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Quarterly Progress Report
Molecular Catalytic Coal Liquid Conversion

United States Department of Energy Grant
#DE-AC22-91PC91056

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I. Abstract

Last quarter, substantial progress has been made in the two general tasks advanced in our research proposal. The first task consists of the development of molecular homogeneous catalysts that can be used in the hydrogenation of coal liquids and in coal conversion processes. The second task concerns the activation of dihydrogen by basic catalysts in homogeneous reaction systems.

With regards to the first task, we have prepared two organometallic rhodium (I) catalysts. These are the dimer of dichloropentamethylcyclopentadienylrhodium, $[RhCl_2(C_5Me_5)]$, and the dimer of chloro(1,5-hexadiene)rhodium We have subsequently investigated the hydrogenation of various aromatic organic compounds using these organometallic reagents as catalysts. Results showed that both catalysts effected the hydrogenation of the aromatic portions of a wide range of organic compounds, including aromatic hydrocarbons and aromatic compounds containing the ether group, alkyl groups, amino and carbonyl groups. However, both compounds were totally ineffective in catalyzing the hydrogenation of sulfur-containing aromatic organic compounds. Nevertheless, both rhodium catalysts successfully catalyzed the hydrogenation of naphthalene even in the presence of the coal liquids.

With regards to base-activated hydrogenation of organic compounds, we have found that hydroxide and alkoxide bases are capable of activating dihydrogen, thereby leading to the hydrogenation of phenyl-substituted alkenes. Thus far, we are the first group to apply this unusual method towards the successful hydrogenation of olefins. More specifically, tetrabutylammonium hydroxide, potassium tert-butoxide and potassium phenoxide were successfully used to activate dihydrogen and induce the hydrogenation of trans-stilbene. Potassium tert-butoxide was found to be slightly more effective than the other two bases in accomplishing this chemistry.

II. Introduction

Our first task concerns the development of molecular homogeneous catalysts that can either be prepared in advance of the hydrogenation or during the conversion of the coal liquid. In this case, the new chemistry is based upon recent work with arene chromium compounds in our laboratory as well as a thorough examination of the current literature. In essence, we are convinved that soluble molecular arene metal compounds that are capable of reducing aromatic compounds or removing heteroatoms need to be investigated as coal liquid conversion catalysts. In addition, rhodium compounds that have been reported to catalyze aromatic compounds ought to be investigated with respect to coal liquid conversion.

The second task will concern the activation of dihydrogen by basic catalysts in homogeneous reaction systems. This elementary concept finds clear precedent in early experimental work, in more recent fundamental gas phase research, in the demonstration that the water gas shift reaction can be catalyzed by bases, and in theoretical analyses of the chemistry. In essence, it has been established that the hydroxide ion, OH^-, converts dihydrogen, H_2, to a hydride-equivalent reagent, $[OH{\bullet}H_2]^-$, that is capable of transferring hydrogen to organic molecules under relatively mild conditions. We shall investigate whether basic catalysts ranging from hydroxide to hydrosulfide ion can accomplish the addition of dihydrogen to coal liquids and the removal of heteroatoms from them.

III. Observations

A. Metal-Catalyzed Hydrogenation

This phase of the project essentially consists of preparing organometallic reagents which are known or have been reported to act as homogeneous hydrogenation catalysts of aromatic hydrocarbons and studying their properties as homogeneous hydrogenation catalysts under various conditions with the ultimate objective of using these compounds to catalyze the conversion of coal liquids.

The hydrogenation experiments utilizing the dimer of chloro (1,5-hexadiene)rhodium as a catalyst were carried out in a Parr stainless steel reactor equipped with a magnetically driven stirrer in the presence of a commercial buffer solution of pH 7.4 and cetyltrimethylammonium bromide as a phase-transfer catalyst. At the operating temperature of 75°C of, a dihydrogen pressure of 30 atm was maintained. A reactant/catalyst ratio of 75:1 was typically maintained. The results of the hydrogenation of three reactants are summarized in Table I.

Table I. Hydrogenation of Organic Compounds Catalyzed by the Dimer of Chloro (1,5-Hexadiene)Rhodium

Expt. No.	Reactants (mmol)	Conditions (Solvent, Temperature, Time, H_2 Pressure (atm)	% Conversion	Products (mmol)
1	Naphthalene (4.7), Catalyst (0.06)	heptane (15 mL), 25°C 3 Hrs., Buffer pH 7.4 (5 mL), Cetyltrimethyl Ammonium Bromide (0.4) 1 atm	25% Conversion	Tetralin (1.1)
2	Naphthalene (4.7) Catalyst (0.06)	heptane (15 mL), 75°C, 3 Hrs., Buffer pH 7.4, (5 mL), Cetyltrimethyl Ammonium Bromide (0.4) 30 atm	100% Conversion	Tetralin (1.3) Decalin (3.0)
3	4-Methyl-Anisole (4.7) Catalyst	heptane (15 mL) 75°C, 3 Hrs., Buffer pH 7.4, (5 mL), Cetyltrimethyl Ammonium Bromide (0.4) 30 atm	100% Conversion	4-Methoxy-methylcyclohexane (4.4)

Table I. Hydrogenation of Organic Compounds Catalyzed by the Dimer of Chloro (1,5-Hexadiene)Rhodium

Expt. No.	Reactants (mmol)	Conditions (Solvent, Temperature, Time, H_2 Pressure (atm)	% Conversion	Products (mmol)
4	Methyl Phenyl Sulfide (4.7) Catalyst	heptane (15 mL) 75°C 3 Hrs., Buffer pH 7.4, (5 mL), Cetyltrimethyl-Ammonium Bromide (0.4), 30 atm	0% Conversion	None

The first two experiments in Table I exhibits the effects of higher temperature and dihydrogen pressure on the extent of hydrogenation of naphthalene. Januszkiewicz and Alper[1] reported that naphthalene was completely hydrogenated (100% conversion) to tetralin and decalin at room temperature and an atmospheric pressure of dihydrogen. Our results indicate that higher temperatures and dihydrogen pressures are required for hydrogenation, using the dimer of Chloro (1,5-Hexadiene)Rhodium as catalyst. The results of the fourth experiment in Table I showed that sulfur-substituted compounds do not undergo hydrogenation, using the rhodium compound as catalyst. This experiment suggests that sulfur-containing compounds may poison the rhodium catalyst.

Furthermore, we have carried out an experiment repeating the conditions of experiment 2 of Table I, except that the reaction was carried out for 12 hours instead of 3 hours, and in the presence of 0.6 grams of coal liquid provided by the Department of Energy. The purpose of this experiment was to determine whether the sulfur-containing coal liquid would inhibit the hydrogenation of naphthalene and measure the extent of inhibition. Upon separation of the coal liquid by column chromatography, the results showed that 91% of the naphthalene was hydrogenated to give 85% tetralin and 5% decalin. Therefore, in comparison with the results of experiment 2, this result indicate that the coal liquid does exhibit substantial inhibiting effect, but the catalyzed hydrogenation still proceeds to a large degree. This is a most encouraging result, since it suggests that the sulfur in coal liquid will not completely inhibit hydrogenation of the aromatic portions of the coal liquid.

Experiments utilizing the dimer of dichloropentamethylcyclopentadienylrhodium, [$RhCl_2(C_5Me_5)$] as catalyst were likewise carried out in the Parr reactor, usually at 75° C, at 50 atm of dihydrogen pressure, and in the presence of triethylamine. A reactant/catalyst ratio of 100:1 was typically maintained. Some results of the hydrogenation experiments utilizing this catalyst are shown in table II.

Table II. Hydrogenation of Organic Compounds Catalyzed by the Dimer of Dichloropentamethylcyclopentadienylrhodium

Expt. No.	Reactants (mmol)	Conditions (Solvent, Temperature, Time, H_2 Pressure (atm)	% Conversion	Products (mmol)
1	Naphthalene (4.7) Catalyst (0.047)	Tert-Butyl Alcohol (25 mL) 75°C, 18 Hrs., Et_3N (1.5), 50 atm	99% Conversion	Octalin (0.2) Decalin (4.0)
2	2-Acetylnaph-naphthalene (4.7) Catalyst (0.047)	Isopropyl Alcohol (25 mL), 75°C, 18 Hrs. Et_3N (1.5), 50 atm	100% Conversion	2-Acetyl-Decalin and Alcohol
3	Methyl Phenyl Sulfide (4.7) Catalyst (0.047)	Isopropyl Alcohol (25 mL), 75°C 18 Hrs., Et_3N (1.5), 50 atm	0% Conversion	None

Like the dimer of chloro (1,5-hexadiene) rhodium, the results of Table II show that the dimer of dichloropentamethylcyclopentadienylrhodium catalyzes the hydrogenation of the aromatic portions of aromatic hydrocarbons and oxygen-substituted organic compounds. In addition, we have also carried out preliminary hydrogenation experiments of 3-toluidine using the dimer of dichloropentamethylcyclopentadienylrhodium as a catalyst. This resulted in a multitude of hydrogenation products together with condensation products which were difficult to identify. However, this definitely indicated that the rhodium compounds do catalyze the hydrogenation of amino-substituted organic compounds., therefore extending the range of organic compounds which can be hydrogenated by the rhodium catalysts.

The third experiment of Table II confirms that sulfur-substituted aromatic compounds do not undergo hydrogenation using dichloropentamethylcyclopentadienylrhodium dimer as catalyst. However, when the hydrogenation of naphthalene was carried out in the presence of the catalyst and sulfur-containing coal liquid, under the conditions of Experiment 1 in Table II, all the naphthalene was hydrogenated to give 30% tetralin, 6% octalin and 60% decalin. Compared to the results of Experiment 1, the coal liquid inhibited the hydrogenation of naphthalene only slightly.

II. Base-Catalyzed Hydrogenation

Our second task is to investigate the chemistry of base-catalyzed hydrogenation of organic compounds with the ultimate objective of applying the chemistry behind this novel concept to the catalytic conversion of coal liquids.

It is not generally known that bases such as the hydroxide ion are capable of activating dihydrogen to form "solvated hydride" or hydride-like species which can effect hydrogenation reactions under the appropriate conditions. Research during the first half of this century has amply demonstrated the feasibility of this concept..[2-4] More recently, Klingler, Krause and Rathke[5] studied the role of this kind of chemistry in the water-gas shift reaction.

So far, only walling and Bollyky[6] have been the only investigators to have applied dihydrogen activation by bases to the hydrogenation of organic compounds. These investigators reported that the base potassium tert-butoxide activated dihydrogen, leading to the hydrogenation of benzophenone to benzhydrol.

In the last quarter, we have succeeded in applying dihydrogen activation by bases towards the hydrogenation of a phenylsubstituted alkene, specifically trans-stilbene. We have found that bases such as hydroxide, phenoxide, tert-butoxide are capable of activating dihydrogen, and in the process effecting the hydrogenation of trans-stilbene to 1,2-diphenylethane. The hydrogenation experiments were carried out in the Parr stainless steel reactor equipped with a magentically-driven stirrer at a temperature of 180°C and a dihydrogen pressure of 100 atm. The results of these experiments are shown in Table III.

Table III. Base-Activated Hydrogenation Reactions of Stilbene

Expt. No.	Reactants (mmol)	Conditions (Solvent, Temperature, Time, H_2 Pressure (atm)	% Conversion	Products (mmol)
1	Trans-Stilbene (4.0) Tetrabutyl-ammonium Hydroxide (24)	1,2-Dimethoxyethane (50 mL), 180°C 18 Hrs. 100 atm	15% Conversion	1,2-Diphenylethane (0.1)
2	Trans-Stilbene (4.0) Potassium tert-Butoxide (24)	1,2 Dimethoxyethane (50 mL), 180°C, 18 Hrs., 100 atm	17% Conversion	1,2-Diphenylethane (0.3)
3	Trans-Stilbene (4.0) Potassium tert-Butoxide (48)	1,2-Dimethoxyethane (50 mL), 180°C, 18 Hrs., 100 atm	19% Conversion	1,2-Diphenylethane (0.3)
4	Trans-Stilbene (4.0) Potassium Phenoxide (48)	1,2-Dimethoxyethane (50 mL) 180°C, 18 Hrs. 100 atm	10% Conversion	1,2-Diphenylethane (0.1)

The results in Table III indicate that hydroxide, phenoxide and tert-butoxide anions activated dihydrogen to effect the hydrogenation of stilbene to give varying low yields of 1,2-diphenylethane. A comparison of Experiments 1 to 4 indicates that the potassium tert-butoxide anion was slightly more effective than potassium hydroxide and phenoxide in effecting this kind of chemistry. Experiments 2 and 3 indicate that doubling the concentration of potassium tert-butoxide did not increase the yield of the hydrogenation product. Overall, the four experiments confirmed the possibilities of this kind of chemistry. Our future work will concentrate on the use of amides and thiolates as bases to activate dihydrogen and and induce the hydrogenation of various organic unsaturated groups.

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