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FACILE REACTION/EXTRACTION OF COAL WITH SUPERCRITICAL FLUIDS

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As part of our program of searching for reagents that can be used for the mild chemical cleavage and solubilization of coal, a systematic study of acid-catalyzed ether cleavage reactions has begun. A variety of ether linkages have been found in coal, Figure 1. Depending on the density of these linkages and

- R-O-R'
- Type 1, R and R' are both alkyl
 - Type 2, R is alkyl and R' is aryl
 - Type 3, R and R' are both aryl
 - Type 4, R, R' and the O form a heteroaromatic ring

Figure 1. Classification of ethers in coal

their importance as cross links in the macromolecular structure of coal, solubilization might be greatly enhanced solely by cleaving ether linkages (see Figure 2). Benzylic ethers, types 1 and 2 with $R = \text{PhCH}_2$, are particularly reactive and have been implicated in the initiation of coal pyrolysis and hydrolysis. Two reagent systems were chosen for initial study, (1) ionic

Figure 2. Depolymerization of Coal by Ether Cleavage.

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hydrogenation in which H is delivered by strong acid and X is a hydrogen delivered by a hydride donor, and (2) the Friedel-Crafts arylation of ethers in which H is again derived from strong acid, but X is an aromatic ring compound.

Ionic Hydrogenation

The chemical compatibilities necessary for a successful ionic hydrogenation system impose some restrictions on the properties of the potential hydride sources, solvents and the catalyzing acids.

The Hydride Source - Triethylsilane (Et_3SiH) is a clean, relatively stable, well studied source of hydride which has often been used in ionic hydrogenations. The silane itself and its product silyl ether are both low-boiling materials which can easily be removed from reaction mixtures. Initial studies have used this hydride source. After demonstrating ionic hydrogenation using triethylsilane, additional sources of hydride (dihydroanthracene, dihydropyrene, p-cymene, etc.) will be investigated.

Solvent Selection - The solvent must dissolve the acid and hydride reagent and be chemically inert in the presence of both. Only hydrocarbons, halocarbons and methanol meet these requirements. Ideally, it should also dissolve large amounts of coaly material such as coal tar and swell or penetrate the coal easily. Benzene, dichloromethane and methanol all meet these requirements and were used in initial experiments.

Evaluation of strong acids - Acids evaluated are listed in Table 1 along with their solubilities in benzene. The two strongest acids, trifluoromethanesulfonic acid and sulfuric acid react directly and rapidly with the triethylsilane to give hydrogen. p-Toluenesulfonic acid was removed from consideration because of its low solubility in benzene. The first four are compatible with triethylsilane and can be used for ionic hydrogenation studies.

Transalkylation Studies

All of the solvents and acids identified as useful for ionic hydrogenation studies can be utilized for transalkylation. In addition, some acids, such as trifluoromethanesulfonic acid, whose reactivity with triethylsilane render them useless for ionic hydrogenation, can still be used as catalysts for transalkylations.

Model Studies

A study of the reactivity of benzyl phenyl ether with strong acids was undertaken. The results are shown in Table 2. The production of ortho-phenylphenol is known to represent an intramolecular pathway, while diphenylmethane (or benzyl methyl ether) formation signals an intermolecular reaction. Changes in the nature of the acid catalyst have little effect on the competition between intra and intermolecular pathways. The acid-catalyzed cleavage takes place readily in benzene, but not in methanol. Since the strongest acid observable in any system is the protonated solvent (for example, hydronium ion in water), in methanol the strong acid, $\text{CH}_3\text{OBF}_3\text{H}^+$, is converted to the weaker acid,

Table 1. Solubility of Strong Acids in Benzene

<u>Acid</u>	<u>Conc. of Acid, mmol/l, 20°</u>
$\text{CF}_3\text{CO}_2\text{H}$	miscible in all proportions
$\text{BF}_3 \cdot 2\text{CH}_3\text{OH}$	380
$\text{BF}_3 \cdot \text{CH}_3\text{OH}$	270
$\text{BF}_3 \cdot \text{H}_2\text{O}$	10
$\text{CF}_3\text{SO}_3\text{H}$	100
BF_3	45
AlBr_3	>>1000
p-TsOH	0.6

Table 2. Reaction Benzyl Phenyl Ether with Acids.

Acid	Solvent	T	(Acid) (PhCH ₂ OPh)	Rate	Yields ^a		
					PhCH ₂ Ph	Benzyl phenol	PhCH ₂ OCH ₃
BF ₃ ·CH ₃ OH	PhH	20°	5.4	<1 min	47%	40%	
	PhH	20°	2.8	20 min	50%	42%	
	PhH	20°	1.1	v. slow			
	PhH	20°	.44	No Rxn			
	PhH	72°	2.8	1 min	49%	49%	
CF ₃ SO ₃ H	PhH	22°	2.3	<1 min	44%	48%	
CF ₃ CO ₂ H	PhH	22°	5.4	No Rxn			
BF ₃	PhH	23°	3.4	7 min	49%	48%	
AlBr ₃	PhH	25°	4.6	5 sec	48% ^b	54% ^c	
BF ₃ ·CH ₃ OH	CH ₃ OH	23°	5.4	No Rxn			
BF ₃ ·2CH ₃ OH	BF ₃ ·2CH ₃ OH	23°	182	Slow		83% ^d	13%
BF ₃ ·CH ₃ OH	PhH/Et ₃ SiH (5 eq)	23°	2.7	2 hrs	45%	40%	
BF ₃ ·CH ₃ OH	PhH/Et ₃ SiH (63 eq)	23°	2.8	6 hrs	16%	59%	

a. GC yields, uncorrected

b. Data of Tarbell and Petropoulos, J. Am. Chem. Soc. 1952, 74, 244; yield is phenol which should be equal to PhCH₂Ph.

c. Data of Tarbell and Petropoulos, J. Am. Chem. Soc. 1952, 74, 244.

d. Detected as its methyl ether.

$\text{H}(\text{CH}_3\text{OH})^+\text{F}_3\text{BOCH}_3$, which is not active as catalyst under these conditions. In summary, model studies have provided the following information.

1. An aprotic solvent will be required for both transalkylation and ionic hydrogenation.
2. A non-nucleophilic solvent will be required for ionic hydrogenation.
3. Intramolecular reaction will occur in the reactions of phenyl ethers.
4. In an aromatic solvent, arylation (transalkylation) occurs in preference to ionic hydrogenation.

Model studies of the ionic hydrogenation were continued using a copolymer of 1,4-bis(bromomethyl)naphthalene and hydroquinone to mimic the solid, insoluble nature of coal. The results are shown in Table 3. Infrared spectra of

products in experiments 1 and 4 are virtually indistinguishable and indicate that none of the original polymer remains. This establishes that the reaction takes essentially the same course in the presence and absence of triethylsilane. However, the solubilities of the products in the presence and absence of triethylsilane is dramatically different. Since solubility is a sensitive function of molecular weight for oligomeric systems, the solubility of the attempted ionic hydrogenation product signals its lower molecular weight. This indicates that hydride has indeed captured enough of the benzylic cations to change the physical properties of the product.

Changes in acid strength (compare experiments 2, 4, and 5) indicate that stronger acids lead to more solubility (lower molecular weight) in the presence of the same molar ratio of hydride source. Experiments 3 and 4 show that increasing hydride concentration beyond six equivalents only slightly increases the solubility of the product. Using these results as a basis, we will next perform both the transalkylation and ionic hydrogenation of coal.

Table 3. Ionic Hydrogenation of a Polymeric Ether^a

EXP. #	Acid (equiv)	Hydride (equiv)	Solvent	Solubilities	
				Solvent	Acetone
1	BF ₃ ·H ₂ O(6)	---	CH ₂ Cl ₂	0%	0%
2	BF ₃ (xs)	Et ₃ SiH(12.5)	CH ₂ Cl ₂	11.3%	100%
3	BF ₃ ·H ₂ O(6)	Et ₃ SiH(6)	CH ₂ Cl ₂	8.8%	100%
4	BF ₃ ·H ₂ O(6)	Et ₃ SiH(12)	CH ₂ Cl ₂	9.0%	100%
5	BF ₃ ·2H ₂ O(6)	Et ₃ SiH(12.5)	CH ₂ Cl ₂	4.5%	20%
6	BF ₃ ·2CH ₃ OH(6)	Et ₃ SiH(12)	CH ₂ Cl ₂	4.2%	16%
7	CF ₃ CO ₂ H	Et ₃ SiH(12)	CF ₃ CO ₂ H	4.0%	20%

a. Copolymer of 1,4-bis(bromomethyl)naphthalene and hydroquinone, see text.