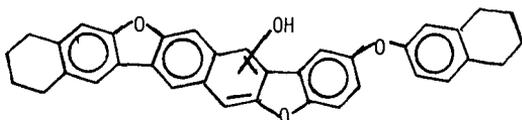


Analytical Cleavage of Diaryl Ethers as Models for  
Asphaltene and Preasphaltene Structures

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Detailed analyses of asphaltene and preasphaltene samples have been previously carried out (1). These materials were solubilized by quantitative radioactive acetylation followed by gel permeation chromatography and determination of the hydroxyl content, the base content, the molecular weight, and nmr parameters for each fraction. This study resulted in model structures for asphaltene and preasphaltene fractions which were quite similar except for molecular weight and neutral oxygen content. An example of the type of structures postulated is shown below:



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The major functionality of oxygen deduced for these models was phenolic hydroxyl and aryl ether groups. Significantly the amount of ether oxygen varied between asphaltenes and preasphaltenes but hydroxyl contents were similar. Nearly all other structural parameters only changed slightly or not at all on comparing the fractions of different molecular weight within a preasphaltene or asphaltene sample. These same parameters were also quite similar when comparing the asphaltene with the preasphaltene sample. Since ether functionality had a major role in distinguishing between asphaltenes and preasphaltenes, an investigation of direct methods for quantitative ether determination was initiated.

Investigation of the ether content of coals and coal-derived materials has been generally approached by a differential determination of unreactive oxygen. Sporadic determination of ether contents by direct cleavage have been reported (2,3) but only recently have selective cleavage reactions been applied (4). Very little systematic work on ether cleavage in coal materials or on coal model compounds has been pursued. Our interest in asphaltenes and preasphaltenes led to an examination of ether cleavage techniques suitable for selective cleavage of ethers in these materials with the objective of their quantitative determination. The focus of this report is the reductive cleavage of arylary ethers.

#### DISCUSSION

Sodium in liquid ammonia has been known to cleave diaryl ethers for some time (5). The low solubility of coal materials in liquid ammonia and a desire to carry out reactions at higher temperatures has led to a study of ether cleavage with sodium and potassium using hexamethylphosphoric triamide (HMPA) as electron transfer agent in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) as solvent (6). The results of treating 1 mole of model ether with 2 to 8 g-atom of sodium and 2 to 8 moles of HMPA are shown in Table 1. Room temperature runs were found to cleave diphenyl ether and other more sensitive ethers (e.g., benzylphenyl and dibenzyl ethers) quantitatively. Dibenzofuran (DF), however, was essentially untouched by these conditions (less than 10% cleavage). Refluxing caused an increase in cleavage but only to 50-60% yields of cleavage products. The problem was traced to the instability of the HMPA solvated

electron system. Since sodium in HMPA has a half life of only several hours (7), the HMPA was replenished periodically at 4-6 hr intervals. Under these conditions, DF could be cleaved quantitatively with one supplementary addition of HMPA (after 4 hr) in 6-8 hr in refluxing THF.

Xanthene, however, was cleaved to a maximum of 69% even at reflux in THF utilizing the sequential HMPA addition. Substitution of potassium for sodium and DME for THF led to quantitative loss of starting material and 91% o-benzylphenol formed along with several minor unidentified products.

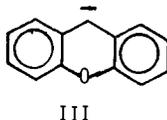
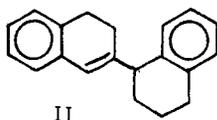
As part of our attempt to cleave all the ethers in asphaltenes and preasphaltenes (from 0 to 50% ether oxygen remained after sodium/HMPA/THF reflux conditions in some preliminary results) we began a survey of likely ether structural types present in these materials which might prevent complete ether cleavage. Two structural types come to mind which might be resistant to reductive cleavage: a) polycyclic aryl ethers b) anionic ethers.

#### a) Polycyclic ethers

If the reduction potential is critical in determining whether an ether cleaves or not, polycyclic ethers which have lower reduction potentials may not cleave. To test this possibility several phenoxyl polycyclic compounds were prepared and treated under ether cleavage conditions. The polycyclic phenyl ethers which have been examined thus far are listed in Table 1. Significantly each of these ethers under the mildest conditions (1, footnote a, Table 1) cleaved essentially quantitatively as judged by the amount of phenol produced. This fact is critical since determination of the increase in hydroxyl content is used to judge the extent of cleavage in coal materials. Two factors, however, enter into the analysis which are detrimental to further examination of the cleaved samples. Birch reduction, even in the absence of an added proton donor, is significant for coal materials as measured by the shift from aromatic to aliphatic protons in the  $^1\text{H}$  nmr spectrum. Either the coal materials themselves (phenol ?) or HMPA act as the proton source. This result is mirrored in the model compounds of Table 1 where various reduced species are produced. Secondly, a curious reductive oligomerization or polymerization occurs with the polycyclic portion of the cleaved model ethers. Mass recoveries are generally low for this portion of the ether. Separate Birch reduction of the polycyclic (naphthalene, anthracene and pyrene) under ether cleavage conditions has in general produced known products with none of the higher molecular weight material seen from ether cleavage. The preliminary ether cleavage results, however, implicated the primary cleavage products, the polycyclic aromatic hydrocarbons, as the precursors of the oligomeric products. Similar products have been observed previously from coal material reductions using sodium and naphthalene as the electron transfer agent (8). Although a pure sample has not been obtained yet, one reduced dimer formed from 1-phenoxynaphthalene has been preliminarily identified as II from  $^{13}\text{C}$ ,  $^1\text{H}$  nmr and ms of this crude sample. Since these materials are not stable to reaction conditions, the exact chemistry of this aspect of the cleavage has not as yet been worked out. Oligomeric materials are observed for all the polycyclic ethers in Table 1. These results point to the possibility that oligomerization may increase, rather than decrease, the molecular weight of coal samples during reductive ether cleavage reactions.

#### b) Anionic ethers

Xanthene was found difficult to cleave with sodium (cf. Table 1). In view of the red color developed during the reaction this resistance to cleavage could have been due to formation of the bridged anion III. The higher reducing power of potassium could have allowed formation and cleavage of the dianion although other mechanisms are possible.



Ignasiak has found that p-phenoxyphenol cannot be cleaved with sodium in liquid ammonia (4); cleavage does result after alkylation of the phenolic group, however. In view of the high oxygen content of our model structure I, anions of this type could very well be generated in the coal materials. We are currently testing this concept to complete the ether cleavage of asphaltenes and preasphaltenes.

#### CONCLUSION

Preliminary data for the reductive cleavage of various types of arylaryl ethers indicates the possibility of directly measuring the amount of different aryl ether types in coal derived materials. Reductive oligomerization, Birch reduction and an incomplete knowledge of ether types present in coal materials remain problems.

#### ACKNOWLEDGMENTS

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Table 1 Cleavage of Polycyclicphenyl Ethers with Sodium and HMPA

<u>Ether</u>	<u>Conditions<sup>a</sup></u>	<u>Phenol Yield<sup>b</sup></u>	<u>Others (% Yield)<sup>c</sup></u>
Diphenyl ether	1	100%	benzene (100), SM (0)
Dibenzofuran	1	--	o-phenylphenol (10), SM (89)
	2	--	o-phenylphenol (100)
Xanthene	2	--	o-benzylphenol (69), SM (30)
	3	--	o-benzylphenol (91), SM (0)
1-Phenoxy-naphthalene	1	97	naphthalene (2), 1,2-dihydro-naphthalene (.7), tetralin (34), SM (3)
9-Phenoxyphenanthrene	1	93	phenanthrene (tr), 9-10-dihydrophenanthrene (tr), SM (tr), others
9-Phenoxyanthracene	1	90 <sup>d</sup>	anthracene (7), 9,10-dihydro-anthracene (52), anthrone (2), others, SM (0)
1-Phenoxy-pyrene	1	102	pyrene (100), SM (2), others

<sup>a</sup>Conditions: 1) 1:7:2 molar ratio ether:sodium:HMPA (except diphenyl ether and 9-phenoxy-pyrene where 1:2:2 was used) in THF at room temperature for 24 hr. All materials were rigorously dried. 2) Same except a 1:7:7 molar ratio was used with HMPA being added in 2-4 portions over 24 hr at reflux (the reaction was complete in 8 hr). 3) Same as 2 except potassium metal and DME were used instead of sodium and THF.

<sup>b</sup>These values were determined by HPLC using a direct calibration method and showed precision of  $\pm 5\%$  with a Waters C-18 Bondapak column and various aqueous acetonitrile concentrations as solvent.

<sup>c</sup>These materials were identified by comparison to known samples. SM = starting material; tr = trace.

<sup>d</sup>Preliminary analysis.