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# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Molecular Research Division

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION  
Quarterly Report, January 1, 1985 - March 31, 1985

H. Heinemann

March 1985

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QUARTERLY REPORT

January 1, 1985 - March 31, 1985

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION

Project 4048

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## I. TECHNICAL PROGRAM FOR FY 1985

### Hydrodenitrogenation - Novel Methods for Nitrogen Removal from Polynuclear Nitrogen Containing Heteroaromatic Coal Compounds

The removal of nitrogen from complex matrices such as coal liquids is an extremely important area to study. We recently discovered that polynuclear heteroaromatic nitrogen compounds can be selectively reduced only in the nitrogen containing ring. We now wish to focus on the aspects of carbon-nitrogen cleavage in the saturated nitrogen heterocyclic ring of model coal compounds in order to better understand how nitrogen can be removed without additional substantial use of hydrogen gas for that reaction to occur. A dual approach will be followed that will provide fundamental information on the cleavage of carbon-nitrogen bonds using metal complexes of rhenium, iridium and ruthenium. The important coordination of metal complexes to saturated nitrogen compounds followed by oxidative addition to a methylene group alpha to the nitrogen atom will allow formation of metalla-azacyclopropanes. These compounds will be reacted with nucleophiles to hopefully afford carbon-nitrogen bond cleavage. The compounds will also be reacted under hydrogenation conditions to provide a similar carbon-nitrogen bond cleavage reaction. The second approach carried out simultaneously will use various zeolite catalysts with incorporated metal ions such as rhodium and ruthenium in addition to hydrogen donors such as long-chain hydrocarbons for catalytic cracking.

## II. HIGHLIGHTS

### NOVEL METHODS FOR HYDROGEN REMOVAL

At 300°C in the presence of 5% rhodium on silica catalyst and hydrogen gas some HDN chemistry prevails with 1,2,3,4-tetrahydroquinoline being converted to quinoline and other as yet not fully identified products containing propylbenzene, 2-propylaniline as well as ammonia. The identified products are presently being analyzed by GC-MS analysis.

### III. PROGRESS OF STUDIES

#### NOVEL METHODS FOR HYDROGEN REMOVAL

In the previous quarterly report, we provided evidence for the reactivity of the nitrogen-carbon bond in model coal compounds with ruthenium clusters and we were in the process of doing a survey of heterogeneous metal catalysts in order to gain insight into the cleavage of the carbon-nitrogen bond under HDN reaction conditions with THQ as the model coal compound. We have continued to survey metal catalysts and in this quarterly report we will discuss the results of this survey with copper, chromia, nickel and 5% rhodium on silica with THQ as the HDN model compound.

#### Copper with THQ

Copper was, unfortunately, an excellent dehydrogenation catalyst for conversion of THQ to quinoline. Thus, in the temperature range 200-400°C only quinoline was found in the presence of hydrogen gas. We also ran THQ with water, thiophene, and as the hydrochloride in water and methanol, but again, only dehydrogenation occurred.



### Nickel and Chromia

The reaction of nickel and chromia at 300°C in the presence of hydrogen provided only starting material and no other product.

### 5% Rhodium on Silica

This catalyst showed considerable reactivity in the reaction with THQ and hydrogen gas. Although, we do not know all the products that were formed, we were able to ascertain, by using GC retention times, several products which we summarize in Table 1.

Table 1. Conversion of 1,2,3,4-Tetrahydroquinoline under HDN Conditions with 5% Rhodium on Silica as the Catalyst

Run #	Temp °C	% Conversion	Products
1	300	86.7	48.7% Quinoline 2.4% Cyclohexenopyridine 49% Unidentified (to be submitted to GC-MS analysis)
2	260	89.9	35.9% Quinoline 19% Cyclohexenopyridine 56% Unidentified
3	200	76	98% Cyclohexenopyridine 1% Quinoline
4	300 (no H <sub>2</sub> gas)	100	99% Quinoline

Thus, Table 1 clearly shows that as the temperature is lowered from 300° to 200°C the dehydrogenation of THQ to quinoline is reduced

substantially and that the major product is cyclohexenopyridine. The other products formed in these reactions will be analyzed by GC-MS and reported in the next quarterly report. Since the regioselectivity in the above-mentioned reaction was totally opposite to our homogeneous and polymer-supported results, i.e., quinoline reduced to THQ under hydrogenation conditions, we speculate that in Run 3 in Table 1 the THQ is dehydrogenated to quinoline and then reduced to cyclohexenopyridine. The change in regioselectivity could be influenced by a catalyst poisoning or surface rearrangement phenomena and we will pursue these results with further experiments.

#### Future Directions

We will study the previously reported dimetalla-azacyclobutenes in hydrogenation reactions and continue the survey of metals in HDN experiments, while trying to further our understanding of the 5% Rhodium on Silica results.

#### Publications

R.H. Fish, A.D. Thormodsen, and T.-J. Kim, "Synthesis of Dimetalla-azacyclobutenes via Reaction of Triruthenium Dodecacarbonyl with Polymuclear Heteroaromatic Nitrogen Compounds. Organometallics 1985 (submitted for publication).

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