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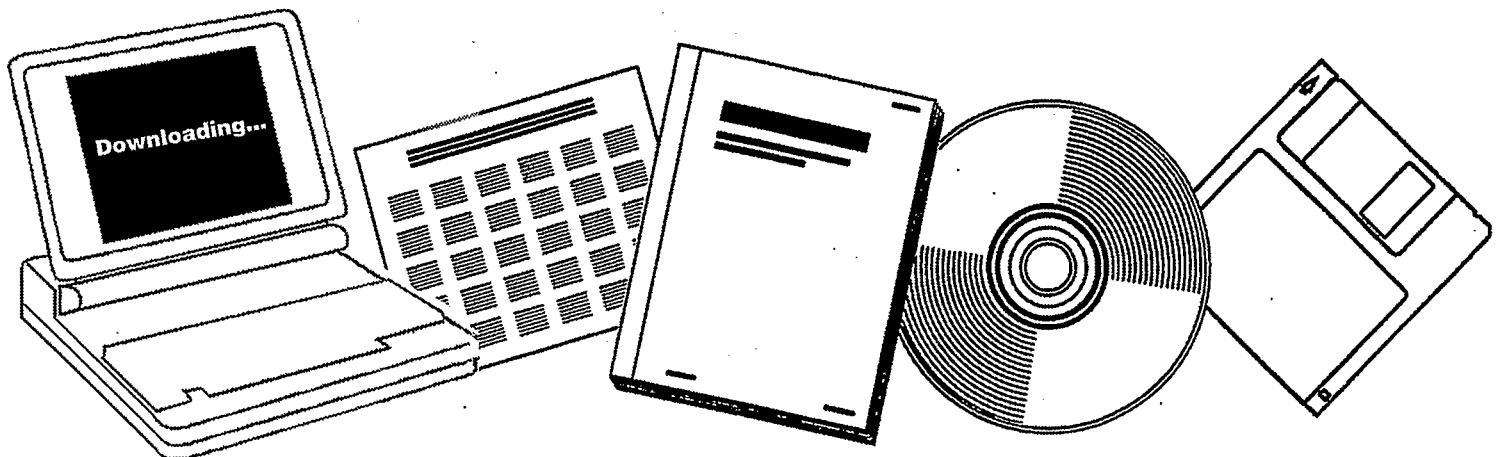
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**CATALYTIC HYDROGENATION OF CARBON
MONOXIDE. PROGRESS REPORT, SEPTEMBER 15,
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CATALYTIC HYDROGENATION
OF CARBON MONOXIDE

Progress Report
September 15, 198~~4~~³ - September 14, 198~~5~~⁴

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N O T I C E

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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 H_2 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 utilizing variation of the macrocycle and central metal (Co,Rh,Ir) are being 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 event 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 1-8.

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

Our present studies are concerned with the detailed examination of reactions such as 1-8 that are relevant to the hydrogenation of CO.

1) Activation of dihydrogen

Activation of H_2 is an essential feature of the hydrogen reduction of CO. We are examining an extensive series of M-M bonded species that may be capable of reaction 1 ($M_2 + H_2 \rightleftharpoons 2MH$).

In addition to $(Rh\ por)_2$ we are examining or reexamining reaction 1 for a series of $(M(CO)_x)_2$ and $(M(CO)_xcp)_2$ complexes.

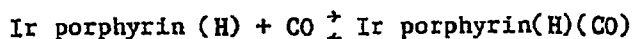
The purpose of this work is to produce a series of well defined metallohydride reducing agents that can be regenerated by reaction with H_2 .

Thermodynamic studies for reaction 1 are being used in evaluating the feasibility of incorporating metallo species in catalytic cycles in addition to evaluating M-H bond energies.

2) Metallo formyl complexes

We have recently shown that reaction 2 ($M-H+CO \rightleftharpoons M-CHO$) is a general reaction for all rhodium porphyrins. (e.g. rhodium octaethyl porphyrin (RhOEP) and Rhodium tetraphenyl porphyrin (RhTPP)). Reaction 2 is presently being extended to related rhodium macrocycle complexes. Preliminary results suggest that several non porphyrinic rhodium macrocycle complexes can produce metallo formyl species. $(Rh\ mac)_2 + H_2 + CO \rightleftharpoons 2 Rh\ mac\ (CHO)$

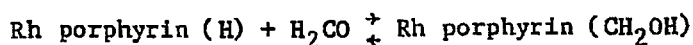
The corresponding Iridium porphyrin and macrocycle complexes do not produce observable quantities of metallo formyl complexes, but instead form only CO adducts of the metallo hydride.



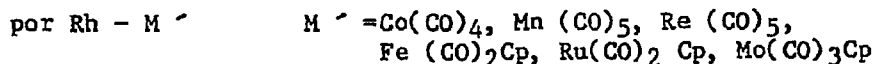
Thermodynamic studies for reaction 2 ($MH+CO \rightleftharpoons MCHO$) are being used to establish criteria for tuning the M-C bond energies which will subsequently be used in guiding the optimization of catalytic properties.

3) H₂ reduction of a metallo formyl

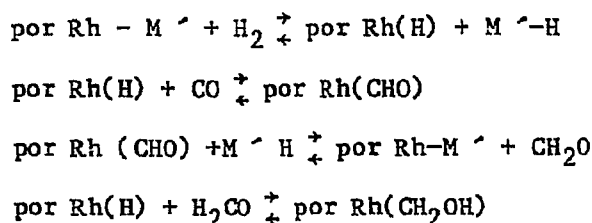
A major focus of our current work is in exploring the hydrogen reduction of metallo formyl and related acyl species (reactions 3 and 5) ($M-CHO+H_2 \rightarrow MCH_2OH$). The purpose of this work is to discover a low energy pathway for the reaction $M_2 + 3H_2+2CO \rightarrow 2 MCH_2OH$. The thermodynamic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



Our approach to the H₂ reduction of the coordinated formyl group is to use a second metallo species that functions as a hydrogen transfer agent. 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.

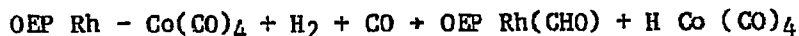


The following set of reactions illustrates the behavior that we are searching for.



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=1at.) to produce the precursors to the hydroxymethyl complex.



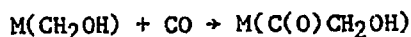
The other bimetallic complexes have similar reactivity and these systems will be evaluated at elevated pressures and temperatures (P<100 at.; T<150°C).

The current focus of this work is on the reactivity of OEP Rh-Ru(CO)₂ Cp 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.

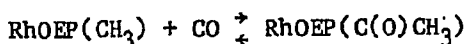
We are presently extending the bimetallic materials to include early transition metals (Zr, Hf) and post transition series metals (In, Tl, Sn).

4) Carbon monoxide insertion (chain lengthening)

One means of producing two carbon and larger organic molecules operates through CO insertion reactions (reaction 4).



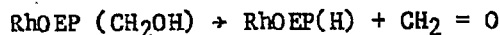
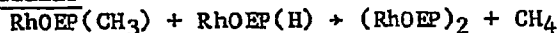
This type of reaction has been demonstrated to occur for Rhodium porphyrin alkyls.



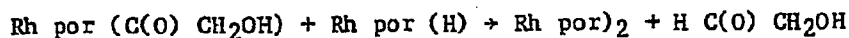
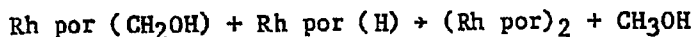
This reaction is currently being evaluated for RhOEP(CH₂OH) in order to obtain the precursor to glycolaldehyde.

5) Reductive elimination reactions

Uni and bimolecular elimination reactions are needed to produce organic products for the organometallic intermediates (reactions 6-8). Both types of eliminations have been demonstrated for Rhodium porphyrin organometallic molecules.

unimolecularbimolecular

The bimolecular elimination of CH₄ demonstrates the feasibility of producing alcohols and aldehydes from rhodium porphyrin catalysis.

Summary

Studies during the first year of this program have contributed to understanding of each of the required steps in the hydrogen reduction of CO (reactions 1-8).

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 to optimize catalyst properties to attain this goal.