Title: **Molecular Catalytic Coal Liquid Conversion**

Authors: Leon M. Stock and Shiyong Yang

Organization: Department of Chemistry, The University of Chicago
5735 S. Ellis Ave., Chicago, IL 60637

Contract No.: DE-AC22-91PC91056

Period of
Performance: September 27, 1992 - March 26, 1996

Objectives: This research, which is relevant to the development of new catalytic systems for the improvement of the quality of coal liquids by the addition of dihydrogen, is divided into two tasks. Task 1 centers on the activation of dihydrogen by molecular basic reagents such as hydroxide ion to convert it into a reactive adduct $[OH\cdot H_2]^-$ that can reduce organic molecules. Such species should be robust withstanding severe conditions and chemical poisons. Task 2 is focused on an entirely different approach that exploits molecular catalysts, derived from organometallic compounds that are capable of reducing monocyclic aromatic compounds under very mild conditions.

Accomplishments and Conclusions:

Task 1 Organic Base-catalyzed Hydrogenation

Introduction

It has been known for a long time that simple basic molecules such as potassium t-butoxide catalyze the hydrogenation of benzophenone [1,2]. Moreover, simple bases such as hydroxide ion and amide ion catalyze the exchange of dideuterium with water and ammonia, respectively [3]. The energy barrier for the exchange of dideuterium with potassium amide in liquid ammonia is less than 5 kcal mol^{-1}, and that for dideuterium exchange in aqueous potassium hydroxide is less than 25 kcal mol^{-1}. Several lines of evidence including the kinetic isotope effects imply that dihydrogen forms an adduct, sometimes referred to as a vander Waals molecule, with hydroxide ion and that exchange occurs within this adduct rather than through free hydride anion. The proposed immediates, the H_3O^- and H_4N^- anions, have been detected in ion cyclotron resonance experiments [4,5], and the nature of the bonding within these species has been investigated theoretically [6]. There are several different structures that differ only modestly in energy content, the most stable ones have long hydrogen-hydrogen bonds, between 0.92 Å and 0.97 Å, compared to 0.73 Å in the dihydrogen molecule. The most stable structures can be described as solvated hydride ions with theoretical binding energies near 20 kcal mol^{-1}. They can rearrange via internal proton motion to dihydrogen complexes, which are 2 to 15 kcal mol^{-1} less stable than hydride adduct. Clearly, the hydrogen-hydrogen bond is greatly weakened in these substances and it is this feature that we sought to exploit for the hydrogenation of aromatic hydrocarbons and coal liquids.

Experimental Section

Hydrogenation of the coal liquid or aromatic hydrocarbon was performed in a Model 4576 HP/HT T316 autoclave system manufactured by Parr Instrument Company. The temperature was controlled by the Model 4842 temperature controller. In a typical experiment, naphthalene (6.4g, 0.05 mole) and freshly distilled hexane (38 ml) were placed in the autoclave, lithium diisopropylamide (0.0125 mole) suspended in hexane (10 wt%, 13.4 ml) was added to the autoclave under dinitrogen. The sealed autoclave was purged with dinitrogen and then with dihydrogen several times to replace the air, before it was filled with dihydrogen at the desired pressure. The mixture was stirred at 200 °C for 18 hrs. The products were isolated in the customary way and the product distribution was determined by GC-MS and ^1H NMR.

Results and Discussion

Base-activated hydrogenation of aromatic hydrocarbons

Several different strong bases were tested as catalysts for the hydrogenation of naphthalene. The results, Table 1, indicate that alkali metal *t*-butoxides (sodium *t*-butoxide, potassium *t*-butoxide and lithium *t*-butoxide) do not effect the hydrogenation of naphthalene at 200 °C and 1000 psig of hydrogen in hexane or *t*-butanol as solvent even though potassium *t*-butoxide does reduce benzophenone to benzhydrol [1,2]. We found that the sodium amide and lithium amide can reduce naphthalene in low yield (1.0% for $NaNH_2$ and 7.0% for $LiNH_2$) at 200 °C and 1000 psig of hydrogen. Even more success was realized with lithium organoamides such as lithium diisopropylamide and lithium dicyclohexylamide. They exhibit very effective catalytic activities for the hydrogenation of naphthalene to tetralin in more than 95% yield at 1000 psig and 200 °C for 5 hrs. The reaction proceeds cleanly with no byproducts.

Table 2 shows the results for a series of lithium organoamides as catalysts for the same hydrogenation reaction. The catalytic activities of the lithium organoamides depend importantly on the ligands. For instance, lithium diisopropylamide can catalyze the hydrogenation of naphthalene to tetralin in 100% yield, but lithium diethylamide and dimethylamide provide only 3 to 7% conversion. Thus, the lithium organoamides with larger aliphatic substituents exhibit higher activities than those with small substituents such as lithium diethylamide, lithium dimethylamide or lithium bis(trimethylsilyl)amide. In addition, the catalytic activities of the alkali metal trimethylsilylamides decrease in the order $K^+ > Na^+ > Li^+$ in toluene solution. Potassium bis(trimethylsilyl)amide, like lithium diisopropylamide, is a very active catalyst. However, the yield of tetralin was decreased when sodium bis(trimethylsilyl)amide and lithium bis(trimehylsily)amide were used as the catalysts under the same conditions.

The reaction was also influenced by the amount of the catalyst. The yield of tetralin reaches about 94% when the mole ratio of the substrate to the catalyst was less than 12.5. The yield depends on the hydrogen pressure, but the reaction proceeds very well (80% yield) even when the dihydrogen pressure is reduced to 300 psig.

Lithium diisopropylamide does not dissolve in hexane at room temperature, so a suspension of the catalyst in hexane was used. Indeed, a clear homogeneous solution was observed when the autoclave was opened after the reaction was completed, then a white solid slowly precipitated. The lithium content of the white solid was determined to be between 31 and 38 wt% by a gravimetric method [7] implying that the solid probably was a mixture of LiOH and Li_2O(Li : 37.7% in the 1:1 mixture). This material was produced by the reaction of lithium diisopropylamide with water.

The substitution of dideuterium gas for dihydrogen gas in the catalytic hydrogenation of naphthalene produced highly deuterated tetralin, indicating that the protons in the reduced aromatic molecule come from the dihydrogen molecules and not the solvents.

Other aromatic hydrocarbons were also investigated. Anthracene was hydrogenated to 9,10-dihydroanthracene in 95% yield and to another unidentified compound in 3% yield. Acridine was converted to 9,10-dihydroacridine in 77% yield and to 9% of another unidentified compound under 1000 psig of hydrogen pressure at 200 °C. At 300 °C, 1-methoxynaphthalene was hydrogenated in 95% yield; the main products are 1,2,3,4,-tetrahydromethoxynaphthalene(63%) and 1,2,3,4-tetrahydronaphthalene(12%).

The results indicate that organoamides, especially lithium diisopropylamide and potassium (trimethylsilyl)amide, are active catalysts for the hydrogenation of bicyclic and polycyclic aromatic hydrocarbons.

Hydrotreating of coal liquids

Coal liquids supplied by The Department of Energy have also been investigated. The results for two bases, lithium diisopropylamide (Catalyst 2) and potassium bis(trimethylsilyl)amide (Catalyst 5), are shown in Table 3. Three experiments with various catalyst loadings were performed with regard to the Catalyst 2. The conversions of the aromatic compounds in the sample were calculated from the decrease in intensity of the absorptions at 321 and 338 nm in UV-Visible spectrum. The conversions reached 82% at 338 nm and 97% at 321 nm when 4 g of Catalyst 2 per 10 g of coal liquids was employed. The elemental analysis for the product obtained under these conditions indicates that the carbon content (89.13%) decreased 0.45 units as the hydrogen content (10.70%) increased 0.62 units. Thus the H/C ratio increased from 1.36 to 1.43.

Catalyst 5 is an even more effective catalyst for the hydrotreating of the coal liquid. VSOH was hydrotreated to form a clear yellow liquid under mild conditions (1000 psig of hydrogen and 200 °C) if 16 mol% of Catalyst 5 was employed. The resonances between 8.0 and 8.3 ppm in ^{1}H NMR spectrum of the product, which are attributed to the protons bonded to aromatic carbon atoms of bi- and tricyclic molecules disappeared as new resonances of protons bonded to aliphatic carbons appeared. In addition, the absorptions at 321 and 338 nm in the UV-Visible spectrum, which are also attributed to the absorptions of polycondensed aromatic hydrocarbons, also completely disappeared, indicating that all the condensed aromatic compounds such as naphthalene derivatives were hydrogenated to the monoaromatic hydrocarbons.

The effects of temperature, catalyst loading as well as hydrogen pressure on the hydrotreating of coal liquids have also been studied. In general, after being hydrotreated, the coal liquid has a lower carbon content and higher hydrogen content than the untreated coal liquid sample.

Task 2 Catalytic Hydrogenation of Aromatic Compounds by Rh Catalysts

Introduction

The advantages of aqueous phase catalysis for hydroformylation and related processes has received considerable scientific scrutiny in recent years. One successful example is the Ruhrchemie/Rhone-Poulenc process in which water-soluble rhodium complexes catalyze the hydroformylation of propene. There are indications that the water, which is used as solvent in the two-phase system, alters the chemistry.

Preliminary research on the use of metal catalysts that was already underway in our laboratory prompted us to consider the use of aqueous systems for the hydrogenation of aromatic compounds in coal liquids.

Results and Discussion

The dimer of chloro(1,5-hexadiene)rhodium is an active catalyst precursor for the hydrogenation of aromatic hydrocarbons and heterocyclic compounds under phase transfer conditions involving tetrabutylammonium hydrogen sulfate (THS) or cetyltrimethylammonium bromide (CTAB) in an aqueous buffer [8]. This catalyst was investigated in more detail in our laboratory using tetralin as the substrate. Table 4 shows the influence of several phase transfer agents on the hydrogenation of tetralin to decalin at [substrate]/[catalyst] = 200/1. It can be seen that the addition of surfactant molecules reduces the activity of the catalyst. The conversion of the tetralin was decreased from 91% to 30% when THS was used. Similar results were obtained for CTAB and other surfactants exhibited even more negative effects on the reaction. It was clear that $[1,5\text{-HDRhC1}]_2$ was a more effective catalyst in the systems which contained low concentrations of the surfactant, and that some surfactants hindered the reaction. It is also noteworthy that $[1,5\text{-HDRhC1}]_2$ does not catalyze the reduction reaction of tetralin when only one of the solvents is used.

The use of buffers as the aqueous phase showed that the pH values and the composition of the buffer both effect the reaction, Table 5. The buffers with same compositions but different pH values and those with same pH value but different compositions all yield different conversions. The high yield (91%) was obtained by using hydion buffer at pH=7.4. In addition, the optimum volume ratios for the aqueous phase to organic phase were in the range 0.3-0.6 with more than 85% of tetralin hydrogenated to decalin under these conditions.

Methylene chloride, chloroform, dimethylethylene oxide alcohols, aliphatic hydrocarbons including hexane, cyclohexane, heptane, and higher homologues were studied. Hexane proved to be the most generally suitable cosolvent.

Other aromatic compounds were also hydrogented with this catalyst system. The reaction process was influenced by the subsituents in the aromatic ring, and the ease of the hydrogenation was found to be in the order benzene, toluene>n-butylbenzene> o-xylene> mesitylene.

Although the catalytic activity of $[1,5\text{-HDRhC1}]_2$ for the hydrogenation of tetralin was very good, the catalyst system had poor stability. The Rh metal aggregated on the wall of the reactor and appeared to be deactivated. We have begun to address this problem. The highest turnover number achieved under the optimum conditions with the [substrate]/[catalyst]=200:1 and the [aqueous phase]/[organic phase]=0.3 was 200. However, we found that small amounts of some surfactants ([surfactant]/[Rh]= 1.0) appear to form an emulsion to stabilize the catalyst without apparently affecting its activity. Under these conditions, the stability of the catalyst was improved greatly. In an experiment that was carried out for eight days, we found the turnover number of the catalyst exceeded 1200.

Our observations suggest that an active, stable catalyst system can be obtained for hydrogenation of monocyclic aromatic compounds under mild conditions. In addition, the noble metal can be separated and recycled. Thus, systems of this kind may prove highly effective for the removal of aromatic compounds from coal liquids.

Future Plans

The research will continue to focus on these two tasks. More work will be done on the rhodium catalyst system to improve its performance and to apply this catalyst system for the hydrotreating of coal liquids. Hydrotreating of coal liquids catalyzed by organic bases will proceed in parallel.

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Table 1 The organic bases used in attempts to activate hydrogen for the reduction of naphthalene

Organic Bases	[Substrate]/ [Base] (mole/mole)	Solvent	Conversion (%)
NaOBu-*t*	4:1	Hexane	0
LiOBu-*t*	4:1	Hexane	0
KOBu-*t*	1:2	Hexane	1
	1:2	*t*-BuOH	0
$NaNH_2$	4:1	Hexane	1
$LiNH_2$	4:1	Hexane	7
$LiN[CHMe_2]_2$	4:1	Hexane	100
$LiN[C_6H_{11}]_2$	4:1	Hexane	95

Conditions: Substrate: naphthalene; Solvent: 50 ml; Temperature: 200 °C; Initial H_2 pressure: 1000 psig; Reaction time: 18 hrs.

Table 2 Influence of ligands on the catalytic activity of lithium amides for the hydrogenation of naphthalene to tetralin

$LiNR_2$	[Substrate]/ [$LiNR_2$] (mole/mole)	Solvent	Conversion (%)
$LiN[CHMe_2]_2$	4:1	Hexane	100
$LiN(C_6H_{11})_2$	4:1	Hexane	95
$LiN[CH_2Me_2]_2$	4:1	Hexane	3
$LiNMe_2$	2:1	Hexane	7
$LiN[SiMe_3]_2$	2:1	Hexane	16
$LiN[SiMe_3]_2$	4:1	Toluene	3
$NaN[SiMe_3]_2$	4:1	Toluene	51
$KN[SiMe_3]_2$	4:1	Toluene	100

Conditions: Substrate: naphthalene; Solvent: 50 ml; Temperature: 200 °C; Initial H_2 pressure: 1000 psig; Reaction time: 18 hrs.

Table 3 Hydrotreating of coal liquid(VSOH) with Catalysts 2 and 5

Catalyst	[VSOH]/ [Catalyst] (g/g)	Temperature (°C)	Yield (%)	Conversion(%)		H/C Ratio
				321nm	338nm	
	VSOH	200	95	0	0	1.38
2	10/1	300	82	22	17	1.41
	10/2	300	81	77	62	1.43
	10/4	300	76	97	82	1.43
5	10/1	200	90	48	32	1.40
	10/2	100	92	95	90.0	1.43
		200	87	100	100	1.45
		250	89	100	100	1.49
		300	95	100	100	1.57
	10/4	200	93	100	100	1.57

Conditions: Solvents: Hexane for Catalyst 2 and Hexane-toluene mixture (2/3 v/v) for Catalyst 5; Reaction volume: 50 ml; Hydrogen pressure: 1000 psig at 25 °C; Reaction time: 24 hrs; Catalyst 2: $LiN(CHMe_2)_2$; Catalyst 5: $KN[SiMe_3]_2$.

Table 4 Effect of surfactants on the conversion of tetralin to decalin catalyzed by [1,5-HDRhC1]$_2$ catalyst

No	[Surfactant]/[Rh] (mole/mole)	Yield(%)		
		Trans-decalin	*Cis*-decalin	Total
None	–	18	74	91
THS	0.5	12	76	87
	8.0	4	26	30
CTAB	0.5	19	81	100
	1.0	21	79	100
	2.0	18	82	100
	4.0	13	61	73
	8.0	7	37	44
Aliquat 336	1.0	12	66	78
Tween 20	1.0	8	38	45
DSS	1.0	17	83	100

Conditions: Substrate: Tetralin(3.3g, 25.0 mmole) Catalyst: [1,5-HDRhC1]$_2$ (58 mg, 0.126 mmole); [Substrate]/[Catalyst]: 200/1; Solvent: Hexane(30 ml); Buffer(pH=7.4): 20ml, [Aqueous phase]/[Organic phase](v/v): 0.60; Temperature: 25 °C; H_2 pressure: 1 atm.

THS: Tetrabutylammonium hydrogen sulfatre,
CTAB: Cetylmethylammonium bromide,
Aliquat 336: Tricaprylmethylammonium chloride,
DDS: Dodecylsulfate sodium salt.

Table 5 Influence of the buffer as the aqueous phase on the biphase hydrogenation of tetralin to decalin catalyzed by $[1,5\text{-HDRhC1}]_2$

No	Buffer	Yield(%)		
	(pH, composition)	*Trans*-decalin	*Cis*-decalin	Total
1	Buffer (pH=7.4, Hydrion)	18	74	92
2	Buffer (pH=7.0, Hydrion)	7	32	39
3	Buffer (pH=8.0, Hydrion)	5	33	37
4	Buffer (pH=7.4, phosphate, 0.1M)	6	29	34
5	Buffer(pH=7.4, Phosphate:0.001M, NaC1: 0.138M, KC1: 0.027M, Tween 20: 0.05 % w/v)	4	36	41
6	Buffer(pH=7.4, Trizma saline: 0.05M NaC1: 0.56 %)	3	25	28

Conditions: Substrate: Tetralin(3.3g, 25.0 mmole); Catalyst: $[1.5\text{-HDRhC1}]_2$ (58 mg, 0.126 mmole); [Substrate]/[Catalyst]: 200: 1; Solvent: Hexane(30 ml); Buffer: 10 ml; [Aq.phase]/[Org. phase]: 0.30; Temperature: 25 °C; H_2 pressure: 1 atm.