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Coal Transformation Chemistry

Second Quarterly Progress Report

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I. Abstract

A review of the information concerning the structure of Illinois No. 6 coal obtained in this laboratory and elsewhere provides the basis for a proposed structure for this bituminous coal. All the available facts concerning reduction, reductive alkylation, hydrogen atom exchange, oxidation, functional group analysis and so forth have been used to define a structural segment consisting of about 1000 atoms with a molecular weight in excess of 6000. This work is discussed in Part A.

The study of the reductive alkylation reaction of Illinois No. 6 coal in liquid ammonia has been directed toward the optimization of the reaction conditions for the achievement of maximum solubility. The latest results indicate that about 55% of the original Illinois No. 6 coal can be converted to products which are soluble in tetrahydrofuran using potassium in liquid ammonia as the reducing agent and n-butyl iodide in tetrahydrofuran as the reducing alkylating agent. These observations are treated in Part B.

The effort on donor solvent coal chemistry during this quarter was directed to the role played by pericyclic reactions in the liquefaction process. The reactivity of a number of donors has been examined including 1,2- and 1,4-dihydronaphthalene. Although the research is not yet complete, the preliminary results indicate that free radical processes occur preferentially. Thus, the pericyclic reactions appear to be unimportant at the threshhold reaction temperatures of 350-425°C. This work is described in Part C.

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 Solublization 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

The information in the literature concerning the structure and the chemical reactivity of Illinois No. 6 coal and other closely related coals has been assembled. The various proposals which have been made in the literature concerning the structure of this coal have been critically assessed. A structure for this coal has been proposed based upon all the available information including research in this laboratory on the reductive alkylation and tetralin-d_{12} exchange reactions. This work is described in Section IVA.

The study of the optimization of the conditions for the reductive alkylation reaction in liquid ammonia has reached completion. Potassium is the best reducing agent in liquid ammonia and the alkylation reaction which proceeds slowly is best accomplished in tetrahydrofuran over 48 hours. The new work is described in Section IVB.

The role of pericyclic reactions in the liquefaction reactions of Illinois No. 6 coal has been considered via the study of 1,2- and 1,4-dihydronaphthalene with selected compounds. The results suggest that free radical processes are much more important than pericyclic processes. The results are discussed in Section IVC.

B. Publications During This Quarter

1. D.E. Hansen, H.H. King, and L.M. Stock, Hydrogen-Deuterium Exchange Reactions of Tetralin with Coal-Related Molecules. Fuel and Petrochemical Division Preprints Am. Inst. Chem. Eng., <u>1</u>, 356 (1980).

2. The Reductive Alkylation of Illinois No. 6 Coal. Seminar Presentation, Gordon Research Conference, June, 1980.

3. The Hydrogen-Deuterium Exchange Reaction of Tetralin-d_{12} with Coal and Coal Molecules, Seminar Presentation, Stanford Research Institute, July, 1980.

C. Summary of Progress to Date

TASK 1 Solublization Reactions

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.

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 by a mixture of tetralin-d_{12} and tetralin 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.

IV. DISCUSSION OF TECHNICAL PROGRESS

PART A

A Structure for Illinois No. 6 Coal

by L.B. Alemany

Suggestions for the structure of coal are not new--Given's in 1960 and Wiser's in 1975 are probably the most frequently cited.[1] Any proposed average structure for a given coal has significant limitations. Foremost, in light of the highly heterogeneous nature of any coal, there is no unique, repetitive structural unit. A proposed structure is merely a synthesis of the data available. Because the available data are limited for any one coal, more than one reasonable structure can be drawn for most coals. A knowledge of the full range of structures present is clearly useful, if not necessary, for predicting the chemical behavior of the coal. Ideally, the proposed structure is consistent with essentially all the information available on macromolecular Illinois No. 6 coal. However, the small, hydrogen-rich molecules trapped within this network are not shown. Presumably this structure will be modified as additional investigations on Illinois No. 6 coal provide more quantitative data of use in the elucidation of structure. For example, we need more quantitative information on the relative amounts of the aromatic systems present, on the nature of the hydroaromatic species present, on the average degree of ring substitution, and on the intrastructural relationship of these units.

The structure presented in Figure 1A has the following features. The structural formula, $C_{456}H_{397}O_{48}S_9N_3$ (MW = 6976), is consistent with the elemental analysis of the coal after a correction[2] is made for the amount of oxygen present in the mineral matter.

Only small aromatic ring systems, most frequently benzene, are present. Several investigations strongly support this feature. Alkaline cupric oxide oxidation of Illinois No. 6 coal has shown that benzene carboxylic acids constitute 69% of the acids identified.[3] Sodium dichromate oxidation of Illinois No. 2 coal, which is similar, has shown that benzene, naphthalene, and phenanthrene moieties constitute over 90% of the aromatic carbocycles and that the number of naphthalene and phenanthrene moieties is less than half the

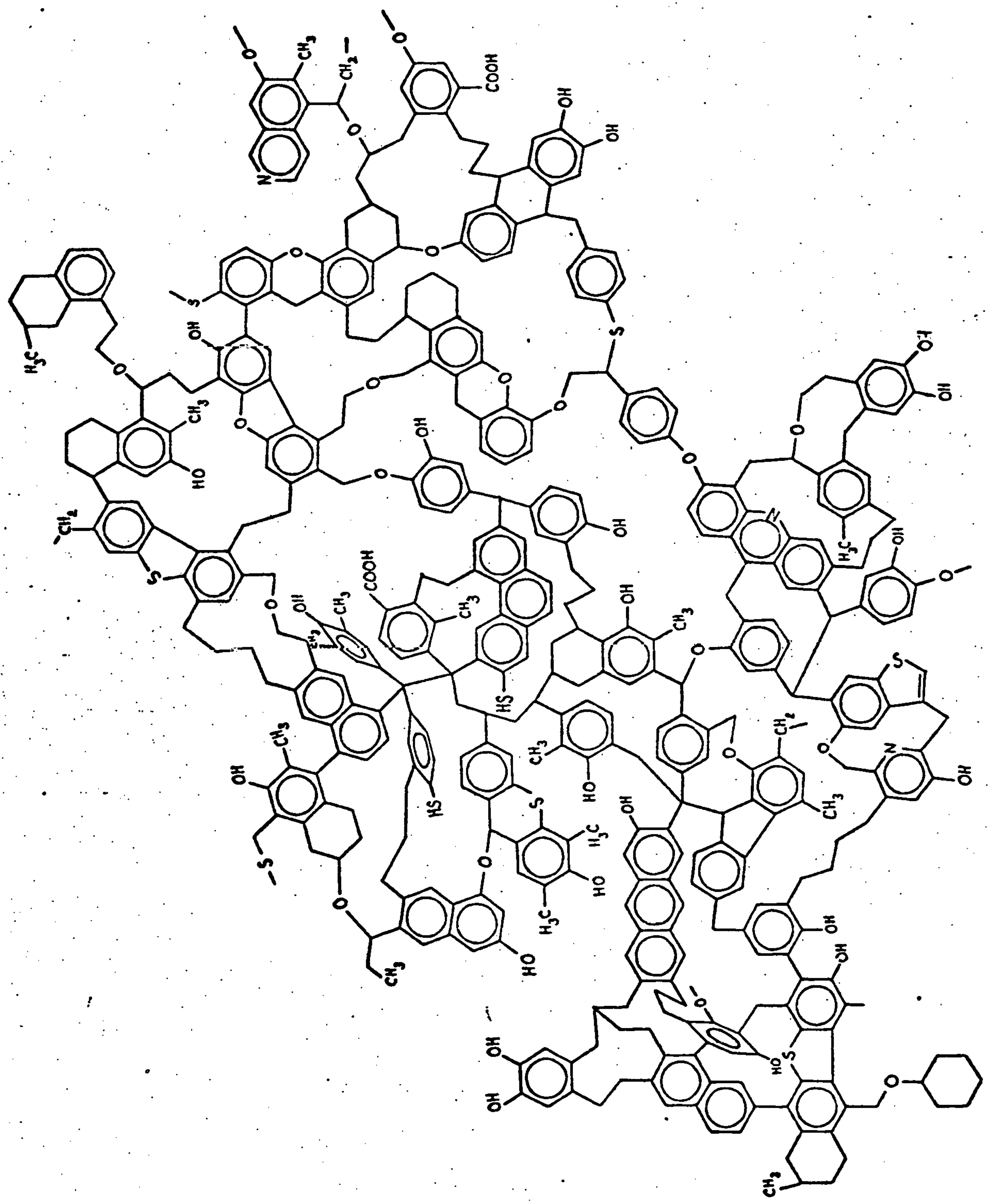

Figure 1A. A structure for Illinois No. 6 coal based on its composition, spectroscopic properties and chemical reactivity.

number of benzene moieties.[4] (The nearly identical values for the ratio of benzene carboxylic acids : naphthalene carboxylic acids given by Illinois No. 2 and No. 6 coals upon alkaline cupric oxide oxidation also supports the belief that these two coals would behave similarly upon sodium dichromate oxidation.[3]) Other investigations, while yielding only qualitative results, are nearly as compelling in requiring that only small aromatic ring systems be present. Rapid (<2 min) thermal liquefaction of Illinois No. 6 coal has shown that the majority of the aromatic systems are benzene and naphthalene.[5] Polycyclic aromatic systems are not hydrogenated under the reaction conditions. Similarly, research with different electron transfer agents has led us to conclude that the reduction and alkylation of large, polycyclic aromatic systems in Illinois No. 6 coal is not a principal reaction. Indeed, all the available evidence forces one to conclude that the aromatic carbon atoms in any bituminous coal are not present in significant amounts as highly condensed rings, rather mono- and diaromatic rings predominate.[1,5]

Sixty-nine percent of the carbon is aromatic. Several cp nmr investigations on Illinois No. 6 coal;[5,6] a pyridine-soluble, toluene-insoluble extract;[7] and the pyridine-insoluble residue[7] suggest that about 70% of the carbon is aromatic. Unfortunately, none of these spectra appear to have been obtained with rapid, magic angle spinning of the sample. Consequently, the aromatic and aliphatic carbon resonance bands overlap, and therefore, the amount of each type of carbon can only be estimated. The slight dependence (several per cent) of the relative amounts of aromatic and aliphatic carbon atom signal intensity on the cross polarization time introduces an additional uncertainty in the cp nmr data for any coal sample.[8,9] Furthermore, in general, the carbon atoms in any sample are not necessarily equally polarized.[10] In spite of these difficulties, cp nmr with rapid, magic angle spinning is at least semiquantitative, as spectra of an unspecified Illinois bituminous coal obtained with and without cross polarization yielded similar values (≃74%) for the percentage of aromatic carbon.[11] Clearly, additional cp nmr studies with rapid, magic angle spinning and a variety of cross polarization times would be useful in providing more detailed information on the relative amounts of aromatic, aliphatic, and etheral carbon atoms in any coal. However, critical analysis of the data suggests that only minor refinements will be necessary.

Cross polarization data on the hydrogen distribution in any coal are very rare and have not been reported for Illinois No. 6 coal. However, Gerstein and his colleagues have obtained such data on Iowa Star vitrain, which is similar (e.g., 71% of the carbon is aromatic as determined by cp nmr with rapid, magic angle spinning), and estimated that 31% of the hydrogen is aromatic.[12] In the proposed average structure for Illinois No. 6 coal, 27% of the hydrogen is aromatic, a modest difference.

Hydroaromatic structures are present in this structure. This very general feature has been well established by studies of catalytic dehydrogenation of Illinois No. 6 coal.[13,14] However, as noted before, much remains to be learned about the hydroaromatic species present.

Forty-two percent of the hydrogen is benzylic, benzhydrylic, or trityl, which is consistent with other research in this laboratory on the exchange reactions of coal with tetralin-$\underline{d}_{12}$ at 400°.

Polyamantanes are not present, as required by the work of Gorbaty and his colleagues.[15]

All the phenols and ethers are reactive and are in a 1 : 1 ratio (4.8 phenols and 4.8 ethers per 100 carbon atoms). Several investigations strongly support this feature. Liotta has shown that Illinois No. 6 coal with 11 oxygen atoms per 100 carbon atoms has very nearly 5 phenols per 100 carbon atoms, all of which react.[16] Given and his colleagues have determined that 50% of the oxygen in hvCb Illinois No. 6 coal is hydroxylic,[17] while Ruberto and Cronauer have determined that the etheral and hydroxylic oxygen in Illinois No. 6 Burning Star coal is in a 7 : 6 ratio.[18] The well established methods used in these three investigations to obtain these values make them particularly significant. In contrast, the oxygen distribution 4 ethers : 5 phenols in the pyridine-insoluble residue remaining after extraction of Illinois No. 6 coal is less secure, as these figures were estimated so as to be consistent with the other data.[7] Nevertheless, the estimated ratio is clearly reasonable in light of the more secure results.

o-Dihydroxybenzene derivatives are present in the proposed structure. Alkaline cupric oxide oxidation of Illinois No. 6 coal has shown that 3,4-dihydroxybenzoic acid forms.[3] Identification of this and other characteristic lignin oxidation products clearly suggests that lignin-like polymers were present in the early stages of coalification.

Tertiary ethers are not present, as the likelihood of such highly branched ethers surviving throughout coalification is low.

Nonaryl carbon bonded to etheral oxygen constitutes 4.6% of the carbon. Mayo and Kirshen have reported that cp nmr indicates that about 4-5% of the carbon in Illinois No. 6 coal is $-CH_2-O-$.[7] The -CH-O-unit is implicitly included in this designation.

Four of the 48 oxygen atoms are in carboxyl groups (0.4 carboxyl group per 100 carbon atoms). Liotta[16] and Ruberto and Cronauer[18] have recently obtained evidence for the presence of a small amount (11% of the oxygen[18]) of carboxylic acid functional groups in Illinois No. 6 coal.

Work in this laboratory has established that O-alkylation with ^{13}C labelled butyl and methyl iodides provides three identifiable O-alkylation products. The structure is compatible with these results. O-Alkylation of the structure shown in Figure A1 would give etheral carbon cmr signal intensities in a 15 : 29 : 2 ratio if none of the ethers underwent a Wittig rearrangement. Three Wittig rearrangements of secondary ethers would give signal intensities in the 15 : 26 : 5 ratio indicated by the cmr spectra. Also in accord with the cmr spectra, similar amounts of C- and O-alkylation would occur.

Most of the sulfur in this structure occurs in aryl sulfides or closely related structures, e.g., dibenzothiophenes. This is in accord with the only organic sulfur distribution reported for Illinois No. 6 coal,[19] with the organic sulfur distribution reported for an unspecified Illinois coal,[20] and with the organic sulfur distribution reported for Illinois No. 2 coal, which is similar.[4]

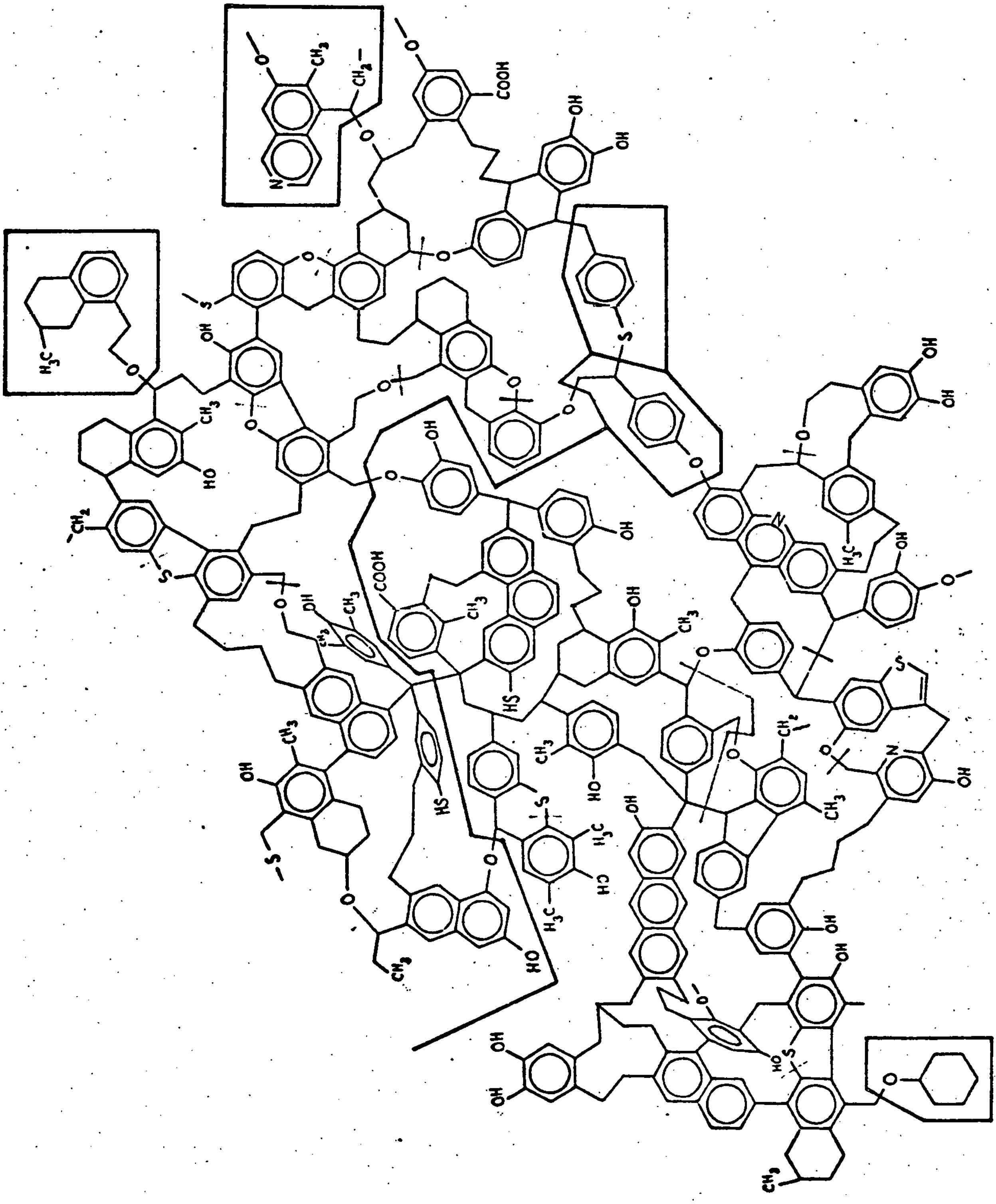

Figure A2.--The bonds that would most likely cleave and the fragments that would form upon reduction.

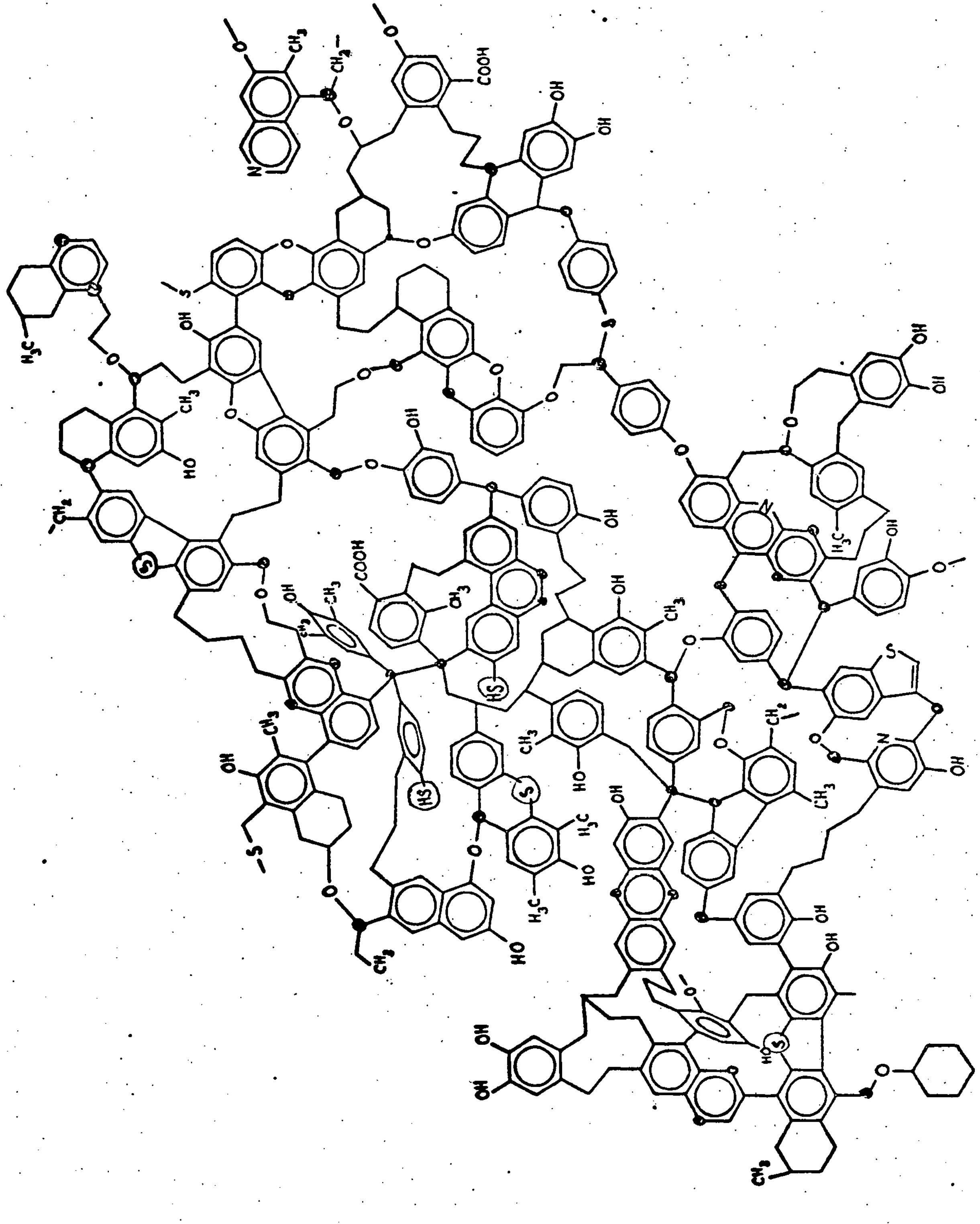

Figure A3.--Sites where C- and S-alkylation could initially occur after reduction and cleavage.

Nitrogen occurs only in aromatic heterocycles, although, a carbazole moiety could have also been included. This is in accord with the organic nitrogen distribution reported for Illinois No. 2 coal.[4] Unfortunately, no such adata have been reported for Illinois No. 6 coal, although the nitrogen distribution in the two coals is probably similar.[21] Work in this laboratory strongly suggests that the nitrogen-containing species are part of large macromolecules following the reductive alkylation reaction.

The chromatograms for the reductively alkylated, soluble coal indicate that a large amount of high molecular weight material consistently formed. Figure A2 shows the same structure as Figure 32 but with lines drawn to indicate the C-C, C-O, and C-S bonds that would most likely cleave upon reduction if no rearrangement reactions occurred. Only four relatively small fragments, with a composite molecular formula $C_{34}H_{41}O_3S$ are cleaved. A fifth fragment ($C_{12}H_{10}ON-$) forms but is bonded to a structure not shown. The remaining structure ($C_{410}H_{346}O_{44}S_8N_2$) is so extensively crosslinked that it can cleave into only two large fragments that are also bonded to structures not shown. While additional bonds can cleave, these two large fragments cannot break down into smaller fragments. Aliphatic chains (except highly arylated ethane derivatives), dibenzofuran moieties, xanthene derivatives, and their sulfur analogs prevent the structure from cleaving into numerous small fragments under such mild conditions. To be sure, some rearrangement reactions would in all likelihood occur. Nevertheless, the qualitative aspects of cleavage would remain the same.

Number average molecular weight characterization of coal-derived products can be very misleading because a relatively large number of small molecules may be produced.[22] Weight average molecular weight characterization is a much more useful approach. The seven fragments shown in Figure A2 illustrate this, as the four relatively small fragments constitute only 7.6% of the weight.

Finally, Figure A3 shows the same structure as Figure A1 but with the sites of C- and S-alkylation indicated. No alkylation is expected at the aryl carbanions formed upon the cleavage of diaryl ethers or thioethers because these strongly basic reagents would preferentially abstract comparatively acidic (e.g., benzhydrylic) protons elsewhere in the coal. The amount of sulfur alkylated is not negligible. Unfortunately, the available data do not distinguish S- from C-alkylation on the basis of C_α chemical shifts. The precise amount of C-alkylation cannot be depicted. The Wittig rearrangement reactions of secondary ethers in this structure would not generate stable carbanions. Finally, structural elements are included in which protons can be abstracted from the reductively alkylated products initially formed to generate resonance-stabilized carbanions that undergo additional alkylation.

Research during the past five years has led to a great increase in the general understanding of coal structure. Because these molecules are so complex it has been necessary to employ a diverse set of experimental procedures to deduce the basic structural elements. Some features remain unestablished and the structure that has been proposed here will require modification. However, this structure satisfies numerous experimental data including proton and carbon solid state nmr data, oxidation chemistry, functional group analysis, and information available from several degradation reactions including reductive alkylation and exchange reactions with tetralin-d_{12}.

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2. Liotta (private communication) has suggested that oxygen by difference be calculated after applying the following correction: % mineral matter = 1.13(% ash) + 0.47(% pyritic sulfur) as proposed by P. Given.

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6. (a) D.D. Whitehurst, M. Farcasiu, and T.O. Mitchell, The Nature and Origin of Asphaltenes in Processed Coals, EPRI-AF-480, Electric Power Research Institute, Palo Alto, Calif., July 1977; (b) Idem, "On the Kinetics and Mechanisms of Solvent Refining Coal," in Preprints of the 1976 Coal Chemistry Workshop, H.M. Peters and D.S. Ross, Eds., Stanford Research Institute, Menlo Park, Calif., 1976, pp. 101-124; (c) D.D. Whitehurst, "A Primer on the Chemistry and Constitution of Coal," in Organic Chemistry of Coal, ACS Symposium Series 71, J.W. Larsen, Ed., American Chemical Society, Washington, D.C., 1978, pp. 1-35.

7. F.R. Mayo and N.A. Kirshen, Fuel, 58, 698 (1979).

8. D. Vucelić, N. Juranić, and D. Vitorović, Fuel, 58, 759 (1979).

9. F.P. Miknis, G.E. Maciel, and V.J. Bartuska, "Carbon-13 NMR Studies of Coals by Cross Polarization and Magic-Angle Spinning," in American Chemical Society, Division of Fuel Chemistry, Preprints of Papers, 24 (2), April 2-6, 1979, pp. 327-333.

10. While protonated carbon atoms can usually be fairly easily completely polarized, non-protonated carbon atoms frequently polarize less efficiently and unequally. However, exceptions in both classes are known: " . . . , polarization transfer does not readily occur in naphthalene or anthracene and only marginal spectra can be obtained. Conversely spectra have been readily obtained on their methyl derivatives." Similarly, hexamethylbenzene shows comparable signal intensities for the six equivalent aromatic and six equivalent aliphatic carbon atoms.

The transfer of spin polarization from ^{1}H to ^{13}C via the static component of the dipolar interaction is clearly not just an intramolecular, nearest neighbor interaction. With apparently more than one pathway for the transfer of spin polarization, ^{13}C atoms in different environments can clearly be unequally polarized, and thus, this can complicate the interpretation of the signal intensities of the various types of ^{13}C atoms. A recent article on cp nmr applied to fossil fuels provides numerous pertinent references that expand upon this very brief discussion.

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22. R.M. Davidson, Molecular Structure of Coal, IEA Coal Research, London, 1980, p. 21.

PART B

Reductive Alkylation of Coal in Liquid Ammonia

by C.I. Handy

Introduction

During this quarter attention has been directed toward the completion of certain aspects of the project. For purposes of comparison with previously obtained data, a reductive alkylation of Illinois No. 6 coal was carried out at -33°C using sodium as the reducing agent. This completes the study of potassium, sodium and lithium as reducing metals. Similarly, Illinois No. 6 coal was reductively ethylated at 25°C and the tetrahydrofuran solubility of the product was determined. This experiment enables a comparison of ethyl and butyl groups for the solubilization of Illinois No. 6 coal. A reductive alkylation of coal incorporating all the reaction conditions believed to be most favorable for enhanced tetrahydrofuran solubility was carried out. In related work a sample of tetrahydrofuran-soluble butylated coal from a reaction in which naphthalene was used as electron transfer agent was reacted with potassium and naphthalene in tetrahydrofuran at room temperature and protonated using ammonium chloride. The tetrahydrofuran-soluble material from this experiment, was fractionated by gel permeation chromatography on Styragel^{R} columns, after removal of reduced and alkylated naphthalenes by conventional column chromatography, using silica gel as the support.

Results and Discussion

The results of the reactions are summarized in the following tables.

Table B1. The Influence of Alkali Metal on the Conversion of Illinois No. 6 Coal to Soluble Butylated Product at -33° in Liquid Ammonia.

Metal[a]	THF solubility, %	Wt of coal alkylate / Wt. of coal
Li	41	1.37
Na	41	1.54
K	52	1.49

[a] The same quantity was used in all these experiments, 0.029 moles/g coal.

Table B2. The Influence of Alkylating Agent on the Conversion of Illinois No. 6 Coal to Soluble Alkylated Product in Liquid Ammonia at 25°C.

Alkylating Agent[a] 0.040 moles/g coal	% THF solubility	Wt. of coal alkylate / Wt. of Coal
EtI	33	1.41
n-BuI	41	1.54

[a] The same quantity of alkylating agent, 0.040 moles/g coal, was used in each experiment.

The results obtained in this research suggest that the conversion of Illinois No. 6 coal to a soluble product is favored when potassium is the alkali metal, n-butyl iodide is the alkylating agent and a substantial reaction time is allotted for the alkylation reaction using tetrahydrofuran as a solvent. These criteria are summarized in Table B3.

A marked improvement was observed. The tetrahydrofuran solubility of the product reached 56% in a first pass experiment, and the ratio of the weight of coal alkylate to the weight of raw coal was 1.55.

Experimental work is now being directed toward the factors governing the solubility of the coal products obtained by reduction, reductive alkylation, etherification etc.. In this connection, a sample of butylated coal obtained with potassium and naphthalene in tetrahydrofuran was treated with potassium and naphthalene in tetrahydrofuran and then with ammonium chloride. The coal compounds which were soluble in tetrahydrofuran were separated from naphthalene

$$\text{Coal} \xrightarrow[C_4H_9I]{K,C_{10}H_8} \text{THF-Sol. Product}$$

$$\text{THF-Sol. Product} \xrightarrow[NH_4Cl]{K,C_{10}H_8} \text{THF-Sol. Product}$$

and its reductive alkylation products and subjected to gel permeation chromatography. The results are summarized in Table B4. The elution profile of the chromatogram is shown in Figure B1 and the general elution pattern is presented in Table B5.

Table B3. Reaction Parameters for Butylation of Coal.

Wt. of coal in g	Moles K / g coal	Coal anion form$^{n.}$ time in hrs.	Coal anion form$^{n.}$ temp in °C	Moles n-BuI / g coal	Alkylation time, hrs.	Alkylation temp, °C	Wt. of coal alkylate in g	THF-soluble material in g	% THF solubility	Wt. of coal alkylate/ Wt. of coal
1.1821	0.030	6.0	-33	0.04 in THF	40	-33 to 25	1.8370	1.0324	56.2	1.55

Table B4. Results from Gel Permeation Chromatography of a Butylated and Subsequently, Protonated Coal.[a]

Fraction No.		Wt. of material, mg
17		0.0
18		2.0
19		19.1
20		21.7
21		13.9
22		11.6
23		12.2
24		10.8
25		11.9
26		11.2
27		11.0
28		11.8
29		13.2
30		10.8
31		7.6
32→40		12.6
	Total	181.4

[a] The soluble product passed a 0.9 to 1.4μ frit. The recovery of material was quantitative.

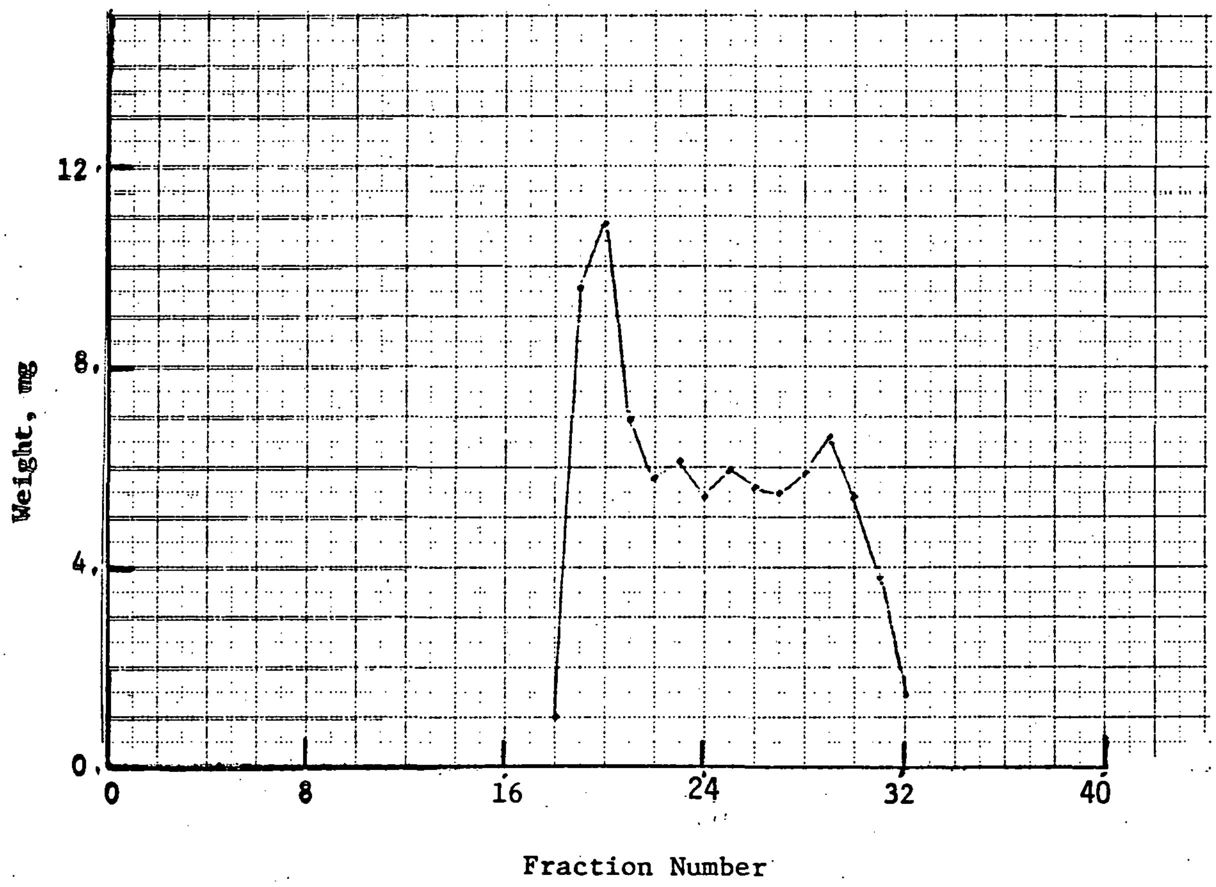


Figure B1.--Elution profile for reductive alkylation product.

Table B5. Approximate Molecular Weight Ranges of Chromatographed Materials.

Range	Material, % K,N,THF[a]	K,N,THF[b]
9,200 < MW < 17,500	28.8	23.6
3,600 < MW < 9,200	10.5	7.7
600 < MW < 3,600	41.1	37.9
MW < 600	19.6	30.9

[a] Butylated Illinois No. 6 coal.

[b] Butylated coal treated with potassium and ammonium chloride.

Conclusions

The results obtained from the experiments confirm that potassium is the alkali metal of choice and that it is superior to lithium and sodium as a reducing metal for the reactions in liquid ammonia. It is possible also to conclude that at 25°C, n-butyl iodide is a better alkylating agent than ethyl iodide, just as in previous experiments it was demonstrated that n-butyl iodide is more effective than methyl iodide, n-butyl chloride or n-butyl bromide at -33° or at -78°C.[4]

Only a few experiments directed toward the identification of the factors governing the solubility of the alkylated coals have been performed thus far. Consequently, no final conclusions can be drawn concerning the elution profile presented in Table B5. However, it is interesting that there appears to be a significant increase in the quantity of low molecular weight material in the product.

Experimental

The alkylation experiments were executed in essentially the same manner as outlined in earlier Quarterly Reports.[2-4] The gel permeation chromatography was carried out using Styragel^R columns (Waters Associates) and distilled tetrahydrofuran as eluant, as described in a previous Quarterly Report.[1]

References

1. Seventh Quarterly Progress Report (September 1, 1978 to November 30, 1978).

2. Eighth Quarterly Progress Report (December 1, 1978 to February 28, 1979).
3. Final Report (March 1, 1979 to February 29, 1980).
4. First Quarterly Progress Report (March 1, 1980 to May 31, 1980).

Part C

Donor Solvent Coal Chemistry

by H.-H. King

Introduction

Virk and his associates have proposed that concerted pericyclic reactions[1] may be significant in the liquefaction of coal.[2-5] They have studied the thermal hydrogen atom transfer reactions of reactive donors, 1,2- and 1,4-dihydronaphthalene, with anthracene and phenanthrene. They reported that 1,2-dihydronaphthalene reduces phenanthrene to 9,10-dihydrophenanthrene 1.6-fold more rapidly than 1,4-dihydronaphthalene. On the other hand, they found that 1,4-dihydronaphthalene reduces anthracene to 9,10-dihydroanthracene about 11-fold more rapidly than 1,2-dihydronaphthalene. These results are in accord with the concepts and advanced by Woodward and Hoffmann concerning supra-supra group transfer reactions.[1]

Research in this laboratory and elsewhere has revealed that hydrogen atom transfer reactions occur readily by free radical processes under the reaction conditions employed by Virk and his coworkers. Moreover, the sample of 1,4-dihydronaphthalene used by that research group was only 64% pure. Accordingly, we reexamined these reactions using pure reagents. In addition, we also studied the reduction of E-stilbene which has the same electronic component ($2\pi e$) as phenanthrene but is more reactive and employed deuterated donors to test whether these reductions proceed by concerted or multistep reactions.

Experimental Part

Equipment.--The equipment used in these experiments was described in a previous report.[6]

Materials.--Many of the compounds used in the new work were described in the vious reports. In addition, 1,2- and 1,4-dihydronaphthalene (97%) were obtained from Chemical Samples Co.. Gas chromatographic and NMR spectroscopic studies showed that the dihydronaphthalenes are at least 97% pure.

Procedures.--The procedures used in these experiments were also described in the previous report.[6] The experimental conditions employed are summarized in Tables I-III.

Reduction of Tetracene by Tetralin-d_{12}.--Tetracene (0.758 mmole), tetralin-d_{12} (0.376 mmole) and tetralin (0.376 mmole) were sealed in a 0.25 cm i.d., 20 cm-long glass tube reactor and heated in a preheated sandbath at 350°C for 20 minutes. The tube was cooled in air and opened. Tetralin and naphthalene were washed out with hexane. The deuterium distribution of 5,12-dihydrotetracene was analyzed by MS. The results are presented in the following section.

Table I. The Hydrogen Transfer Reactions[a]

Reaction	Temp., °C	Time, min.	Donor (mmole)	Acceptor (mmole)
320	400	120	tetralin (0.758)	phenanthrene (0.575)
321	400	120	1,2-dihydronaphthalene (0.759)	phenanthrene (0.757)
322	400	120	1,4-dihydronaphthalene (0.756)	phenanthrene (0.758)
323	300	120	tetralin (0.758)	anthracene (0.757)
324	300	120	1,2-dihydronaphthalene (0.759)	anthracene (0.757)
325	300	120	1,4-dihydronaphthalene	anthracene (0.758)
326	300	120	tetralin (0.758)	E-stilbene (0.758)
327	300	120	1,2-dihydronaphthalene (0.759)	E-stilbene (0.758)
328	300	120	1,4-dihydronaphthalene (0.756)	E-stilbene (0.758)
329	300	10	tetralin (0.758)	benzyl phenyl ether (0.761)
330	300	10	1,2-dihydronaphthalene	benzyl phenyl ether (0.760)
331	300	10	1,4-dihydronaphthalene	benzyl phenyl ether (0.762)
332	400	240	tetralin (0.758)	1,2-diphenylethane (0.759)
333	400	240	1,2-dihydronaphthalene	1,2-diphenylethane (0.760)
334	400	240	1,4-dihydronaphthalene (0.756)	1,2-diphenylethane (0.760)

[a] The reactants were sealed in a 0.25 cm i.d., 20 cm-long glass tube reactor.

Results and Discussion

The thermal stabilities of 1,2- and 1,4-dihydronaphthalene were determined in preliminary control experiments. The results are summarized in Table II.

Table II. The Thermal Stabilities of Dihydronaphthalenes[a]

					Product Dist. (%)[b]		
Reaction	Temp., °C	Time, min.	Reactant	% Conversion	T	DHN	N
335	300	120	1,2-DHN	35.8	15.8	1.0	19.0
336	300	120	1,4-DHN	64.2	14.5	28.7	21.0
337	400	5	1,2-DHN	64.0	30.0	0.6	33.4
338	400	5	1,4-DHN	92.7	27.8	2.10	43.9

[a] Dihydronaphthalene (0.76 mmole) was sealed in a 10 cm-long glass tube reactor.

[b] T = tetralin, 1,2-DHN = 1,2-dihydronaphthalene, 1,4-DHN = 1,4-dihydronaphthalene, N = naphthalene.

These results indicate that dihydronaphthalenes are thermally unstable and either rearrange to the other dihydro isomer or disproportionate to tetralin and naphthalene. 1,4-Dihydronaphthalene is significantly more reactive than 1,2-dihydronaphthalene and rearranges to form 1,2-dihydronaphthalene quite readily. On the other hand, only a very small amount of 1,4-dihydronaphthalene accumulates in the reaction solution when 1,2-dihydronaphthalene is employed as the starting material.

The results for the hydrogen transfer reactions are summarized in Table III.

Table III. The Hydrogen Transfer Reactions

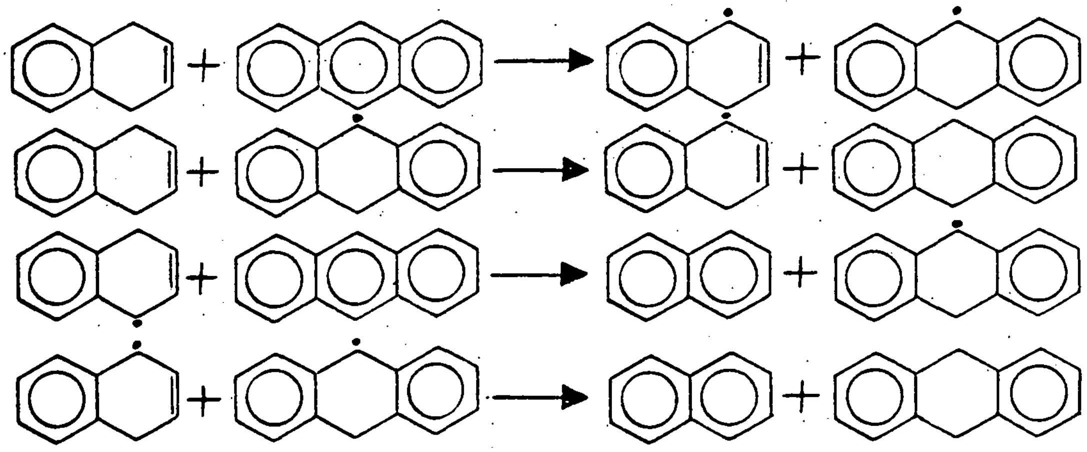
			Conversion (%) in Donor		
Temp., °C	Time, min.	Acceptor	Tetralin	1,4-Dihydronaphthalene	1,4-Dihydronaphthalene
400	120	Phenanthrene[a]	2	16	10
300	120	Anthracene[a]	3	5	58
400	120	Phenanthrene	5	11	12
300	120	Anthracene	1	13	53
300	120	E-stilbene	1	6	17

Table III.--Continued

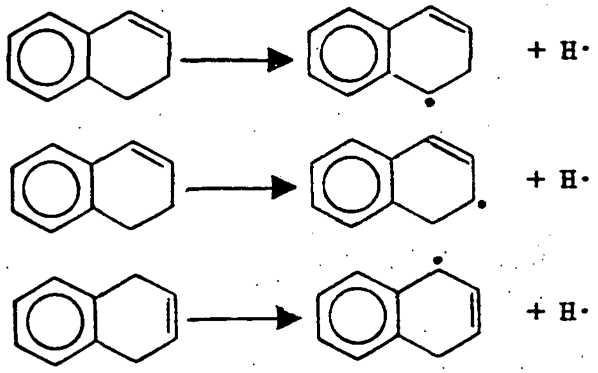
Temp., °C	Time, min.	Acceptor	Conversion (%) in Donor Tetralin	1,4-Dihydronaphthalene	1,4-Dihydronaphthalene
300	10	Benzyl phenyl ether	0.7	0.4	0.5
400	240	1,2-Diphenylethane	5	5	4

[a] Ref. 3.

The results obtained by Virk and his associates[3] and in this laboratory are, in general, quite comparable. However, there is a significant difference in the measured reactivity of 1,2-dihydronaphthalene with phenanthrene. Whereas the previous work suggested that 1,2-DHN was about 1.6-fold more reactive than 1,4-DHN with phenanthrene, the new work indicates that there is no essential difference in reactivity. The results in Table II show that the dihydronaphthalenes disproportionate to tetralin and naphthalene within several minutes at 400°C, therefore, the actual initial donor is tetralin rather than dihydronaphthalene. Thus, it is not surprising that the conversions of phenanthrene with 1,2-DHN and 1,4-DHN are the same. The lower temperature reactions with anthracene and E-stilbene show that 1,4-dihydronaphthalene reduces the substrates more rapidly than 1,2-dihydronaphthalene. These results are at variance with the predictions of the Woodward-Hoffman rules for concerted pericyclic reactions. Therefore, these reactions must occur in a stepwise fashion. A reasonable formulation for 1,4-dihydronaphthalene is presented in the equations.



Theoretical calculations of the BDE's based on Benson's group additivity method give the results shown below.



$BDE_1 = 82.8$ kcal/mole

$BDE_2 = 80.0$ kcal/mole

$BDE_3 = 81.6$ kcal/mole

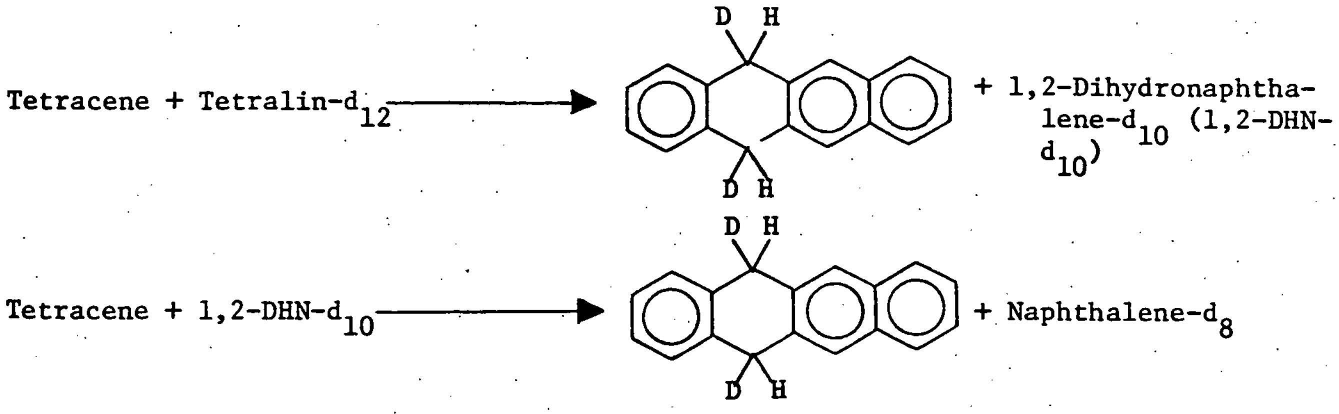
The difference between BDE_2 and BDE_3 may be of the consequence of ring correction of the heat of formation. A ring correction of 4.8 kcal/mole, which is based on ring correction for 1,3-cyclohexadiene, is introduced for the heat of formation of 1,2-dihydronaphthalene. On the other hand, a ring correction of only 0.5 kcal/mole based on the correction for 1,4-cyclohexadiene is used for the heat of formation of 1,4-dihydronaphthalene. Since the carbon-carbon bond length in the benzene ring is different from that of the olefinic double bond, these ring corrections of steric strain for the cyclohexadienes may not be applicable for the cases of dihydronaphthalenes. Either the theoretical estimations cannot give the accurate BDE's without further modification or the BDE's are not adequate guidance here. In addition, the reactivity of 1,4-dihydronaphthalene is more favorable than that of 1,2-dihydronaphthalene by a statistical factor of 2. At any rate, all the available facts shown in Table II suggest that 1,4-dihydronaphthalene is more reactive than 1,2-dihydronaphthalene. Therefore, the reduction of unsaturated hydrocarbons by 1,4-dihydronaphthalene will usually be faster than those by 1,2-dihydronaphthalene and the reactions will not depend upon the orbital characteristics of the substrates.

Virk also suggested that the decomposition of 1,2-diphenylethane or benzyl phenyl ether may proceed via the pericyclic pathways.[2] The results in Table III show that the decomposition rates of 1,2-diphenylethane and benzyl phenyl ether are independent of the donor type. Therefore, the thermal decomposition of 1,2-diphenylethane or benzyl phenyl ether is most logically formulated as a unimolecular reaction to form a pair of radicals which abstract a hydrogen atom from the donor.

$$C_6H_5CH_2CH_2C_6H_5 \rightarrow 2C_6H_5CH_2\cdot$$

$$C_6H_5CH_2\cdot + DH \rightarrow C_6H_5CH_3 + D\cdot$$

The experimental results mentioned in the preceding paragraphs favor a stepwise free radical mechanism for the hydrogen transfer reactions. To provide further experimental evidence, 100 parts of tetracene was reduced by a mixture of 50 parts of tetralin-d_{12} and 50 parts of tetralin. According to the predictions of the pericyclic pathway two hydrogen or deuterium atoms must be transferred from one donor molecule to the acceptor molecule in each reaction. Therefore, only



5,12-dihydrotetracene-d$_0$,d$_2$ and d$_4$ should be produced. However, 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. Control experiment shows that the exchange reaction between tetralin-d$_{12}$ and 5,12-dihydrotetracene is relatively slow, these results favor the stepwise free radical mechanism. Work on this project continues.

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