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DISCUSSION

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LOW SEVERITY COAL CONVERSION BY IONIC HYDROGENATION
Final Report for the Period July 7, 1986—December 1989

By
John W. Larsen
James Maioriello
Jane C. Cheng

August 17, 1990

Work Performed Under Contract No. FG22-85PC80908

For
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
Lehigh University
Bethlehem, Pennsylvania

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LOW SEVERITY COAL CONVERSION BY IONIC HYDROGENATION

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July 7, 1986 to December, 1989

John W. Larsen, James Maioriello
and Jane C. Cheng

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August 17, 1990

PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY
Under Contract DE-FG22-85PC80906

OBJECTIVE AND SCOPE OF WORK

Objectives

1. To develop favorable reaction conditions under which only carbon-heteroatom linkages of coal are cleaved.
2. To explore the ionic hydrogenation of low rank coals using $\text{BF}_3 \cdot \text{H}_2\text{O}$ as the acid and hydrogen gas as hydride donor in the presence of catalytic quantities of transition metal complex.

Scope of Work.

1. Reactions with model compounds will be studied to explore and characterize novel ionic hydrogenation chemistry. They will be followed using standard, appropriate techniques such as NMR and gas chromatography.
2. Interesting new ionic hydrogenation systems will be applied to coals in an attempt to develop efficient low temperature coal conversion chemistry. The degree of hydrogenation, depolymerization and other chemical changes will be evaluated by applying standard analytical techniques to the pyridine and toluene extracts of the reacted coals as well as to the solid products.

INTRODUCTION

The work accomplished in this project will be reported in two parts. Part one will focus on the development of catalytic ionic hydrogenation reactions utilizing a transition metal-H₂ complex as the hydride donor and BF₃:H₂O as proton donor. This part reports the results of preliminary work leading to the development of a new catalytic ionic hydrogenation system (MeCN)₂PtCl₂/H₂/BF₃:H₂O. The results from some of this work have been published and the paper is included as the appendix. The second part focuses on the newly developed catalytic and other well characterized ionic hydrogenation reactions applied to lignites (Beulah-Zap), sub-bituminous (Wyodak), and bituminous coals (Pittsburgh #8).

The goal of this research is to explore the low severity ionic hydrogenation of low rank coals and lignites. Ionic hydrogenation of organic compounds involves a two stage reaction; 1) formation of a carbocation in the presence of acids either by protonation of an unsaturated functional group or by cleavage of a carbon-heteroatom bond in groups such as alcohols or ethers, and 2) reduction of the cation by hydride abstraction from some donor, such as triethylsilane, isopropanol, or hydrogen gas in the presence of a proper catalyst. This reaction is selective since only functional groups which are sufficiently basic to be protonated by any particular acid will be reduced. Consequently, the reducing capability of a system can be controlled by proper choice of acid.

The ionic hydrogenation system, CF₃CO₂H/Et₃SiH is most common and has been thoroughly studied.^{1,2} This system is capable of reducing carbonyl compounds to either: 1) alcohols and ethers, or hydrocarbons, depending on the structure of the compound; 2) tertiary alcohols to hydrocarbons; and 3) tri or tetra substituted olefins to the corresponding hydrocarbons, all in good yields. When Et₃SiH is used in the presence of BF₃:H₂O (a much stronger acid than CF₃CO₂H), less basic functionalities also undergo reduction.³ For example, this pair is capable of deoxygenating or desulfurating molecules such as α -methoxynaphthalene and 1-naphthalenethiol, reductions which cannot be achieved with weaker acids such as CF₃CO₂H.

Triethylsilane and other silanes are expensive reagents and their oxidized forms are sometimes difficult to separate from the desired reduced products. Consequently, their use in low severity coal conversion is not attractive. Hydrogen gas can be activated as a hydride donor for ionic hydrogenation reactions⁴ and it regenerates a proton on reaction. These systems are catalytic in acid, and both hydrogen atoms added ultimately come from hydrogen gas, while still maintaining the selectivity typical of stoichiometric ionic hydrogenation reactions. While the literature contains sporadic evidence that this chemistry is feasible^{4,5}, it has not been thoroughly explored and warrants study and extension.

Our approach was to develop systems of acid and soluble transition metal complex which will activate hydrogen gas as a source of hydride ion for ionic hydrogenation reactions. The activity of potential systems can be determined by studies of small molecules emphasizing compounds that typify coal structure. Coal itself, is too complex to use for probing new reaction systems. Once found and well characterized, the new systems were applied to low rank coals and lignites in attempts to selectively depolymerize and hydrogenate coals.

The only published application of ionic hydrogenation to coals used super acids and hydrogen gas for the nonselective depolymerization of the coals^{6,7}. A more selective depolymerization reaction would consume hydrogen more selectively, provide feedstock for catalytic upgrading, and give an interesting array of products which might provide insight into coal structure. Ionic hydrogenation reactions employing $\text{BF}_3 \cdot \text{H}_2\text{O}$ as proton donor in the presence of Et_3SiH as hydride donor³, are capable of cleaving aromatic ethers and phenols, functionalities which are prevalent in low rank coals and lignites⁸. The ability of $\text{BF}_3 \cdot \text{H}_2\text{O}$ to protonate oxygen containing PNA's makes it an attractive choice as acid for this reaction, since this will result in cleavage of crosslinking sites that perpetuate throughout the macromolecular structure of low rank coals and lignites. It is also inexpensive, compatible with water, and is now used commercially.

We began by replicating a literature process as shown below using a Teflon lined autoclave (Berghoff, 250 mL).⁹

With some modifications, complete reaction was achieved. Not all acid/transition metal complex pairs were effective in the reduction of triphenylmethanol to triphenylmethane. In particular, $(\phi_3\text{P})_2\text{PtCl}_2$ in $\text{BF}_3\cdot\text{H}_2\text{O}$ was not effective in this reduction. This catalyst is insoluble in this acid. Since we valued the attractive features of $\text{BF}_3\cdot\text{H}_2\text{O}$ for the ionic hydrogenation of coals, we sought catalysts that were soluble in this acid, small to facilitate mass-transport into the coal, and active in the reduction.

The most active catalyst tried was $(\text{MeCN})_2\text{PtCl}_2$ ¹⁰. This platinum complex is both soluble in $\text{BF}_3\cdot\text{H}_2\text{O}$ and active at 50°C , using 500 psi of hydrogen, and 1 mol% of catalyst for 24 hrs. In general, this system is capable of cleaving aryl ethers to a mixture of saturated and partially saturated products. Nitrogen containing aromatics are partially saturated and no carbon-nitrogen bond cleavage occurs. As might be expected, reduced forms of sulfur (thiophenol, diphenyl sulfide, benzothiophene) poison the catalyst. Oxidized forms of sulfur (sulfoxides and sulfonic acids) are not poisons and are not reduced. Part 1 of this report describes the results of our work on the development of new and interesting catalytic ionic hydrogenation systems.

$\text{NaBH}(\text{OAc})_3$ was screened as a potential hydride donor for use in ionic hydrogenation reactions. This compound is known to react faster with the more electrophilic aldehydic than ketonic carbonyl¹¹. In fact, this absolute rate difference is used to selectively reduce aldehydes

in the presence of ketones. This reagent to be a poor hydride donor for ionic hydrogenation reactions because it is consumed rapidly by reacting with the acid to give hydrogen gas and its use results in the formation of complex product mixtures.

Part 2 will detail our work on the application of catalytic ionic hydrogenation using $(\text{MeCN})_2\text{PtCl}_2/\text{H}_2/\text{BF}_3\cdot\text{H}_2\text{O}$ and other more traditional ionic hydrogenation reactions to coals and/or their extracts. Applications of the above reaction (using the same conditions, but with 10% wt of $(\text{MeCN})_2\text{PtCl}_2$) to Wyodak coal (74% C, dmmf. Argonne), resulted in no increase in tetrahydrofuran (THF) extractability (6.7% wt for nonreacted coal vs. 5.8% wt for hydrogenated coal). No improvement was observed when reaction period was extended to two weeks. Elemental analysis of the reacted coals showed no increase in hydrogen content over that of the nonreacted coals.

We also attempted to react Beulah Zap lignite with the sulfur tolerant heterogeneous catalyst MoS_2 , impregnated as a water soluble tetrathiomolybdate complex according to a procedure recently published¹². The lignite was significantly altered from this procedure and therefore this reaction proved to be useless for our purpose.

Wyodak coal contains a small amount of sulfur (0.63 %, dry basis) which is a catalyst poison. To determine whether this was repressing the reaction, we obtained from Dr. Ron Liotta of Exxon, a sample of Texas lignite in which all of the organic sulfur had been oxidized to sulfoxides and sulones. These are not poisons. Many of the benzylic positions in the coal were also oxidized. Our attempts to reduce this lignite also failed demonstrating that poisoning by sulfur was not the reason for the failure of the reaction.

Mass transport into solid coal or rapid condensation reactions may be preventing the ionic hydrogenation. To minimize these problems, our studies were extended to the ionic hydrogenation of THF extracts obtained from several coals (Wyodak and Pittsburgh #8). Ionic hydrogenation of these extracts gave products whose number average molecular weight M_N (determined by gel permeation chromatography, GPC) increased. Elemental analysis revealed that a modest amount of hydrogen was incorporated into the coal.

Coal and coal extracts were not depolymerized ionic hydrogenation reactions. In fact, extracts were observed to polymerize in the presence of acid, probably via Freidel-Craft type alkylation reactions. In our systems, transalkylation appears to competes quite effectively with hydride abstraction even when triethylsilane is employed as the donor. This is consistent with the observation that extracts obtained from lower rank coals such as Wyodak (consequently more polar and with higher oxygen content) underwent larger increases in $\bar{M}_N$. New and interesting ionic hydrogenation chemistry has been developed, but it is not effective at depolymerizing or hydrogenating coals.

PART 1

CATALYTIC IONIC HYDROGENATION USING H_2 AS A HYDRIDE DONOR

EXPERIMENTAL

Chemicals were used as purchased except for trifluoroacetic acid which was distilled from concentrated sulfuric acid. Borontrifluoride monohydrate ($BF_3 \cdot H_2O$) was prepared by bubbling BF_3 into water, the ratio of $BF_3 \cdot H_2O$ was monitored by weight increase. Reactions were carried out in a 50 mL glass erlenmeyer flask, whose bottom was made concave (to facilitate stirring), half-embedded with sand in a Teflon-lined stainless steel 250 mL autoclave (Berghof) with magnetic stirring. The product(s) and, when the reaction was incomplete, the unreacted starting material, were isolated from the reaction mixture by neutralizing it with aqueous base, followed by extraction with either methylenechloride or diethyl ether. Individual components were separated by silica gel flash chromatography or preparative thin layer chromatography (methylene chloride or hexanes-methylene chloride as eluant). The products were identified by comparing their 1H and ^{13}C NMR spectra (JOEL FX 90Q Spectrometer), and gas chromatography retention times (Hewlett-Packard 5880A series with crosslinked methyl silicone capillary column) with those of known compounds. When necessary, further structural data was obtained by means of GC-MS measurements (Supelco fused silica capillary column, Finnegan 4023 GC/MS/DS system operating at 70 eV), and by elemental analyses (Robertson Laboratory, Inc., Madison, NJ).

GENERAL REACTION PROCEDURE.

The general procedure for conducting the reactions described in this report will be included in this section. More complete experimental procedures can be found in the appendix at the end of the report, which contains our published results. The solid catalyst was first introduced into a 50 mL erlenmeyer flask and then dissolved in the acid. The substrate to be reduced was added and the flask was placed in a Teflon lined autoclave. The reactor was

purged with 50 psi of hydrogen three times. Slowly, the reactor was charged to the appropriate pressure with hydrogen and brought to reaction temperature in about 45 min. After the reaction period was complete, the autoclave was allowed to cool (1 hr.) and was slowly (1 hr) depressurized. The reaction mixture was dissolved in dichloromethane and neutralized with either a saturated aqueous sodium bicarbonate or 4N aqueous sodium hydroxide solution. The two layers were separated and the aqueous phase was extracted several times with additional dichloromethane. All organic layers were combined, dried over anhydrous magnesium sulfate, and filtered. The reaction product mixtures were concentrated in vacuo, and analyzed as described above.

SOLUBILITY MEASUREMENTS OF AROMATIC COMPOUNDS IN $\text{BF}_3\cdot\text{H}_2\text{O}$

Sample preparation. A mixture of aromatic compound (250 mg) and $\text{BF}_3\cdot\text{H}_2\text{O}$ (7 mL) in a 15 mL vial equipped with a Teflon-lined lid was stirred at 22°C for 2 days. The mixture was left undisturbed (no stirring) until the undissolved aromatic compound floated to the top of the dense acid and the saturated $\text{BF}_3\cdot\text{H}_2\text{O}$ layer was clear. A small portion of the liquid was transferred with a syringe to a UV cell (1 mm. path length) for measurement at 22°C. For anthracene, the solution was diluted to 1% of its saturated concentration (5 μL of saturated solution and 0.5 mL fresh $\text{BF}_3\cdot\text{H}_2\text{O}$) before measurement. The remainder of the above mixture was stirred at 50°C for 1 day. The same procedure described above was followed except for the temperature which was kept at 50°C.

Determination of solubility by UV spectroscopy. All the UV spectra were measured with a Perkin Elmer Lambda 5 UV/VIS spectrophotometer at either 22°C or 50°C. Since benzene, naphthalene, and phenanthrene were mainly unprotonated in $\text{BF}_3\cdot\text{H}_2\text{O}$ and their UV spectra were essentially identical to those measured in organic solvents, the molar extinction coefficients of benzene in hexane ($\log \epsilon$ 3.9, λ_{max} 198 nm), naphthalene ($\log \epsilon$ 5.1, λ_{max} 220 nm) and phenanthrene ($\log \epsilon$ 4.7, λ_{max} 250 nm) both in ethanol were used for solubility calculations¹⁴. For anthracene, which was mainly protonated in $\text{BF}_3\cdot\text{H}_2\text{O}$, a molar extinction coefficient of protonated anthracene ($\log \epsilon$, 4.5, λ_{max} 425 nm) in concentrated sulfuric acid was

used¹⁵. For 1- and 2-methylnaphthalene, the necessary molar extinction coefficients were determined by UV measurements on freshly prepared $\text{BF}_3\cdot\text{H}_2\text{O}$ solutions of these compounds of known concentrations: 1-methylnaphthalene, $\log \epsilon$ 4.1, (λ_{max} 387 nm); 2-methylnaphthalene, $\log \epsilon$ 3.8, (λ_{max} 389 nm).

DISCUSSION

We began by replicating a literature process (see Table 1), and with some modifications, were able to achieve quantitative reduction. Under milder reaction conditions than reported in the literature (e.g., 500 psi of hydrogen, 50°C, 1 mol% of catalyst, and 24 hrs., 72%), excellent yields were obtained. Table 1 shows the results from a series of reactions using trifluoroacetic acid as a reaction medium and $(\phi_3P)_2PtCl_2$ as the catalyst under a variety of conditions. As expected, the reaction yields increase with increased hydrogen pressure, increased mole percent of catalyst, increased reaction temperature, and increased reaction times (see Table 1). Entries 4, 6, and 7, 8 indicate that comparable yields can be obtained using less platinum complex but longer reaction periods. It is obvious that the reaction is not first-order with respect to $(\phi_3P)_2PtCl_2$. With no catalyst or with added Pt^0 , the starting material was unchanged after one day (entries 10,11).

The activity of $(\phi_3P)_2PtCl_2$ in reducing triphenylmethanol under catalytic ionic hydrogenation conditions is also sensitive to the acid solvent used to form the carbenium ion (Table 2). Surprisingly, $BF_3:H_2O$ (acid strength similar to 100% H_2SO_4 ¹⁶) did not cause conversion of triphenylmethanol to triphenylmethane (Table 2, entries 3--5). UV measurement of the platinum complex in $BF_3:H_2O$ indicated that little, if any, of this catalyst was dissolved in this acid.

Quantitative formation of triphenylmethane was observed when either $Et_2O:BF_3$ or $BF_3:MeOH$ (50% w/w) were used as acid (Table 2, entries 6,7). $TsOH:H_2O$ /toluene ($TsOH$ is p-toluenesulfonic acid) system seems quite promising since $TsOH:H_2O$ is cheap, non-fuming and mild. This system led to the formation of triphenylmethane in 90% yield, despite low solubilities of ϕ_3COH , $TsOH:H_2O$, and $(\phi_3P)_2PtCl_2$ in toluene.

Similar reactions of 1-methoxynaphthalene and 1-tetralone in trifluoroacetic acid were attempted and representative results are shown in Table 3. Both materials are less reactive than triphenylmethanol under the reaction conditions used. Unlike ionic hydrogenation using $Et_3SiH/BF_3:H_2O$, which reduced 1-methoxynaphthalene first to the more reactive

intermediate 1-tetralone then to tetralin³, the $(\phi_3P)_2PtCl_2$ system converted 1-methoxynaphthalene only to 1-tetralone. We have no explanation for this interesting selectivity difference between the platinum complex and the silane hydride donors, nor why 1-tetralone survives in the system.

All the acids listed in Table 2 were also employed for hydrogenation of 1-methoxynaphthalene using 4.2 mol % of platinum complex. Only trifluoroacetic acid was promising, the rest of the acids causing neither tetralin nor tetralone formation.

$(\phi_3P)_2PtCl_2$ is insoluble in $BF_3 \cdot H_2O$ and probably accounts for its lack of activity in this acid. The attractive features of using $BF_3 \cdot H_2O$ as acid prompted a search for smaller, preferably $BF_3 \cdot H_2O$ soluble (or water soluble¹⁴) catalysts. Other transition metal complexes were also studied. $Pd(OAc)_2$ is soluble in three acids tested (Tables 4 and 5, entries 5-7), but hydrogenation was observed only CF_3CO_2H . In CF_3CO_2H , this catalyst is capable of reducing triphenylmethanol to triphenylmethane in 65% yield (Table 4, entry 5), and 1-methoxynaphthalene to a mixture of tetralone (21%) and tetralin (79%) (Table 5, entry 5).

Only $PtCl_2$ (insoluble in $BF_3 \cdot H_2O$) was active in $BF_3 \cdot H_2O$. This system can hydrogenate triphenylmethanol to triphenylmethane (10% yield, see Table 4, entry 8) and 1-methoxynaphthalene to 1-tetralone (19% yield, see Table 5, entry 8) in low yields. Reactions of triphenylmethanol or 1-methoxynaphthalene in CF_3CO_2H with $PtCl_2$ as catalyst yielded aliphatic hydrocarbons as major or only products (entry 4). Similar reactions employing $PdCl_2$, a weaker catalyst than $PtCl_2$, did not yield any reduced products (entries 8,9).

The low activity of $PtCl_2$ and $(\phi_3P)_2PtCl_2$ as ionic hydrogenation catalysts is probably due to their insolubility in $BF_3 \cdot H_2O$. $(P\phi_3)_2PtCl_2$ may be insoluble because of the bulky organic triphenylphosphine ligands and $PtCl_2$ is polymeric with bridging chlorine. Small neutral ligands (CO or CH_3CN) may provide a monomeric, soluble, and more active catalyst. The first such ligand tried was CH_3CN .

The best catalyst and therefore used most frequently is bis(acetonitrile)-platinum(II)dichloride $((CH_3CN)_2PtCl_2)$. It is much smaller than $(\phi_3P)_2PtCl_2$, and soluble in

$\text{BF}_3\cdot\text{H}_2\text{O}$. $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$, another soluble catalyst, is less reactive than its platinum analog, but demonstrates a selectivity that is different from its platinum counterpart. We will elaborate on this point later in this section. $(\text{CH}_3\text{CN})_2\text{Pt}(\text{O}_2\text{CCF}_3)_2$ was also found to be a potentially useful catalyst although it is slightly less reactive than $\text{Pt}(\text{MeCN})_2\text{Cl}_2$ (Tables 6 and 7, entries 1-3).

Since an inorganic black precipitate was observed after hydrogenation of model compounds in the $(\text{CH}_3\text{CN})_2\text{PtCl}_2/\text{BF}_3\cdot\text{H}_2\text{O}$ system, we intentionally hydrogenated $\text{Pt}(\text{CH}_3\text{CN})_2\text{Cl}_2$ in $\text{BF}_3\cdot\text{H}_2\text{O}$ without substrates. The reduced species (Pt^0) shows very low catalytic activity (Tables 6 and 7, entries 5 and 6) suggesting that the $(\text{CH}_3\text{CN})_2\text{PtCl}_2$ catalyzed ionic hydrogenation reactions are largely homogeneous. The appendix includes other experimental evidence supporting a homogeneous reaction.

The effect of aromatic thiols, sulfides, and thiophenes, which are the major forms of organic sulfur in coals, on the catalyst was investigated. As expected, these compounds all poison the catalyst $(\text{CH}_3\text{CN})_2\text{PtCl}_2$ (Tables 6 and 7, entry 4). A cupric salt (CuCl_2) was added to the reaction mixture in an attempt to inhibit poisoning by complexing the sulfur. The copper had no effect (Table 6, entry 8; Table 7, entry 9). When oxidized (Tables 6 and 7, entry 7), these sulfur containing compounds do not stop the ionic hydrogenation reactions, but decreased catalytic activity was observed (Table 7, entry 7). These oxidized sulfur forms are not reduced during the reaction (Table 8, entries 11-13).

The formation of 1-naphthol from 1-methoxynaphthalene is a result of hydrolysis. It is observed (Table 7) when the catalyst is reduced (5a and 6a), retarded, (7), poisoned (9), or absent (6b and 8). Reduced hydrogen pressure (100 psi) favors its formation. Otherwise 1-naphthol is reduced to D as the major product (Table 8, entry 4; also Table 7, entries 1 and 5b). 1-naphthol formation is less favored at room temperature (8b). It is not clear why it is not observed in reaction 4 (Table 7).

Generally, about 15% (wt) of unknown dimers were observed (GC-MS) for the reactions listed in Table 7. These dimers are formed with or without hydrogen and/or catalyst

and are believed to result from acid catalyzed condensation reactions.

Table 8 includes a summary of the results of ionic hydrogenation of model compounds for coals. A variety of oxygenated compounds were subjected to the ionic hydrogenation reaction $(\text{CH}_3\text{CN})_2\text{PtCl}_2/\text{H}_2/\text{BF}_3\cdot\text{H}_2\text{O}$ and generally deoxygenated and fully saturated products were formed. In addition to the results described in previous tables, Table 8 also lists the results of other reactions: phenolic hydroxyl groups (entry 4) were partly removed and the starting material was completely converted to a mixture of partially saturated, fully saturated, and deoxygenated products. 1-tetralone (entry 3) shows some resistance to reduction by this method as this substrate was only partly converted to reduced products. Interestingly, the product distribution contained no tetralin, a typical product usually obtained from more traditional ionic hydrogenation methods². Xanthene (entry 5) was reduced to bicyclohexylmethane (50%) and other partially reduced products (35%). On the other hand, dibenzofuran (entry 6) was only partially converted to a mixture of reduced products (bicyclohexylmethane yield was 16%). Anthrone and anthraquinone (entries 7 and 8) were reduced to a mixture of fully and partially saturated compounds, generating the same products in different distributions. No starting material remained for either substrate.

The ability of this reaction to reduce aromatic nitrogen containing compounds was also studied (Table 8, entries 9-11). These reactions resulted in partial saturation of aromatic rings without cleavage of C-N bonds. Hydrogenation occurred preferably on the ring without the nitrogen resulting in partially hydrogenated products. Presumably, the nitrogen bases required diprotonation and the second protonation will occur selectively on the ring furthest away from the ammonium ion. Reaction of the nitrogen-bearing ring is prevented by its low basicity, which results from nitrogen protonation. Hydrogenating indole yielded dimers, trimers and other by-products in addition to its reduction product, indoline (<30 %).

The ionic hydrogenation of aromatic hydrocarbons was also studied, and we observed surprising structure-reactivity relationships. Benzene and naphthalene (Table 8, entries 12 and 13) which are not reduced by $\text{BF}_3\cdot\text{H}_2\text{O}/\text{Et}_3\text{SiH}$, are completely reduced to cyclohexane and

decalin, respectively. These reactions demonstrate the stronger hydrogenating power of $(\text{CH}_3\text{CN})_2\text{PtCl}_2/\text{H}_2/\text{BF}_3\cdot\text{H}_2\text{O}$ over that of $\text{BF}_3\cdot\text{H}_2\text{O}/\text{Et}_3\text{SiH}^{3,10}$. 1-methylnaphthalene (Table 8, entry 14) is hydrogenated to 1-methyldecalin and a minor amount of 5-methyltetralin (3%). 2-methylnaphthalene (entry 15) is not easily reduced (79% recovered). We have no explanation for this unusual selectivity. There are large differences in reactivity for large PNA's. Anthracene and phenanthrene (entries 16 and 17) show a large difference in reactivity, which is presumably caused by the difference in basicity of the two molecules. Anthracene is about 10^8 more basic than phenanthrene¹⁷. We will address the reactivity difference later in this section. Chrysene is not reduced at all, despite our attempts to optimize reaction conditions for its reduction. It is well known that the basicity of PNAs increases with molecular weight, but the increased basicity for large PNAs does not appear to enhance their reactivity, because $\text{BF}_3\cdot\text{H}_2\text{O}$ is acidic enough to cause hydrogenation of benzene, which is a 10^{13} -fold weaker base than anthracene¹⁷. Other factors such as decreased solubility (Table 9) for larger PNAs in $\text{BF}_3\cdot\text{H}_2\text{O}$ seem to outweigh their increasing basicity. Phenanthrene is intermediate in basicity between benzene and anthracene, but is less reactive than either.

It is not clear why 2-methylnaphthalene is more difficult to reduce than its 1-isomer. Solubility and H/D exchange studies (Tables 9 and 10) show that both molecules are soluble in and protonated by $\text{BF}_3\cdot\text{H}_2\text{O}$. Clearly, protonated 1-methylnaphthalene accepts hydride much more readily than the 2-isomer. It is easy to speculate about steric effects, but pointless until the active hydride donor is characterized.

There is also a large difference in reactivity between anthracene and phenanthrene, with phenanthrene being quite unreactive. Anthracene is about 10^8 times more basic than phenanthrene. Solubility decreases with molecular size. Anthracene, being the most basic molecule, is significantly protonated and so its solubility is higher. The least soluble molecule, phenanthrene, is the least reactive. All of these molecules undergo H/D exchange in $\text{BF}_3\cdot\text{D}_2\text{O}$. This demonstrates that hydride abstraction is the rate limiting step. Although quite basic, chrysene is not reduced. Apparently it is insoluble due to its large size and strong crystal

interactions.

1-Naphthoic acid was not reduced under standard reaction conditions. We believe that the presence of a strong electron withdrawing group such as $-\text{COOH}$ (or $-\text{SO}_3\text{H}$, $-\text{SO}_2-$) decreases the basicity of the parent molecules enough to prevent protonation, thus stopping the reaction.

Table 11 displays the results of catalytic ionic hydrogenations reactions employing $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ as catalyst on a select group of substrates. The first point to note is $(\text{MeCN})_2\text{PdCl}_2$ is less reactive than its platinum analog. But, the most interesting feature is the difference in selectivity between the two catalysts. The palladium catalyst is capable of reducing both 2-methyl and 2-ethylnaphthalene to a mixture of partially and fully reduced products. The platinum catalyst was shown to be ineffective in reducing these same compounds. We have no explanation for this difference in reactivity.

CONCLUSION

A newly developed reaction system consisting of $(\text{CH}_3\text{CN})_2\text{PtCl}_2/\text{H}_2/\text{BF}_3\cdot\text{H}_2\text{O}$ was applied to the ionic hydrogenation of aromatic and functionalized aromatic compounds. Hydrogenations are carried out in this aqueous system at 50°C and 500 psi of hydrogen. Aryl ethers are hydrogenated and cleaved yielding deoxygenated, fully saturated compounds as the major products. Reactions of nitrogen-containing aromatic compounds resulted in partial saturation of aromatic rings without cleavage of the C-N bonds. Aromatic and PNA compounds can be fully or partially hydrogenated depending on their structures. Aromatic thiols, sulfides, and thiophene poison the catalyst; the oxidized sulfur forms (sulfonic acids and sulfones) are not reduced and do not poison the catalyst.

Table 1. Ionic hydrogenation of triphenylmethanol in trifluoroacetic acid.

Entry	Reaction code No.	(Ph ₃) ₂ PtCl ₂ (mmol %)	P(H ₂) (psi)	Time (hr)	Yield (%)	Turnover number
1	J-1:1	4.2	1300	45	100	24
2	J-1:2	4.2	1000	45	100	24
3	J-1:14	4.2	500	24	95	23
4	J-1:11	4.2	500	12	67	16
5	J-1:3	1.0	1000	45	100	100
6	J-1:13	1.0	500	24	72	72
7	J-1:10	1.0	500	12	50	50
8	J-1:12	.25	500	24	50	200
9	J-1:9	.25	500	12	29	116
10	J-1:12'	0.0	500	24	0	0
11	J-1:8	Pt ⁰	500	26	0	0
12	Literature ⁷ (20°C)	4.2	1470	150	19	4.5

TABLE 2. The effect of acid on ionic hydrogenation of triphenylmethanol.

$$\text{Ph}_3\text{COH} \xrightarrow[\text{24 hr.}]{\text{H}_2, (500 \text{ psi}) / (\phi_3\text{P})_2\text{PtCl}_2 (1 \text{ mole\%})} \text{Ph}_3\text{CH}$$

Entry	Reaction code No.	Acid used	Temp (°C)	Yield (%)
1	J-1:18	CF ₃ COOH	22	6
2	J-1:15	CF ₃ COOH	50	70
3	J-1:19	BF ₃ :H ₂ O	22	0
4	J-1:22	BF ₃ :H ₂ O	50	0
5	J-1:23	BF ₃ :H ₂ O/CH ₂ Cl ₂	50	0
6	J-1:16	BF ₃ :Et ₂ O	50	100
7	J-1:17	BF ₃ /2MeOH	50	100
8	J-1:20	CF ₃ SO ₃ H	50	0
9	J-1:21	TsOH/toluene	50	90

TABLE 3. The effect of reactants on ionic hydrogenation.

reactant	product	yield(%)
Ph ₃ COH	Ph ₃ CH	95
1-tetralone	35
tetralin	10

Reaction condition

H₂ (500 psi), (φ₃P)₂PtCl₂ (4.2 mole %), TFA, 50°C, 25 hr.

Table 4. Ionic Hydrogenation of Triphenylmethanol

$\text{Ph}_3\text{COH} \xrightarrow[24 \text{ hr}]{500 \text{ psi H}_2, 50^\circ\text{C}} \text{Ph}_3\text{CH}$					
Entry	Reaction code	Catalyst (mol %)	Acid used	Yield (%)	Comment
1	J-1:24	L_2PtCl_2 (1)	$\text{TsOH-CH}_2\text{Cl}_2$	94	$\text{L}=\text{Ph}_3\text{P}$
2	J-1:25	L_2PtCl_2 (1)	TsOH-PhOH	0	$p\text{-Ph}_3\text{C-C}_6\text{H}_4\text{-OH}$ (100%)
3	J-1:17	L_2PtCl_2 (1)	$\text{BF}_3\text{-2MeOH}$	100	
4	J-1:26	PtCl_2 (1)	CF_3COOH	0	$\text{Ph}_3(\text{Alkyl})$, etc. $\text{H(ar)}:\text{H(al)} \approx 1:10$ ($^1\text{H NMR}$)
5	J-1:27	Pd(OAc)_2 (1)	CF_3COOH	65	
6	J-1:28	Pd(OAc)_2 (1)	$\text{BF}_3:\text{MeOH}$	0	
7	J-1:29	Pd(OAc)_2 (1)	$\text{BF}_3:\text{H}_2\text{O}$	0	
8	J-1:30	PtCl_2 (1)	$\text{BF}_3:\text{H}_2\text{O}$	10	
9	J-1:31	PdCl_2 (1)	$\text{BF}_3:\text{H}_2\text{O}$	0	

Table 5. Ionic Hydrogenation of 1-Methoxynaphthalene

Entry	Reaction code	Catalyst (mol %)	Acid used	Yield (%)	Comment
1	J-2:12	L ₂ PtCl ₂ (4)	TsOH-CH ₂ Cl ₂	0	L=Ph ₃ P
2	J-2:13	L ₂ PtCl ₂ (4)	TsOH-PhOH	0	"
3	J-2:14	L ₂ PtCl ₂ (4)	BF ₃ :MeOH	9	"
4	J-2:15	PtCl ₂ (4)	CF ₃ COOH	0	Aliphatic prod. 100%
5	J-2:16	Pd(OAc) ₂ (1)	CF ₃ COOH	21	 79%
6	J-2:17	Pd(OAc) ₂ (1)	BF ₃ :MeOH	0	
7	J-2:18	Pd(OAc) ₂ (1)	BF ₃ :H ₂ O	0	
8	J-2:19	PtCl ₂ (1)	BF ₃ :H ₂ O	19	
9	J-2:20	PdCl ₂ (1)	BF ₃ :H ₂ O	0	

Table 6. Ionic Hydrogenation of Triphenylmethanol

Entry	Reaction code	Catalyst (mol %)	Yield (%)	Comment
1	J-1:32	$\text{L}'_2\text{PtCl}_2$ (1)	53	$\text{L}' = \text{CH}_3\text{CN}$
2	J-1:33	$\text{L}'_2\text{PdCl}_2$ (1)	29	
3	J-1:34	$\text{L}'_2\text{Pt}(\text{TFA})_2$ (1)	50	$\text{TFA} = \text{CF}_3\text{CO}_2$
4a	J-1:35a	$\text{L}'_2\text{PtCl}_2$ (1)	53	no sulfur compd. (control exp.)
4b	J-1:35b	$\text{L}'_2\text{PtCl}_2$ (1)	4	10 mol%
4c	J-1:35c	$\text{L}'_2\text{PtCl}_2$ (1)	0	10 mol%
4d	J-1:35d	$\text{L}'_2\text{PtCl}_2$ (1)	0	10 mol%
a _{5a}	J-1:36a	Pt^0 (1)	9	reduced mixture $\text{L}'_2\text{PtCl}_2/\text{BF}_3:\text{H}_2\text{O}$ was used
5b	J-1:36b	$\text{L}'_2\text{PtCl}_2$ (1)	58	(control exp.)
a _{6a}	J-1:37a	Pt^0 (1)	4	Pt^0 (fresh) + $\text{BF}_3:\text{H}_2\text{O}$ (fresh)
a _{6b}	J-1:37b	$\text{L}'_2\text{PtCl}_2$ (1)	0	$\text{BF}_3:\text{H}_2\text{O}$ (Pt^0 removed)

Table 6: (cont.)

Entry	Reaction code	Catalyst (mol %)	Yield (%)	Comment
7a	J-1:38a	L_2PtCl_2 (1)	73	10 mol% SO_3H
7b	J-1:38b	L_2PtCl_2 (1)	57	10 mol%
7c	J-1:38c	L_2PtCl_2 (1)	52	10 mol%
8a	J-1:39a	L_2PtCl_2 (1)	0	10 mol% SH 10 mol% $CuCl_2$
8b	J-1:39b	L_2PtCl_2 (1)	4	10 mol% SH 10 mol% $CuCl_2$
8c	J-1:39c	L_2PtCl_2 (1)	0	10 mol% SH 10 mol% $CuCl_2$
8d	J-1:39d	—	0	10 mol% SH 10 mol% $CuCl_2$
8e	J-1:39e	—	0	10 mol% $CuCl_2$

a: A yellow solution of $(CH_3CN)_2PtCl_2/BF_3 \cdot H_2O$ was reduced (500psi H_2 , $50^\circ C$, 24hr) to form a clear solution with black precipitate. This mixture was used for reaction 5a. To test the completeness of this $(CH_3CN)_2PtCl_2$ reduction, another experiment was performed: a mixture of the black precipitate, separated from its clear solution, and freshly added $BF_3 \cdot H_2O$ was used in reaction 6a; the resulting clear solution was used in reaction 6b.

Table 7. Ionic Hydrogenation of 1-Methoxynaphthalene

Entry	Reaction code	Catalyst (mol %)	Product (Yield %)	Comment
a ₁	J-2:21	L ₂ PtCl ₂ (1)	B(69) D(19)	L' = CH ₃ CN
2	J-2:22	L ₂ PdCl ₂ (1)	B(7) C(4)	
3	J-2:23	L ₂ Pt(TFA) ₂ (1)	B(46) C(17)	TFA = CF ₃ CO ₂
4a	J-2:24a	L ₂ PtCl ₂ (1)	B(34)	no Sulfur compd (control exp.)
4b	J-2:24b	L ₂ PtCl ₂ (1)	(0)	10 mol%
4c	J-2:24c	L ₂ PtCl ₂ (1)	(0)	10 mol%
4d	J-2:24d	L ₂ PtCl ₂ (1)	(0)	10 mol%
b _{5a}	J-2:25a	Pt ⁰ (1)	A(16) B(9) E(60) other prods(-15)	reduced mixture L ₂ PtCl ₂ /BF ₃ :H ₂ O was used
a _{5b}	J-2:25b	L ₂ PtCl ₂ (1)	B(2) D(9) F(66)	(control exp.)
b _{6a}	J-2:26a	Pt ⁰ (1)	A(28) B(6) E(41)	Pt ⁰ (fresh) + BF ₃ :H ₂ O(fresh)
b _{6b}	J-2:26b	L ₂ PtCl ₂ (1)	A(6) E(40)	BF ₃ :H ₂ O (Pt ⁰ removed)

Table 7. (Cont.)

Entry	Reaction code	Catalyst (mol %)	Product (Yield %)	Comment
7a	J-2:27a	L_2PtCl_2 (1)	A(15) B(29) E(32)	10 mol%
7b	J-2:27b	L_2PtCl_2 (1)	A(14) B(54) E(8)	10 mol%
7c	J-2:27c	L_2PtCl_2 (1)	A(13) B(55) E(9)	10 mol%
8a	J-2:28a	—	A(19) E(43)	
8b	J-2:28b	—	A(24) E(10)	room temp, no H_2
8c	J-2:28c	—	A(5) E(47)	50°C, no H_2
9a	J-2:29a	L_2PtCl_2 (1)	A(18) E(50)	10 mol% 10 mol% $CuCl_2$
9b	J-2:29b	L_2PtCl_2 (1)	A(24) E(41)	10 mol% 10 mol% $CuCl_2$
9c	J-2:29c	L_2PtCl_2 (1)	A(18) E(44)	10 mol% 10 mol% $CuCl_2$
9d	J-2:29d	—	A(10) E(52)	10 mol% 10 mol% $CuCl_2$
9e	J-2:29e	—	A(12) E(51)	10 mol% $CuCl_2$

a: A difference in product distribution from reactions with same scale was observed as a result of using glass test tubes with different sizes. From reactions J-2:25 (entry 5) and on, larger test tubes were used, which generates more hydrogenated products.

b: See footnote a of Table I.

Table 8. Ionic Hydrogenation Results

reactant		(MeCN) ₂ PtCl ₂ (1 mole % of reactant)			product(s)				
		H ₂ (500psi), H ₂ O:BF ₃ , 50°C, 24 hr							
entry	reactant	product (% of product)			total yield %	recovered reactant %	comment		
1	Ph ₃ COH	Ph ₃ CH (53-58)			53-58	44-39	a		
2a		(2)	(9)	(66, 86% cis)	77	none	b		
2b	..	.. (37)	.. (4)	.. (39, 96% cis)	80	none	21°C, b		
3		(4)	(33, 84% cis)		37	36	b		
4		(10)	(11)	(60, 86% cis)	81	none	b		
5		(50)	other prod ^c (-35)		-85	none	b		
6		(17)	(16)	...	33	55	a		
7		(48)	(38)	(4)	90	none	a		
8		.. (81)	..	.. (10)	91	none	b		
9		(49)	(25)	(7)	81	none	b		
10		(1)	(75)		76	4	b		
11		(81)			81	none	b		
12		(47) ^d			47	none	b		
13		(83, 90% cis)			83	none	b		
14		(70)	(3)		73	none	b		
15		(13)			13	79	a		
16		(4)			4	86	a		
17		(22)	(13)		81	6	b
		(13)	(33)						

a. NMR yield. b. Isolated yield. c. Partially reduced products. d. The product cyclohexane was partially lost during depressurization even when two consecutive cold-traps (liquid nitrogen) were used.

Table 9. Solubility of Aromatic Compounds in $\text{H}_2\text{O}:\text{BF}_3$ ^a

compd	pK_B (in HF) ^b	major form in $\text{H}_2\text{O}:\text{BF}_3$	solubility (mol/L) ^c	
			22°C	50°C
9.2	unprotonated	2.2×10^{-3}	2.9×10^{-3}
4.0	unprotonated	1.3×10^{-4}	1.8×10^{-4}
^d	1.7	protonated	1.7×10^{-3}	1.8×10^{-3}
^d	1.4	protonated	3.9×10^{-3}	4.2×10^{-3}
3.5	unprotonated	2.4×10^{-5}	1.0×10^{-4}
^e	-3.8	protonated	7.0×10^{-2}	4.4×10^{-2}

^a. Measured by UV spectroscopy, see Experimental Section.

^b. Brouwer, D. M.; Mackor, E. L.; MacClean, C. In Carbonium Ions; Olah, G. A.; Schleyer, P. v. R. Eds.; Wiley Interscience: New York; 1970; Vol. 2, pp 837-897.

^c. Determined from the major form of the aromatic compound in $\text{H}_2\text{O}:\text{BF}_3$, i.e., either protonated or unprotonated. See Experimental Section for the molar extinction coefficients used in the calculations.

^d. Methyl rearrangement was observed. For 1-methylnaphthalene, the ratio of 1-methylnaphthalene to 2-methylnaphthalene was 1:1; for 2-methylnaphthalene, the ratio was 1:9. No demethylation was detected.

^e. Diluted to 1 % of the original concentration, i.e., 0.5 mL of fresh $\text{H}_2\text{O}:\text{BF}_3$ was added to 5 μL of original solution.

Table 10. Deuteration of Aromatic Compounds^a

compd	H-D exchange(%) ^b	comments
91	: = 1:1
94	: = 1:9
93	

a. Reaction conditions: 350 mg of aromatic compound in 7 mL of D₂O:BF₃, 22°C, 43 hr with stirring. For analysis of deuterium exchange, see ref. 8.

b. The highest possible H-D exchange is 96% based on the exchangeable aromatic protons and available deuterium from D₂O:BF₃.

c. No H-D exchange was observed for methyl protons, but rearrangement of methyl group, yielding a mixture of 1-methyl- and 2-methylnaphthalene-d₇, was observed by ¹H NMR.

Table 11. Ionic Hydrogenation Results Employing $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ as Catalyst

Substrate	Pd(CH ₃ CN) ₂ Cl ₂ (1 mol%) H ₂ (500 psi), BF ₃ :H ₂ O, 50°C, 24 hrs.		Product(s)	Total Yield (% yield)	Recovered Reactant
Substrate	Product(s) (% yield)
(45)	(28)		74	none
(5)	(41)	Partially Reduced products	61	<10
(17)	(27)	(25)	71	none
(9)	(26)	(20)	55	none
(9)	(34)	(19)	62	none
(9)	(34)	(19)	76	none

PART 2

LOW SEVERITY IONIC HYDROGENATION OF COAL

The organic portion of coals consists primarily of a cross-linked macromolecular network. Ether groups are common in lignites and low rank coals⁸. Any reaction capable of cleaving ether groups is expected to form large amounts of lower molecular weight and soluble materials. Ionic hydrogenation is a reaction with an inherent selectivity towards the cleavage of ether groups. The ability of this reaction to cleave aryl ethers and similar functionalities has been demonstrated. The ionic hydrogenation of coals and coal extracts using several different reagents has been attempted. The hydrogenated coals were characterized by their extractabilities and elemental analysis. Hydrogenated extracts were analyzed by gel permeation chromatography (GPC) and elemental analysis.

EXPERIMENTAL

Chemicals were used as purchased except where otherwise noted. $(\text{CH}_3\text{CN})_2\text{PtCl}_2$ and $\text{BF}_3\cdot\text{H}_2\text{O}$ were prepared by the same methods as described in Part 1. All Soxhlet extractions were conducted at the solvents reflux temperature. For hydrogenation reactions involving whole coals, the extent of coal depolymerization and hydrogenation was determined by comparing extractabilities and elemental analyses. When coal extracts were used as starting material for hydrogenation reactions, the extent of depolymerization and hydrogenation was determined by comparing the molecular weight distributions (gel permeation chromatography, Waters ALC 201 HPLC equipped with mass analyzer and 4 μ -styragel columns: 100, 500 1000, and 10,000 Å), ^1H NMR (JOEL FX 90Q Spectrometer), and elemental analysis (Galbraith Laboratory Inc, Knoxville Tn) of the hydrogenated material with that of the non-hydrogenated material.

Volumetric Swelling of Wyodak Subbituminous Coal with $\text{BF}_3\cdot\text{H}_2\text{O}$ Approximately 150 mg. of Wyodak subbituminous coal (Argonne premium sample, dried to constant weight, non-extracted) was introduced to an 8 mm. O.D. pyrex tube sealed at one end. The coal was centrifuged to about 5 min. and its height recorded (h_0). Approximately 2.0 g. of $\text{BF}_3\cdot\text{H}_2\text{O}$ was added to the tube and the tube was capped with a septum. The coal- $\text{BF}_3\cdot\text{H}_2\text{O}$ suspension was allowed to interact for 24 hours, occasionally shaking it vigorously to insure proper mixing. Unlike conventional volumetric swelling measurements, the coal floats to the top of the more dense $\text{BF}_3\cdot\text{H}_2\text{O}$. Therefore, the upper and lower boundaries of the coal were impossible to see. The upper boundry was identified by adding a small portion of either cyclohexane, or chloroform which floated to the top of the coal. The tube was inverted and the mixture was centrifuged. The lower boundry was identified by removing part of the black $\text{BF}_3\cdot\text{H}_2\text{O}$ with a syringe and injecting a plug of air which pushed the coal above the $\text{BF}_3\cdot\text{H}_2\text{O}$ layer. Now the height of the swollen coal (h_1) has determined. Q values for duplicate samples: 2.40 (cyclohexane), 2.59 (chloroform).

General reaction procedure for ionic hydrogenation of Wyodak Coal. Tetrahydrofuran

(THF) was dried over potassium hydroxide pellets. Wyodak coal was obtained from the Argonne National Laboratory Premium Coal Sample Bank. The coal containing ~29 wt% of moisture was either dried to constant weight in a vacuum oven at 110°C, saturated with BF₃ gas before hydrogenation or direct THF extraction. The coal (~4 g., dry weight) was hydrogenated in an autoclave (vide supra) with or without the catalyst (CH₃CN)₂PtCl₂ under the conditions indicated in Table 2. The resulting mixture was neutralized with 4N sodium hydroxide (aq) while cooling in an ice-bath. After filtration, the solid was washed three times with distilled water (~200 mL each). The workup was done under nitrogen atmosphere. The wet coal was dried to a constant weight in a vacuum oven at 110°C. The dried coal or BF₃ saturated coal was soxhlet extracted with 150 mL of THF for one week. Solvent was evaporated from the extract *in vacuo*. The coal extracts and residues were dried to a constant weight in a vacuum oven at 110°C. The THF extractability and elemental analysis data are shown in Tables 2 and 3.

Ionic Hydrogenation of Oxidized Texas Lignite with (CH₃CN)₂PtCl₂\BF₃:H₂O\H₂

The selectively oxidized lignite, as received from Dr. Ron Liotta (Exxon Research and Engineering Co) was dried in a vacuum oven (T=110°C) for 24 hours. 5.61 g. of oxidized Rawhide was transferred to a Teflon-lined Burgoff autoclave (250 mL), and a solution of (CH₃CN)₂PtCl₂ in BF₃:H₂O (82.5 mg. catalyst in 20 mL of acid) was added. An egg shaped stir bar was added, and the reactor was quickly sealed and purged 3 times with 50 psi H₂. The reactor was charged with 500 psi H₂ (room temp.), and slowly brought to reaction temperature (50°C). The reactor was allowed to stir at this temperature for 24 hours. Afterwards, the heating mantle was removed, and the autoclave was allowed to cool to room temperature, prior to depressurization. After the reactor was depressurized, the contents of the autoclave were poured into 100 g. of ice and neutralized with 30 mL aq. 4N NaOH. The neutralized coal was then vacuum filtered through a qualitative filter paper and washed with 5x100 mL of distilled water. The precipitate was transferred to a tared screw vial and dried in a vacuum oven (T=110°C) for 4 days (5.9 g recovered, 105% recovery).

THF Extraction of Untreated and Treated Texas Lignite. Approximately 5.76 g. of oxidized Rawhide and 3.5 g. of the hydrogenated product were transferred to 33x94 mm cellulose extraction thimbles and extracted under N_2 with 250 mL THF for 2 days. Following the extraction, the THF was removed *in vacuo*, and the extracts were dried in a vacuum oven ($T=110^\circ C$) for 1 week. The extractability of the hydrogenated Rawhide showed no increase over that of the starting coal (7% vs. 5%, respectively).

Ionic Hydrogenation of Beulah-Zap Lignite with $BF_3 \cdot H_2O / MoS_2 / H_2$. H_2S was bubbled through an aqueous solution containing 871 mg. (1% wt, Mo/Coal) of ammonium heptamolybdate (Fisher) for 30 min. This solution was poured onto the coal, and the mixture was allowed to stir for 30 minutes. The impregnated coal was dried in a vacuum oven at 110° for 3 days. A tubing bomb, charged with the dry impregnated coal, was immersed in a sand bath ($430-450^\circ C$) for 2 hrs. under a constant flow of N_2 . This procedure results in the decomposition of the tetrathiomolybdate to the disulfide.¹⁸ The impregnated coal was mixed with $BF_3 \cdot H_2O$, and allowed to react under H_2 (500 psi, cold) at $100^\circ C$ for 24 hours. The reaction mixture was neutralized with 4 N NaOH and filtered. The filtrate was washed with distilled water (3×100 ml), and dried under vacuum ($110^\circ C$) for 2 days.

Ionic Hydrogenation of the Pyridine Soluble Portion of an Ion-exchanged Wyodak Subbituminous Coal. The pyridine extract of an ion-exchanged Wyodak Subbituminous coal was reduced using two different ionic hydrogenation procedures. The two hydrogenation systems used were $BF_3 \cdot H_2O / Et_3SiH$ and $BF_3 \cdot H_2O / H_2 / (MeCN)_2PtCl_2$.

Ion-Exchange Procedure. 1 liter of an aqueous 1.0 M citric acid solution was added to 40 g. of Wyodak (Argonne) in a 2 liter round bottom flask. The mixture was refluxed for 20 hours under N_2 . The ion-exchanged coal was filtered through a tared Soxhlet extraction, and extracted with distilled water until the siphon wash was neutral to blue litmus (7 days). The coal was dried in a vacuum oven ($T=114^\circ C$) for 2 days. The extract was obtained by Soxhlet extraction of the ion-exchanged coal with pyridine for 2 days. The extract (4.57 g., 15% wt)

was isolated by removing the pyridine under vacuum, and drying the extract in a vacuum oven (110°C) for 2 days.

Reaction 1. Ionic hydrogenation of the extract employing $\text{BF}_3 \cdot \text{H}_2\text{O} / \text{Et}_3\text{SiH}$. A 300 mL. round bottom flask was equipped with a condenser, and a mechanical stirrer. The apparatus was purged continuously with N_2 . After the flask was immersed into an ice-water bath, 22 mL (460 mmol) of ice-cold $\text{BF}_3 \cdot \text{H}_2\text{O}$ was introduced into the flask and 1.98 g. of extract was added to the rapidly stirred liquid. The flask was equipped with a 100 mL equilibrated addition funnel containing 40 mL (250 mmol) of Et_3SiH . The silane was added dropwise (5 min), and the reaction mixture was allowed to stir at room temperature overnight. The reaction was quenched by pouring the mixture into 115 mL of 4N. NaOH-ice slurry. The neutralized mixture was filtered, washed with 6x 50 mL of distilled water, and dried in a vacuum oven (110°C) for 4 days. 1.35 g. (68%) of reaction product was obtained. Elemental analysis results are shown in Table 5.

Reaction 2. Ionic Hydrogenation of the extract using the system $\text{BF}_3 \cdot \text{H}_2\text{O} / (\text{CH}_3\text{CN})_2\text{PtCl}_2 / \text{H}_2$. An ice-cold solution of $(\text{CH}_3\text{CN})_2\text{PtCl}_2$ in $\text{BF}_3 \cdot \text{H}_2\text{O}$ (291.4 mg of catalyst in 30 mL of $\text{BF}_3 \cdot \text{H}_2\text{O}$) was introduced into a Teflon-lined autoclave (Bergoff, 250 mL). The mixture was magnetically stirred and 2.1 g. of extract was added. The autoclave was sealed and purged with 50 psi of hydrogen three times. The reactor was charged with 500 psi of hydrogen (room temperature) and brought to reaction temperature (50°C) in 25 minutes. After a reaction period of 24 hours, the heating mantle was removed and the reactor allowed to cool to room temperature. Once cooled, the final pressure in the reactor was 475 psi. The reactor contents were poured over 300 g. of ice, and neutralized with 4 N NaOH. The recovered residue was filtered, washed with 4x200 mL of distilled water and dried in a vacuum oven (110°C) for 2 days to yield 1.92 g. (91%) of product. Elemental analysis results are shown in Table 5.

Hydrogenation of the THF Soluble Portion of Bruceton with Organic Acids and Et₃SiH in THF. The ionic hydrogenation of the THF soluble portion of Bruceton (17%) was attempted by the dropwise addition of the extract dissolved in THF, to a 1 M. solution of either TsOH:H₂O, CF₃CO₂H, or CH₃SO₃H in THF. This was followed by the addition of Et₃SiH. A typical experimental procedure is described below. A 500 mL three neck round bottom flask was equipped with a N₂ line, condenser, mechanical stirrer, and equilibrated addition funnel. The flask was immersed in an ice-water bath, purged with N₂, and 100 mL of the acid/THF solution was introduced to the flask. A solution of approx. 1.5 g. of extract dissolved in 50 ml of THF was slowly added dropwise (30-45 minutes), followed by the dropwise addition (10 min.) of 7 ml (106 mmol) of Et₃SiH. The ice-water bath was then removed and the mixture was allowed to stir overnight at room temperature. Afterwards, the reaction mixture was poured into an aqueous NaOH bath (approx. 4.5 g. of NaOH, 100 ml of distilled water, 175 g. ice). The neutralized reaction mixture was vacuum filtered under N₂. The filtrate was diluted with an equal volume of distilled water to precipitate additional material. This suspension was poured over the previously filtered coal, and the precipitate was washed with distilled water, and dried with a vacuum oven (110°C) to constant weight (2-4 days).

The number average molecular weights (M_N) were obtained by GPC analysis of a 1% solution of either the starting extract or the hydrogenated material, in pyridine. The H/C values were obtained by elemental analysis of the material (Galbraith Labs, Knoxville Tn.). The results obtained for these reactions are summarized in Table 6.

Ionic Hydrogenation of THF Soluble Portions of Bruceton or Ion-exchanged Wyodak with Et₃SiH and Acid as Solvent The THF soluble portions of either Bruceton (17%) and citric acid treated Wyodak (25%) were subjected to ionic hydrogenation using acids as the solvent. The acids chosen for these reactions were BF₃:H₂O, CF₃CO₂H, TsOH:H₂O/chlorobenzene, and CH₃SO₃H. A 200 mL three neck flask round bottom flask was equipped as described previously in this report. The acid was introduced to the flask, and the coal extract was added. Subsequently, the flask was fitted with an equilibrating addition

funnel and 20 mL (125 mmol) of Et_3SiH was slowly added dropwise (15-25 min). The ice-water bath was removed and the reaction mixture was allowed to stir overnight. No ice-water bath was used for reactions in which $\text{CH}_3\text{SO}_3\text{H}$ was used as solvent since this acid freezes at 20°C . To quench the reactions, the mixture was poured over aqueous NaOH ice-water bath, and the neutralized reaction mixtures were vacuum filtered under a blanket of N_2 . The precipitate was washed several times with distilled water and dried to constant weight in a vacuum oven (110°C).

M_N were obtained as described previously. The results for the hydrogenation of the extracts of Bruceton and the citric acid washed Wyodak are summarized in Table 7 and 8 respectively.

Ionic Hydrogenation of THE Soluble Portion of Ion-exchanged Wyodak with $\text{CH}_3\text{SO}_3\text{H}$ using Et_3SiH as Solvent. A 200 mL three neck round bottom flask, equipped as described previously was purged with N_2 , and charged with 21 mL Et_3SiH (138 mmol) at room temperature. 1.54 g. of extract was added to the liquid and the suspension stirred for 10 minutes. Afterwards, 10 mL (154 mmol) of $\text{CH}_3\text{SO}_3\text{H}$ was introduced dropwise (17 minutes), and the mixture was allowed to stir overnight. The reaction was quenched by pouring the mixture into an aqueous alkaline solution (5 g. NaOH , 100 mL distilled water, 100 g. ice). The neutralized mixture was vacuum filtered under N_2 , and the precipitate was washed with distilled water (4×100 mL) and dried in a vacuum oven to constant weight (110°C). The M_N values obtained by GPC are summarized in Table 8.

Reduction of triphenylmethanol using $\text{NaBH}(\text{OAc})_3$ as Hydride Donor in $\text{CH}_3\text{SO}_3\text{H}$. 2 mL (31 mmol) of $\text{CH}_3\text{SO}_3\text{H}$ was added to a 15 mL round bottom flask equipped with a magnetic stirrer. 517 mg (2.4 mmol) of $\text{NaBH}(\text{OAc})_3$ was added as a solid, to the stirring acid. The resulting mixture was thick and viscous, and some H_2 evolution was evident. To the acid/hydride mixture, 614 mg (2.4 mmol) of triphenylmethanol was added and the mixture was stirred at room temperature for 30 minutes. The reaction mixture was quenched with ice, neutralized with 8 mL of 4N NaOH and the organic material was dissolved by adding 2 mL of

dichloromethane. The layers were separated and the aqueous phase extracted with additional dichloromethane. All organic layers were combined, washed with distilled water, and dried with MgSO_4 . After filtering, the solvent was removed in vacuo. A ^1H NMR of the product mixture indicated that a 50% yield of triphenylmethane had been obtained.

Reduction of α -Tetralone with $\text{Na}(\text{BHOAc})_3$ and $\text{CH}_3\text{SO}_3\text{H}$ as Ionic Hydrogenation Pair. A typical reaction procedure involved adding 275 mg. (1.9 mmol) of tetralone to 2.4 mL (36 mmol) of $\text{CH}_3\text{SO}_3\text{H}$ in a 15 mL round bottom flask. 1.52 g. (7.2 mmol) of $\text{NaBH}(\text{OAc})_3$ was slowly added to the stirring substrate/acid mixture. The amount of hydrogen generated during the reaction was measure $\text{NaBH}(\text{OAc})_3$ consumed to generate H_2). The mixture was allowed to stir for 40 minutes, or until the starting material had been consumed (reaction followed by TLC). The reaction was quenched with ice, neutralized with aq. NaOH and dissolved in 3 mL of CH_2Cl_2 . The resulting layers were separated and the aqueous phase extracted with 3x5 mL of dichloromethane. All organic layers were combined, washed with 3x5 mL of distilled water, and dried with MgSO_4 . The dried organic solution was concentrated under a stream of N_2 to yield the crude reaction product mixture (87% recovery). The crude residue analyzed by TLC (developed in cyclohexane) showed the presence of 4 compounds. Two were identified as unreacted starting material and tetralin, by comparing the R_f values with authentic compounds (starting material; tetralin). Tetralin was isolated by preparative TLC (250 μ Silica, developed in cyclohexane) in 22% yield. Other compounds isolated from this separation were not typical reduced products and consequently they were not characterized further.

RESULTS AND DISCUSSION

Elemental analysis of the coals used in this study is shown in Table 1. Our initial hydrogenation target was Wyodak subbituminous coal (%C 76, dmmf). We anticipated facile reduction of this highly oxygenated coal. Applied first was the newly developed catalytic ionic hydrogenation reaction (Part one) under conditions identical to those used for model compounds studies ($\text{BF}_3\cdot\text{H}_2\text{O}/\text{H}_2/(\text{MeCN})_2\text{PtCl}_2$, 24 hrs., 500 psi of hydrogen, 50°C). No increase in the THF extractability over that of the starting coal was observed (Table 2). The occurrence of coal reactions requires mass transport of the catalyst into the coal and perhaps 24 hours is not sufficient time. The reaction period was extended to 2 weeks and no significant increase in extractability occurred. Elemental analyses of the coals that were reacted for 24 hours and two weeks are included in Table 3. For comparison, the analyses obtained for the dried starting coal and that reported by Argonne are also included. The data show that no appreciable incorporation of hydrogen into the coal occurred. The ionic hydrogenation reaction failed with Wyodak coal.

Perhaps mass transport of the catalyst into the coal is slow. Ion-exchange will alter mass transport and allow the catalyst to penetrate more rapidly. Wyodak coal was ion-exchanged with 1M aq. citric acid under reflux for one day. After ionic hydrogenation under standard conditions for one day, the dried coal was extracted with THF. The extractability (10.4%) was higher than those samples that were not treated with citric acid and hydrogenated (5.8%), but lower than a citric acid treated Wyodak coal sample (25%). There is a significant decrease in extractability upon treatment of citric acid washed Wyodak with $\text{BF}_3\cdot\text{H}_2\text{O}/\text{H}_2/(\text{CH}_3\text{CN})_2\text{PtCl}_2$, consistent with acid catalyzed polymerization. This is surprising since the $\text{BF}_3\cdot\text{H}_2\text{O}$ is expected to immediately convert all carboxylate groups to their acid form.

In order for catalytic ionic hydrogenation to be effective with coals, the solvent, $\text{BF}_3\cdot\text{H}_2\text{O}$, must interact with the coal to generate carbocations, and carry the catalyst to the cation. The coal-acid interaction can be monitored by measuring coal volumetric swelling ratio

(Q) using $\text{BF}_3\cdot\text{H}_2\text{O}$ as the solvent. Unlike conventional volumetric swelling measurements with organic solvents (densities are lower than coals), our measurements used $\text{BF}_3\cdot\text{H}_2\text{O}$ which is more dense than coal. Therefore, a third component —an inert, nonswelling organic solvent— was required to define the upper surface of the swollen coal for height (h_1) measurements. The volumetric swelling Q values of 2.40 and 2.59 obtained after 24 hours indicate that $\text{BF}_3\cdot\text{H}_2\text{O}$ swells Wyodak coal.

A severe deficiency of the $\text{PtCl}_2(\text{CH}_3\text{CN})_2$ system is its poisoning by sulfur. We began a search for sulfur-tolerant materials which would activate H_2 for ionic hydrogenation and attempted to hydrogenate a Beulah-Zap lignite with impregnated MoS_2 , using a procedure recently published by Derbyshire.¹² Although the hydrogenated coal showed a significant increase in extractability (30% wt, pyridine) over the parent coal (<1% wt, pyridine), this method proved to be fruitless for our purposes, since the extracted material showed little resemblance to coal derived extracts (FT-IR, ^1H NMR, and GPC analysis). The thermal treatment (430-450°C for 2 hours) of the ammonium tetrathiomolybdate impregnated coal, which is required to generate MoS_2 , drastically altered the structure of the lignite.

Oxidized forms of sulfur do not poison $(\text{CH}_3\text{CN})_2\text{PtCl}_2$.¹⁰ We attempted the ionic hydrogenation of a selectively oxidized Texas lignite. All of the sulfur in the lignite was oxidized to sulfoxides and sulfones¹⁹. The ionic hydrogenation system $(\text{CH}_3\text{CN})_2\text{PtCl}_2/\text{BF}_3\cdot\text{H}_2\text{O}/\text{H}_2$ applied to oxidized lignite had no effect on the extractability of this material. THF extraction of the hydrogenated product resulted in a 7% yield of extractable material while the non-hydrogenated coal yielded 5% extractable material (Table 4). Also, the H/C ratio of the oxidized Rawhide did not increase (Table 4). The lack of change in the extractability and the H/C ratio for the oxidized coal indicates no favorable reaction had occurred. Since it is unlikely the catalyst was completely poisoned by sulfur at this loading (1.5% wt.), the failure of the hydrogenation reaction must not be due to poisoning by sulfur.

Our attempts to depolymerize/hydrogenate whole coals failed. The most obvious cause

for the failure is slow mass transport. In our first series of experiments using whole Wyodak, we were able to show that extending reaction periods to two weeks had no effect on the extractability or H/C ratio. This experiment does not allow us to completely rule out slow mass transport. It could be very slow. Alternatively, rapid reactions occurring in the solid coal may compete with the hydrogenation/depolymerization reactions.

To determine if coal functional groups can be hydrogenated and/or depolymerized by ionic hydrogenation, we used extracts as starting material for the reaction. This eliminates the possibility of rate limiting mass transport of reactants into the coal. Reactions enhanced by propinquity in the solid will also be reduced. The effect of the reaction can be conveniently monitored by standard solution methods of analysis (GPC) allowing more effective evaluation of the ionic hydrogenation reactions.

Attempts to hydrogenate the pyridine soluble portion of an ion-exchanged Wyodak coal (15% pyridine extractability), with two different ionic hydrogenation procedures (reaction 1; $\text{BF}_3\cdot\text{H}_2\text{O}/\text{Et}_3\text{SiH}$, reaction 2; $\text{BF}_3\cdot\text{H}_2\text{O}/\text{H}_2/(\text{CH}_3\text{CN})_2\text{PtCl}_2$) gave products which were only partially soluble in pyridine. Approximately 25% of the product from reaction 1, and 14% from reaction 1 was pyridine soluble compared to 100% for the starting extract. We believe that $\text{BF}_3\cdot\text{H}_2\text{O}$ caused polymerization of the extract forming the insoluble material. Elemental analysis (Table 5) revealed that a modest amount of hydrogen had been incorporated into the extract (H/C ratios for starting extract was 0.84, for product from reaction 1 was 0.90, and for product from reaction 2 was 0.97). As expected, the product from reaction 2 ($\text{BF}_3\cdot\text{H}_2\text{O}/\text{H}_2/(\text{CH}_3\text{CN})_2\text{PtCl}_2$ system) possessed the greatest H/C ratio. The $\text{BF}_3\cdot\text{H}_2\text{O}/\text{H}_2/(\text{CH}_3\text{CN})_2\text{PtCl}_2$ ionic hydrogenation system has been shown to be much more effective in the reduction of model compounds than $\text{BF}_3\cdot\text{H}_2\text{O}/\text{Et}_3\text{SiH}$.⁴

Since we discovered that $\text{BF}_3\cdot\text{H}_2\text{O}$ may cause the polymerization of the pyridine soluble portion of Wyodak coal, we used several organic acids in conjunction with Et_3SiH as the hydrogenating pair in the ionic hydrogenation of the THF soluble portions of two coals, Bruceton and ion-exchanged Wyodak. Ionic hydrogenation systems employing

$\text{CF}_3\text{CO}_2\text{H}/\text{Et}_3\text{SiH}$ as the hydrogenation pair have been thoroughly explored.¹ $\text{CF}_3\text{CO}_2\text{H}$ may not be sufficiently acidic to cleave aromatic ether linkages, consequently we extended this ionic hydrogenation reaction to stronger organic acids, even though the use of stronger acids with Et_3SiH for ionic hydrogenation has not been fully explored. Et_3SiH was found to co-exist (i.e. no hydrogen evolution) with $\text{TsOH}:\text{H}_2\text{O}$ and $\text{CH}_3\text{SO}_3\text{H}$ when in THF solution. Consequently these acids along with $\text{CF}_3\text{CO}_2\text{H}$ were used as proton sources. THF was used to extract the coals since this solvent is less basic than pyridine, compatible with the chosen acids, and eliminates the possibility of a leveling effect. The reactions were conducted under a variety of conditions, and the product's molecular weight distributions were measured using GPC. The first series of ionic hydrogenation reactions were conducted employing THF as solvent. The second series of reactions were run in either liquid acid or Et_3SiH as solvent. The coal extracts were only slightly soluble in the two reactants.

The ionic hydrogenation of the THF soluble portion of Bruceton employing $\text{CH}_3\text{SO}_3\text{H}/\text{Et}_3\text{SiH}$ as the acid/hydride pair in THF as solvent showed the greatest incorporation of hydrogen into the extract (Table 6). There was also a marked increase in $\overline{M}_N$ for the extract. All acids used in these reactions resulted in condensation as evident by the increase in $\overline{M}_N$ values (Table 6). Quenching the $\text{CH}_3\text{SO}_3\text{H}/\text{Et}_3\text{SiH}$ reaction after stirring for 2.5 hours had no effect on H/C or $\overline{M}_N$. This result indicates that both hydrogenation and condensation may be complete in less than three hours. The other acids used in these reactions ($\text{CF}_3\text{CO}_2\text{H}$ and $\text{TsOH}:\text{H}_2\text{O}$) resulted in similar increases in $\overline{M}_N$.

The data summarized in Tables 7 and 8 show that coal extracts undergo condensation reactions under ionic hydrogenation conditions resulting in the formation of higher molecular weight material. This increase in molecular weight was found to be most pronounced for Wyodak extracts (Table 8). Wyodak coal (16.90% O, dmmf) is more highly oxygenated than Bruceton (6.9% O, dmmf) and this may favor condensation reactions. The higher $\overline{M}_N$ for both reacted extracts suggest condensation competes more effectively than hydrogenation. Apparently, hydride abstraction from Et_3SiH by the carbenium ion is slow compared to alkylation. The data from Table 8 shows that using Et_3SiH as solvent and slowly adding

$\text{CH}_3\text{SO}_3\text{H}$ did not eliminate condensation, although it certainly decreased.

$\text{NaBH}(\text{OAc})_3$ was screened as a possible alternative to Et_3SiH in ionic hydrogenation reactions. Since this reagent can selectively reduce only aldehydes even when other types of carbonyls are present,¹¹ it may react slowly with acids and carbenium ions would compete effectively for the hydride. The rate of hydrogen evolution was measured to determine the half-life of $\text{NaBH}(\text{OAc})_3$ in three different strong acids: $\text{CF}_3\text{SO}_3\text{H}$, $\text{CH}_3\text{SO}_3\text{H}$, and $\text{CF}_3\text{CO}_2\text{H}$ (Table 9). Grinding the $\text{NaBH}(\text{OAc})_3$ prior to mixing it with an acid only increased the rate of hydrogen evolution. As expected the rate increased with increasing solvent acidity. However, the rate of H_2 evolution is sufficiently slow that carbenium ions may be able to compete effectively for the hydride. $\text{CH}_3\text{SO}_3\text{H}$ was chosen as solvent for the model compounds since it represents a compromise between high acidity and compatibility with $\text{NaBH}(\text{OAc})_3$.

When the $\text{NaBH}(\text{OAc})_3/\text{CH}_3\text{SO}_3\text{H}$ ionic hydrogenation system was applied to the reduction of triphenylmethanol using stoichiometric quantities of $\text{NaBH}(\text{OAc})_3$, a 50% yield of triphenylmethane was obtained. The $\text{NaBH}(\text{OAc})_3/\text{CH}_3\text{SO}_3\text{H}$ system was applied to a variety of model compounds to determine the utility of the reaction (Figure 1). These reactions resulted in either recovery of the starting material or formation of complex reaction mixtures. Reduced products were formed at best in modest yields (for example, reduction of α -tetralone gave tetralin in 22% yield; and benzophenone was reduced to diphenylmethane in 66% yield). Using $^1\text{H-NMR}$, we were able to determine the major product in many of these reaction were the acetylated compounds. Apparently, the acetate ion from the hydride donor reacted with the carbenium ions forming compounds that were stable in this acid mixture. Since the major products in these reactions were not the reduced products, use of $\text{NaBH}(\text{OAc})_3$ as a hydride donor in ionic hydrogenation was abandoned.

CONCLUSION

The newly developed catalytic ionic hydrogenation system $(\text{MeCN})_2\text{PtCl}_2/\text{H}_2/\text{BF}_3\cdot\text{H}_2\text{O}$, which we have shown to be successful in the hydrogenation and deoxygenation of model compounds, does not depolymerize or hydrogenate low rank coals. Slow mass transport of reagents into the coal is not the determining factor, nor is catalyst poisoning by sulfur.

Exposing extracts of Bruceton or ion-exchanged Wyodak to ionic hydrogenation conditions resulted in their polymerization to form higher molecular weight material as evident from increased M_N values and decreased solubility in the extracting solvent. The occurrence of Friedel-Craft alkylation are consistent with our observation. The THF extracts from Wyodak show the greatest increases in M_N when subjected to ionic hydrogenation. This is consistent with F/C alkylation because Wyodak is a highly oxygenated coal and oxygen substituents on aromatic groups (i.e. $-\text{OH}$, $-\text{OR}$) greatly activate the ring to alkylation more so than aromatics where no such groups are present.

TABLE 1. Elemental Analysis^a of Beulah-Zap
lignite, Wyodak and Pitt. No. 8 Coals.

Coal	% C	% H	% N	% O
Beulah-zap	74.05	4.90	1.17	19.13
Wyodak	76.04	5.42	1.13	16.90
Pitt. No. 8	84.95	5.43	1.68	6.90

a. data for Argonne premium samples, dmmf basis.

TABLE 2. THF Extraction of Wyodak^a Coal

Pretreatment of coal	Hydrogenation ^b (with or w/out catalyst)	Residue(%)	Coal Extract(%)
as received	no	92 ^c	6.7 ^c
BF ₃ saturated	yes (w catalyst)	98	5.8
BF ₃ saturated	yes (w/o catalyst)	94	9.6
dried	no	103	4.6
dried	yes (w catalyst)	101	9.6

a. Argonne Premium Coal

b. Reaction condition: 500 psi of H₂, 10% (wt) of Pt(CH₃CN)₂Cl₂, 50°C, 24 hr.

c. Based on an estimated dry weight of starting coal

TABLE 3. Elemental Analysis of Wyodak^a Treated by Ionic Hydrogenation^b

Sample	Treatment	Portion (%)	%C	%H	%Ash
as received	dried	whole	67.06	5.13	9.62
as received	a) dried	residue(103)	64.82	4.53	9.70
	b)THF extraction	extract(4.6)	60.74	8.38	17.49
	c)dried				
hydrogenated	a)BF ₃ saturation				
	b)24 hr. reaction	residue(98)	59.17	4.19	17.00
	c)THF extraction	extract(5.8)	65.43	6.71	11.94
	d)dried				
hydrogenated	a)BF ₃ saturation				
	b)2 wk reaction	residue(100)	63.30	4.24	13.96
	c)THF extraction	extract(5.6)	33.80(?)	5.81	19.18
Argonne analysis		whole	74	5.8	8

a. Argonne Premium Coal.

b. standard conditions with 10% (wt) of (CH₃CN)₂PtCl₂

TABLE 4. Elemental Analysis, H/C ratios^a and THF extractability for Selectively Oxidized Texas Lignite and its Ionic Hydrogenation^b Product

Sample	%Carbon (wt/wt)	%Hydrogen (wt/wt)	%Ash (wt/wt)	H/C	THF extractability (wt %)
Texas Rawhide ^c	59.95	3.77	2.23	0.75	5
Same Coal After 60.17 Hydrogenation		3.77	3.75	0.75	7

a. calculated from elemental analysis.

b. BF₃:H₂O/H₂/(CH₃CN)₂PtCl₂ 500 psi H₂, 50°C, 24 hr.

c. coal treated with K₂S₂O₇

TABLE 5. Elemental Analysis for Pyridine Soluble Portion of an Ion-Exchanged Wyodak Coal and their Hydrogenation Products

Sample	% Carbon (wt/wt)	% Hydrogen (wt/wt)	% Ash (wt/wt)	H/C Ratio (wt/wt)
Wyodak Extract	74.47	5.28	0.43	0.84
Product of Reaction 1 ^a	72.72	5.49	3.28	0.90
Product of Reaction 2 ^b	68.21	5.56	9.95	0.97

a. $\text{BF}_3\text{:H}_2\text{O}/\text{Et}_3\text{SiH}$ Ionic Hydrogenation System.

b. $\text{BF}_3\text{:H}_2\text{O}/\text{H}_2/(\text{MeCN})_2\text{PtCl}_2$ Ionic Hydrogenation System

Table 6. Ionic Hydrogenation of the THF Soluble Portion of Bruceton With Acid, Et_3SiH , and THF as Solvent

Bruceton THF Solubles + Acid + Et_3SiH			r.t.; stirred overnight THF Products	
Acid Used	Molar Ratio %C ^c /acid/ Et_3SiH	Mass Balance	H/C ^a mol/mol	$\bar{M}_N^b$
d	-----	-----	0.83	1600
$\text{TsOH}:\text{H}_2\text{O}$	1/1/1	64%	0.81	2600
$\text{CF}_3\text{CO}_2\text{H}$	1/1/1	65%	0.77	2300
$\text{CH}_3\text{SO}_3\text{H}$	1/1/1	67%	0.93	2900
$\text{CH}_3\text{SO}_3\text{H}^{\text{e,f}}$	1/1/1	61%	0.91	2800

a. Calculated from elemental analysis

b. GPC., Polystyrene standard

c. Based on %C (wt/wt) in Bruceton (85%, dmmf)

d. analysis of coal extract used as starting material

e. Stirred for 2.5 hrs.

f. an additional 220 mg (14%) of coal product isolated from the filtrate with pyridine possessed an $\bar{M}_N$ value of 1400.

Table 7. Ionic Hydrogenation of the THF Soluble Portion of
Bruceton With Et_3SiH , and acid as Solvent

Bruceton THF Solubles +		r.t.; stirred overnight Et_3SiH Acid		Products
Acid Used	Molar Ratio %C ^c /acid/ Et_3SiH	Mass Balance	H/C ^a mol/mol	$\bar{M}_N^b$
d	-----	-----	0.83	1600
$\text{BF}_3 \cdot \text{H}_2\text{O}$	1/5/1.2	87%	0.79	3300
$\text{CF}_3\text{CO}_2\text{H}$	1/5/1.3	91%	0.87	2800
$\text{TsOH} \cdot \text{H}_2\text{O}^e$	1/1.2/1.2	68%	0.81	2300

a. Calculated from elemental analysis

b. GPC., Polystyrene standard

c. Based on %C (wt/wt) in Bruceton (85%, dmmf)

d. analysis of coal extract used as starting material

e. chlorobenzene as solvent

Table 8. Ionic Hydrogenation^a of the THF Soluble Portion of
Ion-exchanged Wyodak With Acid and Et_3SiH

Molar Ratio %C ^b /acid/ Et_3SiH	Solvent	Mass Balance	H/C ^c mol/mol	$\bar{M}_N^d$
-----	-----	-----	1.35	8600
1/1.5/1.3	Et_3SiH	49%	1.12	48,000
1/1.5/1.3	$\text{CH}_3\text{SO}_3\text{H}$	45%	1.09	38,000

a. Reaction conditions; stirred at room temp. (25°C) for 18 hrs.

b. Based on %C (wt/wt) in Wyodak (76%, dmmf)

c. Calculated from elemental analysis

d. Calculated by GPC, polystyrene standard.

TABLE 9. HALF-LIFE OF $\text{NaBH}(\text{OAc})_3$ WHEN MIXED WITH ACID		
ACID	$\text{P}k_{\text{A}}^{\text{c}}$	HALF-LIFE (min)
$\text{CF}_3\text{CO}_2\text{H}$	-0.3	18
$\text{CH}_3\text{SO}_3\text{H}^{\text{a}}$	-1.9	10
$\text{CH}_3\text{SO}_3\text{H}^{\text{b}}$	-1.0	3
$\text{CF}_3\text{SO}_3\text{H}$	-5.1	<1

a. $\text{NaBH}(\text{OAc})_3$ used as received

b. $\text{NaBH}(\text{OAc})_3$ pulverized with mortar and pestle prior to mixing

c. Stewart, R.; in *The Proton: Applications to Organic Chemistry*, Academic Press, Orlando Fl., 1985, pp17

SUBSTRATE

COMMENTS^c

22% tetralin^b
10% starting material^b
other products had formed

a

66% diphenylmethane
33% starting material

14% fluorene

75% starting material
25% other products

complex mixture had formed
no reduced products

a

FIGURE 1 (continued)

SUBSTRATE + $\text{NaBH}(\text{OAc})_3$ $\xrightarrow[\text{CH}_3\text{SO}_3\text{H}]{25^\circ\text{C, 30 min.}}$ PRODUCT(S)	
SUBSTRATE	COMMENTS ^c
a
complex mixture
complex mixture
a

- a. starting material recovered
 b. isolated yields
 c. NMR yields

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