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DOE/PC/40810--3

DE83 001110

SYNTHESIS OF OLIGOMERIC MODELS OF COAL-DERIVED
MATERIALS FOR USE WITH GPC CALIBRATION

Quarterly Report for the Period

June 1982 - August 1982

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Date Published - September, 1982

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I. ABSTRACT

One important facet of the characterization of coal derived materials is that of molecular weight determination. Number average molecular weight is usually obtained by vapor pressure osmometry measurements. However, no satisfactory method is available for determining weight average molecular weights. The latter values are useful in predicting rheological properties. Gel permeation chromatography (GPC) is a technique which should be most readily adaptable for this measurement. The other techniques of ultracentrifugation and light scattering are not as readily available as GPC. At this time, satisfactory GPC calibration standards which possess chemical structures similar to coal derived materials are non-existent.

The purpose of this study is to develop a useful set of GPC calibration standards for asphaltene and preasphaltene analyses. Our previous results suggest models in which coal derived preasphaltenes and asphaltenes are composed of oligomeric aromatic ethers of both diaryl and furan types. We plan to synthesize a series of model oligomers that are in agreement with the average structural formulas of some selected coal preasphaltenes as determined by pmr, elemental analyses and various oxygen derivatization procedures. These model compounds will be tested for use as calibration standards for both high pressure gel permeation chromatographic and vapor pressure osmometric procedures. Their response and retention times will be compared with coal preasphaltenes to determine the suitability of the model compounds as calibration standards.

II. Objective and Scope of Work

Task.1 Syntheses of Model Oligomers

Previous studies of the structure of asphaltenes and preasphaltenes suggest these coal derived materials are composed of a carbon skeleton composed of 2-4 ring aromatic centers connected by etheral or furan linkages. Model oligomers based on these types of structures will be synthesized in the molecular weight range of 300 to 800 g/mol. Oligomers will be synthesized with and without phenolic groups added to the structure.

Task.2 Vapor Pressure Osmometry

The molecular weights of the model oligomers will be measured by vapor pressure osmometric techniques. The model oligomers will be sent out for analysis by light scattering in order to compare the number average and weight average molecular weights. The number average molecular weight of several preasphaltene and asphaltene samples will be measured by vapor pressure osmometric techniques. Prior to analysis the samples will be separated into narrow molecular weight ranges by preparative column GPC techniques.

Task.3 Gel Permeation Chromatography

A series of model oligomers will be used to calibrate a high pressure gel permeation chromatographic column. Samples of the relatively narrow molecular weight ranges of preasphaltenes or asphaltenes will be tested on the column to determine if retention times are linear functions of the vapor pressure osmometric values. Several commercial packings, both high pressure and open column materials, will be tested.

Summary of Progress to Date

Analysis of two asphaltene and six preasphaltene samples have shown that 60-80% of the total oxygen is accounted for as phenol and carbonyl groups. Thus, ethers make up no more than 40% of the oxygen in these samples. Modification of the proposed models, particularly the preasphaltenes, by incorporation of carbonyl moieties is therefore warranted.

Thirty diaryl ethers and oligo(aryl oxides), both with and without phenolic OH groups, ranging from 186 g/mole to 538 g/mole have been synthesized as model asphaltenes. Preasphaltene models have been modified to include carbonyl groups (generally as quinones). The synthesis of the first of these new models has been accomplished and work on the preparation of other models is in progress.

PROGRESS TO DATE

TASK I Selection and Syntheses of Model Oligomers

A. Selection of Appropriate Models

The selection of model oligomers as GPC calibration standards for asphaltenes and preasphaltenes should reflect the known structural features and molecular weight ranges of these coal derived materials. Thus, a discussion of previous and ongoing analytical work designed to elucidate structural parameters is warranted.

Under a current contract¹, Baltisberger, et al, have been examining lignite derived asphaltenes and preasphaltenes prepared under a variety of liquefaction conditions. Among the structural parameters analyzed for are molecular weight, hydroxyl oxygen content, other (etheral) oxygen content, the fraction of aromatic carbon (f_a) and the degree of aromatic condensation (D).

The number average molecular weight is determined by vapor pressure osmometry (VPO), following fractionation of the sample into molecular size ranges by GPC. Asphaltenes tend to maximize at approximately 400 g/mole, whereas preasphaltenes tend to maximize at approximately 600 g/mole. However, both asphaltenes and preasphaltenes exhibit molecular weight distributions ranging from 250-1500 g/mole.

The oxygen functionality was measured for asphaltene and preasphaltene samples isolated from six runs which were carried out at the Grand Forks Energy Technology Center in a continuous stirred autoclave using an anthracene donor solvent. The details of the solvent extraction isolation of the two samples and their preparation is described in earlier reports.¹ The hydroxyl content of the samples is measured by formation of a ¹⁴C acetate derivative which is subsequently measured by combustion or hydrolysis and counting. The quinone (carbonyl) content is determined by reaction of the sample with hydroxylamine in pyridine solvent to form an oxime (eq. 1):

The resulting oxime is quantitated by measurement of the nitrogen content before and after derivatization.

Table 1 shows the results of the oxygen analysis. Total oxygen was determined by difference using the carbon, hydrogen, nitrogen and sulfur analyses. A typical analysis for 32 was 82.85%C, 5.26%H, 1.66%N, 0.50% sulfur and 9.75% oxygen. Approximately 50% of the oxygen is hydroxyl. Fifteen to twenty percent of the oxygen is present as carbonyl types as analyzed by oxime formation.

In summary, the data show that 60-80% of the oxygen is present as hydroxyl or carbonyl types. At the most, etheral groups make up only 40% of the total oxygen in these samples. The implication is that the target model compounds used for our GPC calibration standards may require modification in the form of (1) more carbonyl oxygen probably as quinones and (2) less ether or furan linkages than first proposed.

Work Forecast:

1

2

Quinones with hydroxyl groups located at a peri position such as the dihydroxyanthraquinones, 1 and 2, shown above may be difficult to react quantitatively with hydroxylamine to form oximes. Reactions with these compounds and their dimethyl derivatives are being studied to determine (1) if the presence of the hydroxyl groups interferes with derivatization and (2) if the alkylation of the hydroxyl group permits subsequent quantitative oxime formation. Reaction of compounds 1 and 2 with hydroxylamine shows that one oxime was formed. At the same time anthraquinone was reacted completely to form the dioxime.

During the next quarter we plan to prepare the dimethoxy derivatives and examine their subsequent reactions with hydroxylamine.

Table 1. Oxygen Functionality of Six GFETC Samples

<u>Sample</u>	<u>Oxygen Analysis, mmol/g^a</u>			<u>%, Accounted For</u>
	<u>Total</u>	<u>OH</u>	<u>C=O</u>	
32-A ^b	4.64	2.57	0.94	76
34-A	4.98	2.50	0.79	70
32-PA	5.19	3.11	1.39	86
34-PA	5.07	2.82	1.07	77
41-PA	3.88	1.79	0.76	65
44-PA	3.42	1.54	0.74	67
45-PA	4.43	1.78	0.95	62
46-PA	2.94	1.17	0.79	61

^aDetails see Quarterly Report, DOE-FC-02101-18. Samples prepared at 460°C, 2000-4000 psig H₂ or H₂:CO(1:1) at the Grand Forks Energy Technology Center (GFETC).

^bA = asphaltene, PA = preasphaltene

B. Synthesis of Model Compounds

1. Asphaltene Models

Table 2 illustrates the materials prepared thus far as models for coal derived asphaltenes. The majority of these ethers are known species and their characterization has been effected through comparison of physical properties (mp,bp) and/or spectra (IR, ^1H and ^{13}C NMR) with literature values. Previously unreported compounds have been submitted for elemental analyses in addition to characterization by the aforementioned techniques.

Three synthetic routes have proven to be useful in the preparation of the diaryl ethers and oligo(aryl oxides) listed in Table 2. These include intermolecular dehydration of a phenolic starting material, a solvent assisted Ullmann reaction and an Ullmann-type reaction employing potassium carbonate as a base. The first two methods have been discussed previously;² only the third one will be described in this report.

The use of finely ground potassium carbonate as a base in the pyridine assisted Ullman ether synthesis³⁻⁵ is demonstrated by the preparation of 1,4'-diphenoxybenzene (entry 13 in Table 2) (eq. 2). This particular reaction illustrates one of the key advantages of the K_2CO_3 modification - preparation of otherwise unobtainable aryl ethers. Neither conventional nor solvent-assisted Ullmann syntheses, both of which require prior formation of the phenoxide salt, afforded 13 from hydroquinone and bromobenzene as

Table 2. Asphaltene Model Compounds

Entry	Name	Structure	MW, g/mole	Preparation ¹
1	3-phenoxyphenol		186	b,d
2	4-phenoxyphenol		186	b,d
3	3-phenoxyanisole		200	b
4	4-phenoxyanisole		200	b
5	3,3'-dihydroxydiphenyl ether		202	b,d
6	4,4'-dihydroxydiphenyl ether		202	b,d
7	3-hydroxy-3'-methoxydiphenyl ether		216	b,d
8	4-hydroxy-4'-methoxydiphenyl ether		216	b,d
9	2-phenoxy-naphthalene		220	c
10	3,3'-dimethoxydiphenyl ether		230	b
11	4,4'-dimethoxydiphenyl ether		230	b
12	1,3-diphenoxybenzene		262	b,c
13	1,4-diphenoxybenzene		262	c
14	2,2'-dinaphthyl ether		270	b
15	1,1'-dinaphthyl ether		270	a,c
16	1,2'-dinaphthyl ether		270	a
17	3,5-diphenoxyanisole		292	b
18	1,4-diphenoxynaphthalene		312	b
19	2,7-diphenoxynaphthalene		312	b,c
20	1,4-bis(4-methoxyphenoxy)benzene		322	b

Table 2 Continued:

Entry	Name	Structure	MW, g/mole	Preparation ¹
21	4,4'-diphenoxybiphenyl		338	c
22	9,10-diphenoxyanthracene		362	b
23	1,4-bis(2-naphthoxy)benzene		362	b
24	1,4-bis(2-naphthoxy)naphthalene		412	b
25	2,7-bis(2-naphthoxy)naphthalene		412	b
26	2,7-bis(1-naphthoxy)naphthalene		412	b
27	4,4'-bis(naphthoxy)biphenyl		438	b
28	penta(phenylene oxide)		446	b
29	4,4'-bis(4-phenoxyphenoxy)biphenyl		522	c
30	sexi(phenylene oxide)		538	c

¹a = Intramolecular dehydration catalysed by NaHSO₄

b = Solvent assisted Ullmann reaction

c = Ullman reaction utilizing K₂CO₃

d = Cleavage of alkyl-aryl ether by treatment with TMSI

starting materials. Similarly, the preparation of 4,4'-diphenoxybiphenyl from 4,4'-dihydroxybiphenyl and bromobenzene was accomplished only by application of the K_2CO_3 -modified Ullman synthesis.

Some other advantages of this method as opposed to a conventional or solvent assisted Ullmann reaction deserve mention: 1) in general, yields are higher by 5-30%. 2) The reaction need not be bathed in an inert atmosphere such as N_2 or Ar. Generation of the reactive species (phenoxide) in situ minimizes oxidation and hence tar formation. 3) Di- and polyhydroxy aromatics are suitable starting materials for this reaction. Since they are more readily available than the corresponding di- and polyhalo aromatics, use of this method affords a greater variety of model compounds. 4) High molecular weight models (500 g/mole) may be obtained in reasonable yield through application of this preparation.

2. Preasphaltene Models

As discussed in part A, modification of the original preasphaltene models⁶ by incorporation of carbonyl groups as quinones has become necessary to fit with recent analytical data.

We have therefore begun the preparation of some new model preasphaltenes, as outlined in Scheme I.

Nitration of anthraquinone with mixed acid yielded 1,5-dinitroanthraquinone (31) as the major product. Minor amounts of other dinitro derivatives, also formed in the reaction, were removed by chromatography. Treatment of 31 with o-chlorophenol and finely ground K_2CO_3 in DMF for two hours at 150° ⁷ afforded 1,5-bis(2-chlorophenoxy)anthraquinone (32) in 90% yield. Photochemical ring closure⁸ was carried out in a Rayonet reactor equipped with low pressure 254 nm mercury lamps. Alternatively, 33 was obtained, in slightly lower yield, from photochemical ring closure of 1,5-diphenoxyanthraquinone (34), employing iodine as an oxidant.^{9,10} By analogy to the preparation of dibenzofuran from diphenyl ether,¹¹ 34 may be converted to 33 through use of palladium acetate as a coupling agent.

The synthetic route illustrated in Scheme I provides a convenient entry into a series of furan-quinone type model preasphaltenes. By varying the starting carbonyl-containing molecule, the following species may be obtained:

Higher molecular weight materials may be produced from dinitro starting materials and/or utilization of naphthols in the etherification step.

Work Forecast

In the coming quarter we plan to complete the synthesis of asphaltene model compounds by preparation of high molecular weight oligo(aryl oxides) containing free phenol groups and more condensed aromatic ring systems (naphthalene, anthracene, phenanthrene). Research on the preasphaltene models will be directed toward syntheses of furan-quinone systems such as 35 - 37, employing the general sequence shown in Scheme I.

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