demonstrated[2C] that fluorine is extremely sensitive to subtle changes of environment. Figure C1 gives ranges of chemical shifts of fluorine for trifluoroacetyl derivatives of alcohols, phenols, thiols, and primary amines. Although spectral overlap of certain functional groups containing different heteroatoms exists, the ^{19}F chemical shift parameter for trifluoroacetyl derivatives is sufficient to allow distinctions within a given series (e.g. alcohols). Since there exists in Illinois Bituminous No. 6 coal a preponderance of oxygen (over nitrogen or sulfur), trifluoroacetylation may be a useful means of structural elucidation. There is much to be done to determine the feasibility of trifluoroacetylation. An experiment analogous to the Sternberg reaction[3C] using trifluoroacetic anhydride instead of an alkyl iodide has been carried out. The solubility in tetrahydrofuran was low and in chloroform even less. The value given as the percent soluble in tetrahydrofuran (33.6) is actually the lower limit of solubility of the coal product. If we assume that the naphthalene dianion reacts with trifluoroacetic anhydride quantitatively, then as much as 1.02 g of the soluble coal product is from the reductive acylation of naphthalene. What is of greatest interest in the NMR signals are observed in the regions expected. Much work needs to be done in the following months to develop this method.

Experimental

Reductive Alkylation of Naphthalene.--A flask equipped with a dry ice condenser, addition funnel, gas inlet, and stirring bar was dried and purged with argon. Sodium (1.5 g) and naphthalene (3.85 g) were added before ammonia (125 ml) was distilled into the flask. After 15 minutes, the reaction was quenched by the dropwise addition of distilled n-butyl iodide (10 ml.) and immediately thereafter, saturated ammonium chloride solution (50 ml) was added. The organic material was extracted with ether and dried over magnesium sulfate. The solution was filtered, the solvent was removed and a yellow oil was collected. Four components of the products with retention times greater than naphthalene were collected from a gc column (20% SE 30 on Chromosorb P, 175°C) and proton nmr spectra were taken. The compounds that have been identified are 2-butyl-1,2-dihydronaphthalene and 1,2-butyl-1,2-dihydronaphthalene (cis or trans).

9-Butylphenanthrene.--To a solution of 9-bromophenanthrene (23 g) in anhydrous ether (100 ml) was slowly added n-butyl lithium (75 ml, 1.6 M in hexane). Precautions were taken to avoid contact with air or moisture. Upon completion of addition, distilled n-butyl iodide (37 ml) was added dropwise. After refluxing for 1.5 hours, the reaction was quenched with water. The organic layer was washed with water and dried. The solvent was removed and the residue was treated with hot petroleum ether (80 ml). Pure 9-butylphenanthrene (14 g, 56%, mp 77°C) crystallized.

Table C1. Butyl Carbon ^{13}C Chemical Shift Data

Compound	δ_{α} (ppm)	δ_{β}	δ_{γ}	δ_{δ}
	32.86	29.01	23.45	13.99
	33.03	32.24	22.82	13.98

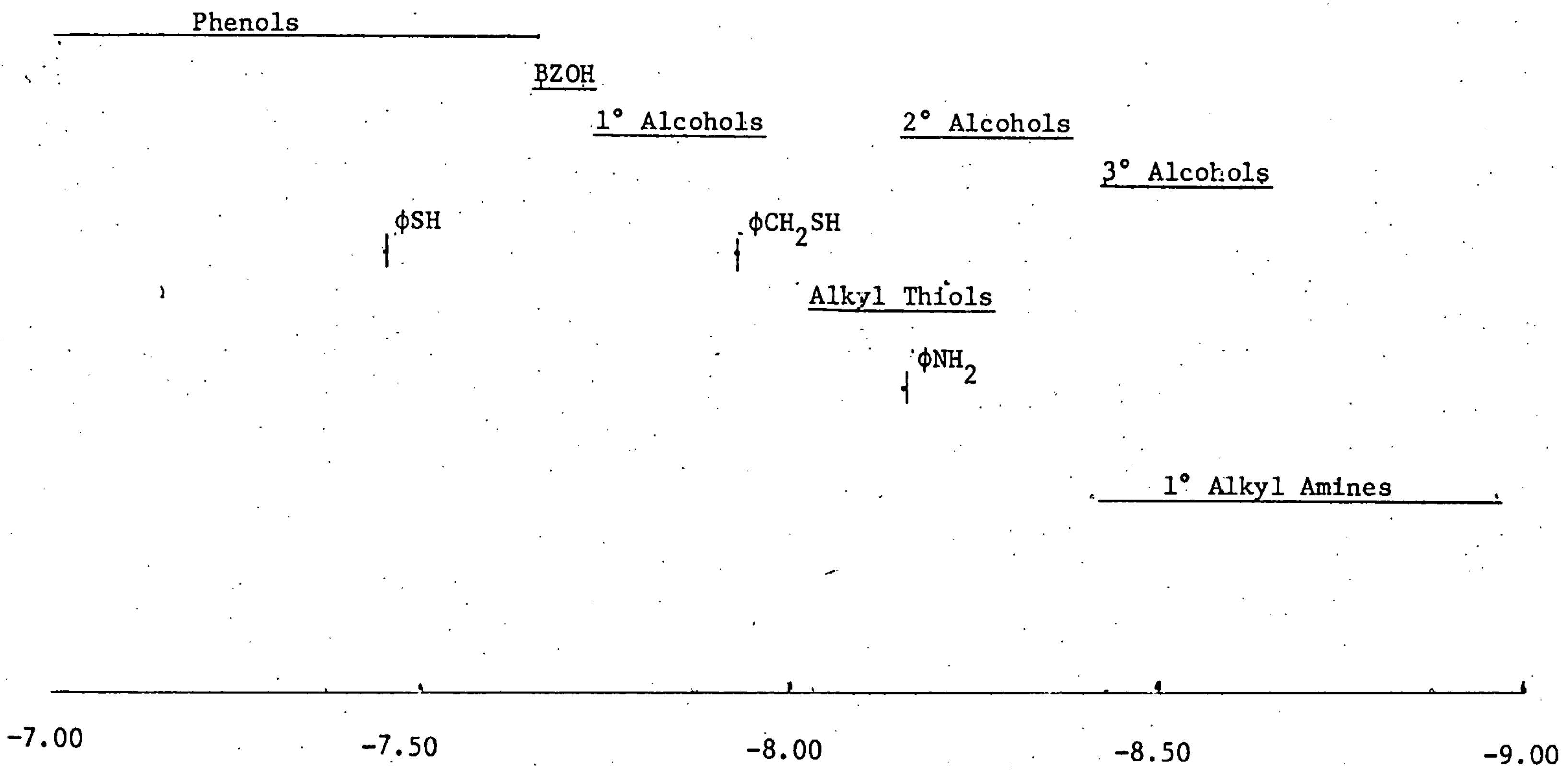
<u>9-Bromo-10-Butylphenanthrene</u>.--Bromine (3.5 g) was added dropwise to a solution of 9-butylphenanthrene (4.7 g) in acetic acid (50 ml). The reaction mixture was allowed to stir at room temperature for 16 hours. The precipitate was filtered and washed with dilute bisulfite solution. Pure 9-bromo-10-butylphenanthrene (5.0 g, 82%, mp 95-97°C) was obtained upon recrystallization in 100% ethanol.

<u>9,10-Dibutylphenanthrene</u>.--In a synthesis analogous to that used for 9-butylphenanthrene, 9-bromo-10-butylphenanthrene (4 g) was dissolved in ether (100 ml) and n-butyl lithium (25 ml, 1.6 M in hexane) was added dropwise. After two hours, n-butyl iodide (5.7 ml) was added dropwise. The workup was accomplished as previously described to give pure 9,10-dibutylphenanthrene (1.89 g, 50.1%, mp 77°C).

<u>Coal Reaction Quench with Trifluoroacetic Anhydride</u>.--The general procedure for this experiment has been outlined in previous reports. The pertinent information can be obtained in Table C2.

<u>Conclusions</u>.--On the basis of what we have seen so far, it appears that trifluoroacetylation has some promise as a probe for coal.

Figure C1[2C] ^{19}F Chemical Shifts for Trifluoroacetyl Derivatives of Heteroatoms[a]



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[a] 0 ppm is $CFCl_2CFCl_2$.

Table C2. Reductive Acylation of Coal in THF-Naphthalene at 25°C

K (g)	Coal (g)	Naphthalene (g)	trifluoroacetic anhydride (ml)	Final wt. of coal product[a]	soluble in THF (g)	insoluble in THF	% soluble in THF
1.0185	1.0242	.4100	4.5	2.3760	1.4760	.9000	33.6

[a] Includes naphthalene and naphthalene byproducts.

Bibliography

1C. L.B. Alemany, Ph.D. Thesis, University of Chicago, 1980, Tables 19 and 20.

2C. P. Sleevi, T.E. Glass, H.C. Dorn, Anal. Chem., 1979, 51, 1931.

3C. Private communication from D. Blain, this laboratory.

Part D

Donor Solvent Coal Chemistry

by H.-H. King

Introduction

The studies of the hydrogen atom transfer reactions with deuterated donors has continued.

Experimental Part

Equipment.--The equipment used in these experiments was described in a previous report.[1D] In addition, the mass spectra were recorded on a Finnigan 1015 mass spectrometer.

Materials.--1,4-Dihydronaphthalene-d_{10} was synthesized by stirring a mixture of naphthalene-d_8 (1.7g) and lithium wire (0.18g) in tetrahydrofuran (25 ml) at room temperature for 3.5 hours. The reaction was quenched by adding ethyl alcohol-O-d (10 ml). After the tetrahydrofuran was removed, the reaction mixture was extracted with methylene chloride, dried with magnesium sulfate, and methylene chloride was removed to give the crude product (1.5g). The crude product was chromatographed on a neutral alumina column three times to give 92% pure 1,4-dihydronaphthalene-d_{10}. The deuterium content is more than 95% at each position.

1,2-Dihydronaphthalene-d_{10} was synthesized by refluxing a mixture of tetralin-d_{12} (5.7g), N-bromosuccinimide (8.9g), and benzoyl peroxide (0.02g) in carbon tetrachloride (25 ml) for 1 hour. The solid was collected and carbon tetrachloride was removed. The brominated product was added to a solution of potassium hydroxide (9g) in ethanol (25 ml) and refluxed for 1 day. The reaction mixture was poured into cold water (100 ml), extracted with methylene chloride, dried with magnesium sulfate, and methylene chloride was removed. The crude product was chromatographed on a silica gel column to give 77% pure 1,2-dihydronaphthalene-d_{10} which is more than 90% deuterated at each position except the 3-position (74% D).

Procedures.--The procedures used in these experiments were also described in the previous report.[1D] The experimental conditions employed are summarized in Table D1.

Results and Discussion

The hydrogen transfer reactions were carried out with deuterated donors to determine whether or not two hydrogen or deuterium atoms were transferred simultaneously from the donor molecule to the acceptor. In each reaction an equimolar mixture of donor and deutereated donor was used. Tetracene was reduced to

Table D1. The Reduction Reactions with Deuterated Donors.

Reaction	Temp., °C	Time, min.	Acceptor	Donor[c]	Reduction of the Acceptor, %	Deuterium Distribution in the Reduced Acceptor, %				
						d_0	d_1	d_2	d_3	d_4
339[a]	350	20	Tetracene (0.758 mmole)	T (0.376 mmole) T-d_{12} (0.376 mmole)	83	54	24	19	2	1
340[b]	300	60	Tetracene (0.252 mmole)	1,2-DHN (0.253 mmole) 1,2-DHN-d_{10} (0.253 mmole)	38	56	27	12	4	1
341[b]	300	20	Tetracene (0.252 mmole)	1,4-DHN (0.252 mmole) 1,4-DHN-d_{10} (0.252 mmole)	70	42	34	18	5	1
342[a]	300	180	E-Stilbene (0.759 mmole)	1,2-DHN (0.382 mmole) 1,2-DHN-d_{10} (0.376 mmole)	7	62	29	7	1	0

[a] A 20 cm glass tube reactor was used. [b] A 10 cm glass tube reactor was used. [c] T = tetralin, T-d_{12} = tetralin-d_{12}, 1,2-DHN = 1,2-dihydronaphthalene, 1,2-DHN-d_{10} = 1,2-dihydronaphthalene-d_{10}, 1,4-DHN = 1,4-dihydronaphthalene, 1,4-DHN-d_{10} = 1,4-dihydronaphthalene-d_{10}.

5,12-dihydrotetracene and E-stilbene to 1,2-diphenylethane. Diels-Alder adducts was formed in the reactions of tetracene with dihydronaphthalenes, the yields were 57% with 1,2-dihydronaphthalene in reaction 340 and 30% with 1,4-dihydronaphthalene in reaction 341. Control experiments established that the exchange reaction between tetralin-d_{12} and 5,12-dihydrotetracene was relatively slow. Consequently, the pericyclic pathway will lead to the formation of only d_0, d_2, and d_4 in the reduced acceptor. However, the results in Table D1 clearly indicate the statistical deuterium distribution in each reaction. Therefore, this hydrogen atom transfer reaction proceeds in a stepwise fashion rather than in a concerted fashion.

Reference

1D. Sixth Quarterly Progress Report.

Part E

Reaction of Phenol and Diphenyl Ether with Inorganic Sulfides

by C.B. Huang

Introduction

The formation of thiophenol in the reaction of phenol or diphenyl ether with iron(II) sulfide or sodium sulfide at 400°C as well as the effects of Illinois No. 6 coal and tetralin as additives on the reactions was investigated.

Experimental

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

Material.--Those compounds used in this quarter's work are: anhydrous sodium sulfide (Alfa); phenol (Mallinckrodt); diphenyl ether (Aldrich); granular ferrous sulfide (Mallinckrodt) and tetrahydronaphthalene (Fisher). Tetralin was purified by distillation.

Procedure.--The procedures used in these experiments have been described previously. In brief, the starting materials were sealed in a glass tube (20 cm) and reacted in the fluidised bath at 400°C. After reaction, the contents of the vessel were washed with dilute hydrochloric acid and then extracted with methylene chloride. The organic phase was dried with magnesium sulfate. The product distribution was determined by gas chromatography using anisole as an interval standard. The experimental conditions are summarized in the tables.

Results and Discussion

The formation of thiophenol has been detected in the reactions of phenol with anhydrous sodium sulfide as shown in the table E2. Iron(II) sulfide does not react with phenol to form the thiophenol (Table E1). Sodium sulfide and iron sulfide do not react with diphenyl ether at 400°C to form the thiophenol (Tables E3 and E4).

The additives, tetralin and coal do not affect the rate of formation of thiophenol in those reactions. Research on the reaction of inorganic sulfides with coal molecules is continuing.

Table E1. Reactions of Phenol with Iron(II) Sulfide.

Reaction	T°C	Time	Additive	C_6H_5SH %
1[a]	400°C	4 hrs	none	0
2	400°C	4 hrs	tetralin[b]	0
3	400°C	4 hrs	coal[c]	0

[a] The mole ratio between phenol and iron sulfide was 1:1 in each reaction. [b] The mole ratio between phenol, iron(II) sulfide and tetralin was 1:1:1. [c] Coal (0.0193g) was added in the mixture of phenol and iron sulfide (0.1932g, mole ratio 1:1).

Table E2. Reactions of Phenol with Sodium Sulfide.

Reaction	T°C	Time	Additive	C_6H_5SH %
4[a]	400°C	1 hr	none	1.9 ± 0.3
5	300°C	1 hr	none	0
6	400°C	1 hr	tetralin[b]	2.1 ± 0.3
7	400°C	1 hr	coal[c]	1.8 ± 0.3

[a] The mole ratio between phenol and sodium sulfide was 1:1 in each reaction. [b] The mole ratio between phenol, sodium sulfide, and tetralin was 1:1:1. [c] Coal (0.0155g) was added to the mixture of phenol and sodium sulfide (0.1558g, mole ratio 1:1).

Table E3. Reactions of Diphenyl Ether with Iron(II) Sulfide.

Reaction	T°C	Time	Additive	C_6H_5SH %
8[a]	400°C	4 hrs	none	0
9	400°C	4 hrs	tetralin[b]	0
10	400°C	4 hrs	coal[c]	0
11	400°C	4 hrs	HCl	2.3 ± 0.3

[a] The mole ratio between diphenyl ether and iron(II) sulfide was 1:1 in each reaction. [b] The mole ratio between diphenyl ether, iron(II) sulfide, and tetralin was 1:1:1. [c] Coal (0.0516g) was added to the mixture of diphenyl ether (0.33 ml) and iron(II) sulfide (0.1761g). [d] The mole ratio between diphenyl ether, iron (II) sulfide and conc. HCl was 1:1:2.

Table E4. Reactions of Diphenyl Ether with Sodium Sulfide.

Reaction	T°C	Time	Additive	C_6H_5SH %
12[a]	400°C	1 hr	none	0
13	400°C	1 hr	tetralin[b]	0
14	400°C	1 hr	coal[c]	0

[a] The mole ratio between diphenyl ether and sodium sulfide was 1:1 in each reaction. [b] The mole ratio between diphenyl ether, sodium sulfide, and tetralin was 1:1:1. [c] Coal (0.0208g) was added to the mixture of diphenyl ether (0.137 ml) and sodium sulfide (0.0608g).