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TITLE: Superacid Catalyzed Coal Conversion Chemistry

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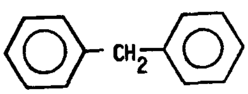
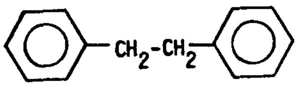
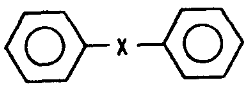
The basis of our studies was a novel, low temperature, mild coal conversion process developed in our laboratory. It involves the use of a superacidic system consisting of HF and BF_3 in the presence of hydrogen and/or a hydrogen donor solvent.

In order to understand the chemistry involved in the process of hydrodepolymerization of coal by $HF:BF_3:H_2$ system a systematic study of a number of coal model compounds was carried out under identical conditions. The model compounds studied in our studies had two benzene, naphthalene and anthracene rings connected either directly or through various bridging units such as alkylidene, ether, sulfide, imino, etc.

Model compounds studied included







X=O, S, NH

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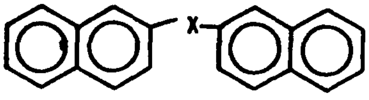
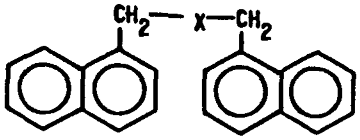
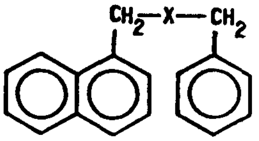
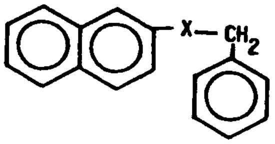
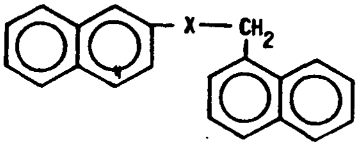


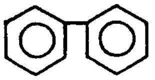
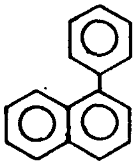
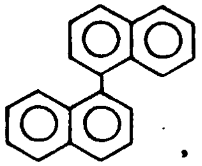
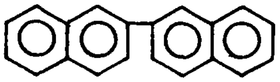


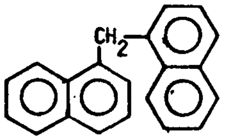






X=O, NH or S

 ,
 ,
 ,




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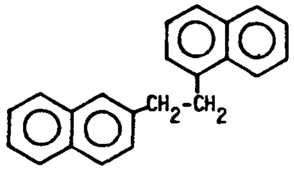

From the results of our studies model compounds can be classified into two categories.

The first category consist of model compounds where two aromatic rings are connected with bridging unit such as -CH$_2$, -CH$_2$-CH$_2$-, CH$_2$-O-, -CH$_2$-O-CH$_2$-, -CH$_2$-S-CH$_2$-, and -CH$_2$-S-CH$_2$-. These model compounds gave near quantitative conversion with HF:BF$_3$ system in the absence of hydrogen under extremely mild condition (mostly room temperature) except in cases of sulfur containing compound where a temperature of 90° C was used. Condensation products such as anthracene and methylanthracene were identified in the products of the conversions. The formation of these undesirable side product could be completely eliminated when a good hydrogen donor such as isopentane was used. Moreover anthracene and methylanthracenes themselves gave appreciable conversion to light hydrocarbons (C_1 to C_4) when treated with $HF:BF_3:H_2$ system at higher temperature (~150° C). The second category of coal models included compound where two aromatic rings are connected either directly (biphenyl, binaphthyl, etc) or through heteroatoms (diphenyl ether, diphenyl sulfide and diphenyl disulfide) as well as heterocyclic compounds such as quinoline. These compounds required relatively higher hydrogen pressure (800-1000psi) and temperature (150-180° C) for good conversion. Lower hydrocarbons (C_1 to C_4) were produced from the conversion of these model compounds. Conversion of these compounds requires hydrogenation of one of the benzene rings followed by cleavage to the observed products.

From our studies it became apparent that high pyridine extractibilities achieved by treating coal at temperature below 100° C results from the cleavage of bridges such as present in bibenzyl, diphenylmethane, dibenzyl ether, dibenzyl sulfide, etc. On the other hand, the increased cyclohexane extractibility and distillability observed at relatively higher temperatures and hydrogen pressures reflects the hydrogenation and cleavage of the aromatic backbone in coal structure similar to what is seen in the conversion of model compounds such as biphenyl, diphenyl ether, diphenyl sulfide, are related naphthalene or anthracene derivatives.

Coupled with our model studies to learn about the mechanism and to expand the scope of the investigation of the $HF:BF_3$ catalyzed reactions of coal and related model compounds, screening of a number of modified and improved superacidic systems was carried out. Trifluoromethanesulfonic acid (triflic acid) was reported in the literature to be thermally very stable at high temperatures. In our studies, however, triflic acid was extensively decomposed in attempted depolymerization reactions of coals (Illinois No. 6) at temperatures of ~250° C or higher. At lower temperatures (~150° C) the activity of triflic acid is insufficient to catalyze the reaction.

It was, however, discovered that a ternary superacidic system composed of CF_3SO_3H-HF-BF_3 is quite effective and can be successfully applied to bring about the depolymerization of coals at 170° C.

In order to improve the liquefaction-depolymerization of coals under studied superacid conditions, we have also studied the functionalization of coals and the effect of functionalization on the liquefaction procedure.

Ethylated coal was prepared by electrophilic ethylation with the highly reactive ethyl fluoride-antimony pentafluoride complex in SO_2 solution at -40° C. The reaction resulted in up to ~50% weight increase of treated coal. Under these mild reaction conditions at -40° C no significant structural changes of coal such as depolymerization or oxidation seem probable.

Pyridine and cyclohexane extractabilities of ethylated coal are 36 and 11%, respectively. Treatment of ethylated coal with the $HF:BF_3$-H_2 system at 90° C for 4 hr gives a product which is 87% extractable pyridine and 5% in cyclohexane. Thus, ethylation of coal seems to render it more susceptible to hydrodepolymerization under the mild liquefaction conditions.

We also prepared nitrated coal by carrying out electrophilic nitration with nitronium tetrafluoroborate in trimethylphosphate solution at room temperature. Nitrated coal showed 25% weight increase. Nitrated coal has 24% extractability in pyridine but is completely insoluble in cyclohexane. Treatment of nitrated coal with the $HF-BF_3-H_2$ system at 90° C for 4 hr resulted in a product coal which has 20% extractability in pyridine and $<1\%$ in cyclohexane. Apparently, nitration of the aromatic backbone of the coal makes it less susceptible to protolytic cleavage. This results in poor depolymerization of nitrated coal. Consequently nitration of coal does not seem to be an effective pretreatment of coal for subsequent liquefaction.

Finally we also carried out exploratory comparative studies of the superacidic coal conversion system with heavy oil residues and tar sand asphaltenes to extend the scope to other carbonaceous materials. The results were encouraging and it will form the topic of a proposal for future research.

Significance to Fossil Energy Program:

Our research project involved the study of a raw comparatively mild coal conversion process. The goal of the project was to study model systems to understand the basic chemistry involved and to provide a possible effective pretreatment of coal which significantly improves liquefaction-depolymerization under mild conditions. The conversion process operates at relatively low temperatures (170° C) and pressures and uses an easily recyclable, stable superacid catalysts ($HF-BF_3$). It consequently offers an attractive alternative to currently available processes.

From the present studies it appears that the modification of coal structure by electrophilic alkylation and subsequent reaction of alkylated coal with $HF-BF_3-H_2$ system under mild conditions considerably improves the extractability of coal in pyridine and cyclohexane. On the other hand, nitration of coal and its subsequent reaction with $HF-BF_3H_2$ decreases the pyridine and cyclohexane extractability. Study of model compounds under conditions identical with the superacidic $HF/BF_3/H_2$ system provided significant information about the basic chemistry of the involved cleavage-hydrogenation reactions.

Articles and Presentations:

Superacid Coal Chemistry. 1. $HF-BF_3$ Catalyzed Depolymerization-Ionic Hydroliquefaction of Coals under Mild Conditions, G. A. Olah, M. R. Bruce, E. H. Edelson, and A. Husain, Fuel, 63(8), 1131 (1984).

Superacid Coal Chemistry. 2. Model Compound Studies under Conditions of $HF-BF_3$ Catalyzed Mild Coal Liquefaction, G. A. Olah and A. Husain, Fuel, 63, 1427 (1984).

Superacid Coal Chemistry. 3. Electrophilic Substitution of Coals under "Stable Ion" Conditions and the Conversion of Functionalized Coals with $HF:BF_3:H_2$ Liquefaction System, G. A. Olah, M. R. Bruce, E. H. Edelson, and A. Husain, Fuel, 63, 1432 (1984).

A paper presented at the 1983 Internation Conference on Coal Science, Pittsburgh, Pennsylvania. A. Husain and G. A. Olah, Proceedings of 1983 International Conference on Coal Science, 1983, page 191.