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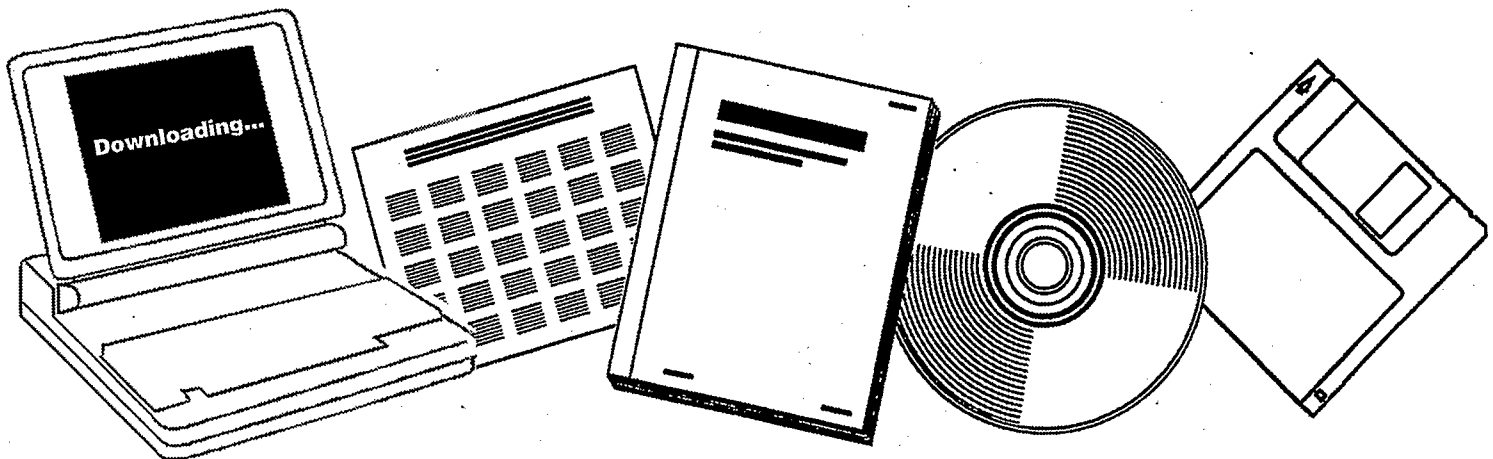
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**CATALYTIC HYDROGENATION OF CARBON
MONOXIDE. PROGRESS REPORT, SEPTEMBER 15,
1984-SEPTEMBER 14, 1985**

PENNSYLVANIA UNIV., PHILADELPHIA

SEP 1985



U.S. Department of Commerce
National Technical Information Service

Received by OSTI

OCT 18 1985

DOE/ER/13133--2

DE86 001547

CATALYTIC HYDROGENATION
OF CARBON MONOXIDE

Progress Report
September 15, 1984-September 14, 1985

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September, 1985.

Prepared for

THE U.S. DEPARTMENT OF ENERGY

AGREEMENT NO. DE-AC02-83ER13133

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INTERIM TECHNICAL REPORT

Contract No. DE-AC02-83ER13133

Project Title

"Catalytic Hydrogenation of Carbon Monoxide"

Abstract

The principal objective of this program is to learn how to utilize the unique properties of Rhodium porphyrins in achieving catalytic hydrogenation of carbon monoxide at mild conditions. Rhodium porphyrins react with H₂ and CO at pressures less than one atmosphere to produce the first intermediate in the hydrogenation of CO and provide a realistic opportunity to participate in the catalytic hydrogenation of CO at low gas pressures. Several catalytic schemes are proposed which take advantage of the unique reactivity of Rhodium porphyrins coupled with the aldehyde-like character of the metallo formyl intermediate. Multifunctional catalysts that utilize Rhodium porphyrins and a second catalyst known to promote the hydrogenation of aldehydes are particularly promising candidates for achieving low pressure hydrogenation of CO. Solvent effects will be explored as one means for tuning the thermodynamic and kinetic parameters for optimum catalytic behavior. Comparative studies used in identifying the essential features required to obtain a catalyst system based on metallo macrocycles.

Progress Report

The principal focus of this project is to gain insight into the sequence of events that occur in the metal catalysed hydrogenation of carbon monoxide and to use this information in designing effective catalyst systems.

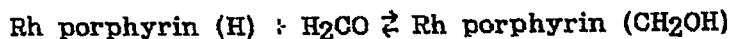
Metal catalysed hydrogenation of carbon monoxide is considered to occur through a series of organometallic intermediates including a metallo formyl (M-CHO) and hydroxymethyl (M-CH₂OH) species. Subsequent CO insertion reactions, carbonyl reduction and elimination reactions result in organic products. One possible scheme for production of glycol aldehyde, ethylene glycol and methanol is given by equations 1-9.

- 1) $M-M + H_2 \rightleftharpoons 2 M H$
- 2) $MH + CO \rightleftharpoons M-CHO$
- 3) $MCHO + H_2 \rightleftharpoons MH + CH_2O$
- 4) $MH + CH_2O \rightleftharpoons M-CH_2 OH$
- 5) $MCH_2OH + CO \rightleftharpoons M-C(O)CH_2OH$
- 6) $M(C(O) CH_2OH) + H_2 \rightleftharpoons M-CH(OH)CH_2OH$
- 7) $MCH(OH)CH_2OH \rightarrow MH + CH(O)CH_2OH$
- 8) $MCH(OH)CH_2OH + MH \rightarrow M-M + (CH_2OH)_2$
- 9) $MCH_2OH + MH \rightarrow M-M + CH_3OH$

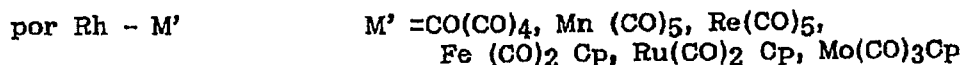
Previous studies from this laboratory have demonstrated that rhodium porphyrin dimers activate dihydrogen to form metallo hydrides that insert carbon monoxide to produce metalloformyl complexes at equilibrium conditions (steps 1 and 2). Present investigations are focused on the following processes;

- 1) hydrogen reduction of the metalloformyl and acyl complexes and subsequent formation of metallo α -hydroxyalkyl intermediates (steps 3, 4, 6)
 - 2) chain lengthening by CO insertion reactions (step 5)
 - 3) reductive elimination reactions that produce organic products (step 7-9)
- 1) H₂ reduction of a metallo formyl

A major focus of our current work is in exploring the hydrogen reduction of metallo formyl and related acyl species (reactions 3 and 5) ($M-CHO + H_2 \rightarrow MCH_2OH$). The purpose of this work is to discover a low energy pathway for the reaction $M_2 + 3 H_2 + 2CO \rightarrow 2 MCH_2OH$. The thermodynamic feasibility of this reaction for the case of rhodium porphyrins has been clearly demonstrated by the reaction of the metallo hydrides with formaldehyde.



Our strategy for accomplishing the H₂ reduction of the coordinated formyl group is to use a second metallo species that functions as a hydrogen transfer catalyst. We have prepared a series of bimetallic complexes that have a metal-metal bond between a rhodium porphyrin and a second metallo species with smaller steric requirements.

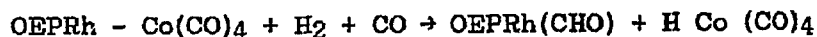


The following set of reactions illustrates the behavior that we are searching for.

- a) $\text{por Rh} - \text{M}' + \text{H}_2 \rightleftharpoons \text{por Rh(H)} + \text{M}'\text{-H}$
- b) $\text{por Rh(H)} + \text{CO} \rightleftharpoons \text{por Rh(CHO)}$
- c) $\text{por Rh(CHO)} + \text{M}'\text{-H} \rightleftharpoons \text{por Rh-M}' + \text{CH}_2\text{O}$
- d) $\text{por Rh(H)} + \text{H}_2\text{CO} \rightleftharpoons \text{H por Rh(CH}_2\text{OH)}$

We are currently in the process of evaluating the reactivity of por Rh-M' compounds with H₂ and CO.

One specific example is OEP Rh-Co(CO)₄ which reacts reversibly with CO and H₂ (P_T=lat.) to produce the precursors to the hydroxymethyl complex.



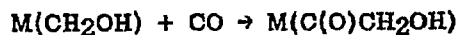
The other bimetallic complexes have similar reactivity and these systems will be evaluated at elevated pressures and temperatures (P<100 at.; T<150°C).

The current focus of this work is on the reactivity of OEP Rh-Ru(CO)₂Cp because H Ru (CO)₅ Cp is known to be an effective catalyst for the H₂ reduction of aldehydes to alcohols. If successful, this study will result in formation of the first hydroxymethyl complex prepared from H₂, CO and a metal complex.

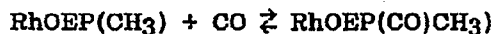
We are presently extending the bimetallic materials to include early transition metals (Zr, Hf) and post transition series metals (In, Tl, Sn).

2) Carbon monoxide insertion (chain lengthening)

One means of producing two carbon and larger organic molecules operates through CO insertion reactions (reaction 5).



This type of reaction has been demonstrated to occur for Rhodium porphyrin alkyls.



This reaction is currently being evaluated for RhOEP(CH₂OH) in order to obtain the precursor to glycolaldehyde.

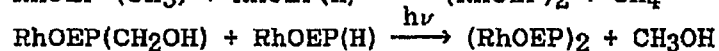
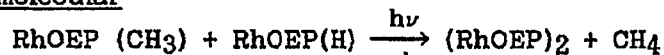
3) Reductive elimination reactions

Uni and biomolecular elimination reactions are needed to produce organic products from the organometallic intermediates (reactions 7-9). Both types of eliminations have been demonstrated for Rhodium porphyrin organometallic molecules.

unimolecular



biomolecular



The biomolecular elimination of CH₄, and CH₃OH demonstrates the feasibility of producing alcohols and aldehydes from rhodium porphyrin catalyst systems.

Summary

Studies during the second year of this program have contributed to understanding of each of the required steps in the hydrogen reduction of CO (reactions 1-9).

Hydrogen reduction of the metalloformyl has been identified as the primary kinetic barrier to the production of organic molecules from H₂ and CO at moderate conditions. Bimetallic compounds are being prepared and evaluated as potential catalysts for this process and encouraging preliminary results have been obtained.

Although catalytic formation of organic molecules from H₂ and CO has not yet been observed at mild conditions, results from this program are establishing criteria and aiding in the development of new strategies to attain this goal.

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