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TRANSITION METAL CHEMISTRY UNDER HIGH CARBON MONOXIDE PRESSURE:
AN INFRARED SPECTROSCOPIC STUDY OF CATALYSIS IN THE FISCHER-TROPSCH REACTION

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January, 1978

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PREPARED FOR THE
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION OF THE
U. S. DEPARTMENT OF ENERGY UNDER CONTRACT EY-76-S-09-0933

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The ultimate aim of this research project is the discovery of fundamental chemistry which will provide a basis for the development of new and improved processes for the conversion of coal to hydrocarbon fuels. In this connection the following two general approaches for the conversion of coal to hydrocarbon fuels are of interest:

(A) Fischer-Tropsch Process

1. Reaction of coal with steam under high temperatures and pressures to produce mixtures of carbon monoxide and hydrogen (the water gas reaction).
2. Reactions of these mixtures of carbon monoxide and hydrogen in the presence of appropriate catalysts to give the hydrocarbon fuels (the Fischer-Tropsch reaction).

(B) Bergius Process

1. The water gas reaction as outlined above.
2. Reaction of the carbon monoxide from the water gas reaction with water in the presence of appropriate catalysis to give hydrogen and carbon dioxide (the water gas shift reaction).
3. Hydrogenation of coal using the hydrogen obtained from the water gas and the water gas shift reactions (steps 1 and 2) (the Bergius Process).

Both of these processes were successfully used by Nazi Germany during World War II for the manufacture of gasoline and other hydrocarbon fuels from coal.

The original specific objective of this research program was the development of experimental techniques for the investigation of infrared spectra of transition metal complexes under pressures of carbon monoxide and/or hydrogen up to 500 atmospheres and temperatures up to 250°C. The rationale behind this work was the identification of metal carbonyl and metal carbonyl hydride species, including those stable only at elevated pressures, which might be catalytic intermediates in the Fischer-Tropsch and related reactions. We have been very successful in the development of this experimental technique, since we now have in routine operation at the University of Georgia an infrared spectroscopic set-up (called a spectraclave) which is used to measure infrared spectra in the metal carbonyl $\nu(\text{CO})$ region at pressures up to 500 atmospheres and temperatures up to at least 200°C. In these spectroscopic studies we use stainless steel high pressure cells with Irtran-1 windows constructed in the machine shop at the University of Georgia.

Our initial studies with the spectraclave have involved reactions of transition metal alkyls with carbon monoxide at elevated pressures. Such reactions relate to the hydroformylation reaction for the synthesis of aldehydes from olefins, carbon monoxide, and

hydrogen since metal alkyls are known catalytic intermediates in such reactions. They also could relate to the Fischer-Tropsch reaction if metal alkyls can be found which can be successively carbonylated to metal acyls and the acyl carbonyl group then hydrogenated to a CH_2 group (Equation 1) thereby resulting in extension of an alkyl chain. However, no

metal alkyls with such chemical reactivity have yet been found. Examples of metal alkyls included in this study are $\text{CH}_3\text{M}(\text{CO})_5$ ($\text{M} = \text{Mn}$ and Re), $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$, and $\text{RM}(\text{CO})_3\text{C}_5\text{H}_5$ ($\text{M} = \text{Mo}$, $\text{R} = \text{CH}_3$, C_2H_5 , $\text{CH}_2 = \text{CHCH}_2$, and $\text{C}_6\text{H}_5\text{CH}_2$; $\text{M} = \text{W}$, $\text{R} = \text{CH}_3$).

A metal of particular importance in the catalysis of hydroformylation reactions is rhodium.² Rhodium is also the metal used as the catalyst in the Union Carbide process of manufacturing ethylene glycol from carbon monoxide and hydrogen.³ Accordingly, we have investigated the reactions of various rhodium compounds with olefins in the presence of carbon monoxide and hydrogen using the spectraclave. Our preliminary results suggest that formation of aldehydes by reactions of olefins with carbon monoxide and hydrogen occurs under conditions where the rhodium is converted to the metal cluster carbonyl $\text{Rh}_4(\text{CO})_{12}$. Furthermore, carbonylation of rhodium systems takes place under far milder conditions than the other transition metal systems investigated in this work. Mechanistic implications of these observations are under investigation.

Use of transition metal complexes as homogeneous catalysts for reactions of carbon monoxide requires the generation of intermediates which can reversibly coordinate carbon monoxide as well as species with which the carbon monoxide is to be reacted.⁴ An interesting class of coordinately unsaturated transition metal complexes are the compounds $[(\text{CH}_3)_5\text{C}_5\text{M}(\text{CO})_2]_2$ (I: $\text{M} = \text{Cr}$, Mo , and W) containing a metal-metal triple bond. Such metal-metal triple bonds can reversibly add carbon monoxide to form the corresponding derivatives with metal-metal single bonds (II) in a manner completely analogous to the hydrogenation of acetylene to give ethane. Accordingly we have prepared samples of the

known⁵ compounds $[(CH_3)_5C_5M(CO)_2]_2$ (I: $M = Cr$ and Mo) and the previously unreported tungsten analogue (I: $M = W$) by reactions of the metal hexacarbonyls with pentamethylcyclopentadiene⁶ in boiling decane. Investigation of the reactions of these metal-metal triple bond species (I) with carbon monoxide at elevated pressures indicates that upon descending the periodic table from chromium through molybdenum to tungsten under corresponding conditions the equilibrium represented by equation 2 lies more to the right with species I being favored for chromium and species II for tungsten.

One of the most effective metals for catalysis of the Fischer-Tropsch reaction is iron which was used by the Germans during World War II^{1,7} and apparently is used by the South Africans in the Sasol process for manufacturing gasoline from carbon monoxide and hydrogen. In accord with our original research proposal suggesting $HFe(CO)_4^-$ as a possible catalytic intermediate⁸ we investigated reactions of $HFe(CO)_4^-$ with carbon monoxide in the spectraclave. Such reactions were found to give $Fe(CO)_5$ with apparent displacement of the hydride ligand in $HFe(CO)_4^-$ by CO. This suggests the following four-step mechanism for the water gas shift reaction:

In accord with this idea, we have found that $HFe(CO)_4^-$ generated from $Fe(CO)_5$ and alcoholic hydroxide, is an effective catalyst for the water gas shift reaction at temperatures around $140^\circ C$ and pressures in the range 15-30 atmospheres. This unexpected discovery that simple (and relatively inexpensive) metal carbonyls such as $Fe(CO)_5$ can be effective catalyst presursors for the water gas shift reaction led us to screen several other simple metal carbonyls as candidates for catalyst precursors of the water gas shift reaction. For these studies we set up several autoclaves with associated equipment for measuring reaction temperatures and pressures as well as a gas chromatograph with a 5A molecular sieve column calibrated for hydrogen analyses. To date we have found that methanol solutions of the metal hexacarbonyls $M(CO)_6$ ($M = Cr, Mo, \text{ and } W$) in the presence of aqueous potassium hydroxide are active homogeneous catalysts for the water gas shift reaction at temperatures above $\sim 120^\circ C$ and pressures in the range 5-10 atmospheres. The hydrogen produced during the water gas shift reactions can be identified by gas chromatography as

outlined above. The carbon dioxide produced during the water gas shift reaction using such catalysts has been identified from its characteristic infrared frequency at 2300 cm.^{-1} when the reaction was done in the spectraclave as well as by gas chromatography with a silica gel column. This work suggests that the range of metal carbonyl derivatives which are effective catalysts for the water gas shift reaction may be much larger than that suggested by previous recent work which uses the relatively rare metals ruthenium⁹ and rhodium.¹⁰ We plan to screen other types of metal carbonyl derivatives for catalytic activity in the water gas shift reaction.

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MEETING PRESENTATIONS FROM THIS PROJECT

- (1) R. B. King, A. D. King, Jr., M. Z. Iqbal, and C. C. Frazier, "Infrared Spectroscopy at High Pressures for the Investigation of Catalysis of Carbon Monoxide Reactions," presented by R. B. King at the 2nd joint conference of the Chemical Institute of Canada and the American Chemical Society, Montreal, P. Q., Canada, May 29-June 2, 1977: paper COLL 25 in abstracts.
- (2) R. B. King, M. Z. Iqbal, C. C. Frazier, and A. D. King, Jr., "Infrared Spectroscopy at High Pressures for the Investigation of Reactions of Cyclopentadienylmetal Derivatives with Carbon Monoxide," presented by R. B. King at the Eighth International Conference on Organometallic Chemistry, Kyoto, Japan, September, 1977.
- (3) R. B. King, A. D. King, Jr., M. Z. Iqbal, C. C. Frazier, and R. M. Hanes, "Metal Carbonyl Catalysis of Carbon Monoxide Reactions," presented by R. B. King at the 2nd International Workshop on "Fundamental Research in Homogeneous Catalysis," Lake Biwa, Japan, September, 1977.
- (4) C. C. Frazier, R. Hanes, A. D. King, Jr., and R. B. King, "Homogeneous Catalysis of the Water Gas Shift Reaction: Pentacarbonyliron and the Metal Hexacarbonyls as Active Catalyst Precursors," paper scheduled for presentation by C. C. Frazier at a symposium on "Inorganic Compounds with Unusual Properties. II. Molecular Catalysis and the Conversion, Production, and Storage of Energy," Athens, Georgia, February, 1978.
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PUBLICATIONS FROM THIS PROJECT

- (1) R. B. King, A. D. King, Jr., M. Z. Iqbal, and C. C. Frazier, "Transition Metal Alkyl Chemistry at Elevated Carbon Monoxide Pressures: An Infrared Spectroscopic Study of Systems Related to Catalytic Intermediates in Homogeneous Hydroformylation Reactions," accepted for publication in J. Am. Chem. Soc.
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