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Quantitation of the Reductive Cleavage of Aryl Ethers of SRC and Coals

Semi Annual Report

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OBJECTIVES AND SCOPE OF WORK

1. To determine the mechanism of cleavage of ethers by reductive means.
2. To determine if and how ether cleavage is controlled by reduction potential, solvent, additives, structure or a combination of these factors.
3. To determine if this technique has the range of applicability, selectivity and quantitative character to be applied to rational coal structure determination.
4. To apply these techniques, if valid, to coal and coal derived material structure determination.

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Task 1 and 2 Ether Synthesis Studies

Objective: To synthesis ethers to be used in the study.

During the first period of this contract our work has focused on synthesis of appropriate aryl ethers to use in testing ether cleavage reactions. Thus, the following ethers have been prepared:

These compounds were prepared by standard literature conditions. Generally an appropriate aryl halide was treated with sodium phenoxide at 150-250°C using a copper powder catalyst. After separating from the copper and extracting the unreacted sodium phenoxide with water, the residual crude phenyl ether was purified by crystallization, distillation or column chromatography. Several grams of each ether has been obtained and preliminary work on their electrochemistry has been initiated.

In future work we expect to complete the synthesis of the ether types to be tested as well as initiate some alkali metal cleavage reactions of them.

Task 1a Electrochemical Studies

Objective: To study the electrochemical reduction and cleavage of aryl ethers as a means of determining the mechanism of cleavage.

The study of the reductive cleavage of ethers by electrochemical means has been initiated. Cyclic voltammetry was used to determine the reduction potentials and radical anion stabilities for a series of aryl ethers in N,N'-dimethylformamide (DMF). Table 1 summarizes the ethers, which have been currently investigated by cyclic voltammetry.

Table I

Aryl Ether	Reduction Potential (Epc vs SCE Reference electrode)	Stability of the Resultant Radical Anion
(Diphenyl ether)	-2.92V	Unstable
(Dibenzofuran)	-2.50V	Stable
(4-Trifluorodiphenyl ether)	-2.55V	Unstable
(4-Cyanodiphenyl ether)	-2.32V	Intermediate Stability
(4-Nitrodiphenyl ether)	-1.14V	Stable.
(4-Cyanoanisole)	-2.50V	Intermediate Stability
(9-Phenoxyanthracene)	-1.80V	Stable

All of the above ethers are reduced to a radical anion in a one-electron step at a platinum electrode in DMF using tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The background limit for the DMF-TBAP solvent system is approximately -3.00 V vs. the saturated calomel reference electrode (SCE). The SCE is +0.242 V of the standard hydrogen electrode (SHE).

The stability of the resultant anion radical of the ether is apparently determined by the ability of the anion to delocalize charge away from the carbon-oxygen bond of the ether. The diphenyl ether radical anion is unstable on the time scale of the electrochemical experiment. For example, the radical anion appears to be virtually absent during the reverse scan at a scan rate of 1.0 V/s. This would imply a half-life of less than 10^{-1} seconds for the radical anion of diphenyl ether. In contrast, the radical anion of dibenzofuran is quite stable on the electrochemical experimental time scale; there appears to be very little decomposition of the radical anion at reverse scan rates of 0.01 V/s. This is indicative of a half-life of greater than 10^2 seconds for the dibenzofuran radical anion at 25°C. At higher temperatures ($\sim 79^\circ\text{C}$), the radical anion of dibenzofuran becomes somewhat less stable. More extensive high temperature-controlled electrochemical experiments need to be carried out on the decomposition of the dibenzofuran radical anion.

The series of substituted diphenyl ethers prepared above were electrochemically studied. Electron-withdrawing substituents were employed to lower the reduction potentials for these ethers. The 4-trifluoromethyldiphenyl ether radical anion is unstable with a half-life of less than 10^{-1} seconds; however, the 4-cyanodiphenyl ether radical anion has a half-life in the range of 0.1 to 1.0 seconds. In contrast, the 4-nitrophenyl radical anion is very stable with a half-life greater than 10^2 seconds.

Thus, as the electron withdrawing ability of the substituent increases, the reduction potential becomes less negative (Table I) as is expected. Concurrently,

as the electron withdrawing ability of the substituent increases, the electron in the anti-bonding orbital can be effectively delocalized away from the carbon-oxygen bond, thus stabilizing the radical anion of the ether toward cleavage. This delocalization is also noteworthy in the radical anion of dibenzofuran; delocalization of charge is attainable through two conjugated phenyl rings, which retain co-planarity at all times.

Arylalkyl ether cleavage studies have also been initiated. The 4-cyanoanisole radical anion has an intermediate degree of stability on the time scale of electrochemical experiment. The half-life is less than 1.0 second, but probably greater than 0.1 second for this radical anion. Preliminary studies indicate cleavage between the oxygen and aliphatic carbon to yield phenoxide ion and a methyl radical. Additional product analysis is necessary to completely elucidate the decomposition pathway for all of the above radical anions, which have a reasonable degree of instability.

Finally, the radical anion of 9-phenoxyanthracene shows a relatively high degree of stability (half-life greater than 10^2 seconds). However, preliminary data indicate that this radical anion can be reduced to a dianion at more negative potentials. The dianion appears to be of an intermediate stability. Experimental work on this system is currently in progress and will be subsequently reported.

Future work includes more extensive studies on the products which result from radical anions of ethers with low or intermediate stabilities. Additional arylalkyl ethers with a polycyclic aryl moiety will be studied (e.g., phenoxypyrene). The relative ease of reduction to their radical anion and dianion, in addition to their respective stabilities, will be studied in DMF. Alkylalkyl ethers will be studied to determine the mode of cleavage for their electrochemically generated radical anions.