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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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This project involves the design and construction of equipment to investigate the infrared spectra of metal carbonyl derivatives in the $1600-2200\text{ cm}^{-1}$ $\nu(\text{CO})$ region at pressures up to 500 atmospheres and temperatures up to 250° followed by the use of this equipment to study the infrared spectra of a variety of transition metal derivatives at elevated pressures of carbon monoxide. The ultimate objective of this work is the discovery of new chemistry leading to the development of new systems which are catalytically active for the conversion of mixtures of carbon monoxide and hydrogen to hydrocarbons in connection with the conversion of coal to hydrocarbon fuels. During the initial period covered by this first progress report a high pressure infrared cell has been designed, constructed, and used for the preliminary investigations of reactions of about 15 transition metal derivatives under elevated pressures of carbon monoxide and hydrogen.

DESIGN AND CONSTRUCTION OF EQUIPMENT

The initial period of this program, spanning roughly two months, involved design work and testing of various components required for the high pressure reaction chamber to be monitored using an infrared spectrometer. Eastman Kodak Company was very helpful at this stage by supplying the principal investigators with free samples of various IRTRAN window materials for testing purposes. Our first preference for window material, IRTRAN 2, was found not to be stable in the presence of hydrocarbon solvents at high temperatures and pressures but instead darkened upon exposure to these conditions. However, IRTRAN 1 was found to be stable under these conditions. IRTRAN 1 does not provide as wide a range of spectral transmittance as IRTRAN 2 but transmits infrared radiation in the region of principal interest (1600 cm^{-1} to 2400 cm^{-1}). In fact IRTRAN 1 offers the following two advantages over IRTRAN 2 which partially offset its lack of spectral transmittance below 1400 cm^{-1} : (a) The modulus of rupture of IRTRAN 1 (21,800 psi at 25°C) is considerably greater than that of IRTRAN 2 (14,000 psi at 25°C) thus providing greater strength for operation at higher pressures; (b) The refractive index of IRTRAN 1 in the infrared region is quite low (1.3 to 1.4) so that light scattering poses less of a problem. All machine work on the prototype autoclave-optical cell resulting from this design work was completed by July 12 and was successfully pressure tested the following week.

Considerable delays were encountered in our efforts to assemble the necessary optics for this project. The most notable delay was encountered in our purchase of an all reflecting 4 X beam condenser. Early in the design phases we decided to use this attachment, an "off the shelf" item, as transfer optics in order not only to remove the unsupported windows of the high pressure cell from the optical axis of the spectrometer but also to maximize the beam intensity at the necessarily small high pressure windows.

This unit was ordered in late May but was not received until October. However, the supplier, Perkin-Elmer Corporation, helped to ease the impact of this delay by sending us a copy of their engineering drawings for this beam condenser. This enabled us to specify completely the outer dimensions of the high pressure cell and even so that construction of the prototype cell and accompanying pressurization system could be completed quite early in the program.

A sketch from a vertical perspective showing the cell and oven in relation to the beam condensing optics is shown in Figure 1. An optical path length of 4 mm. is shown here for the sake of clarity. Much shorter pathlengths (1.0 to 0.1 mm.) are of course used in the infrared measurements. Figure 2 shows a lateral perspective of the assembled high pressure optical cell, reservoir, and agitator. The agitator is activated magnetically by an air-cooled solenoid coil mounted externally.

The spectrophotometer chosen for this project is a Perkin-Elmer model 281. This instrument is particularly well suited for these experiments since its modular design allows the monochromator to be separated from the control console and recorder. This allows the operator to be shielded from the high pressure optical cell at all times. An additional feature of this spectrometer of particular importance is the fact that all abscissa functions are microprocessor controlled thus allowing the wavelengths of the narrow $\nu(\text{CO})$ frequencies to be determined very accurately. This instrument was received on January 10 and will be placed in operation in the very near future.

Figure 3 is a block diagram showing the various components of the completely assembled system. The gas pressurization system uses a Teledyne Sprague Model S 216 CR-300 pump P driven by air stored in cylinder A. The output of this pump compresses the gas (or gaseous mixture) contained in the upper compartment of the free piston pump F. This highly compressed gas is introduced into the high pressure autoclave-cell heated by an oven C. Any reactions are monitored using the infrared spectrometer S.

The internal pressure of the autoclave-cell is recorded using a Bourdon gauge B. Valve V is a vent valve while R designates a regulator used to set the operating pressure within the system. This system, as designed, is capable of delivering binary mixtures of hydrogen and carbon monoxide at pressures up to 2000 atmospheres, although the optical components are currently designed to a 500 atmospheres upper limit.

Figure 4 is a rough sketch showing the proposed configuration of the Perkin-Elmer 281 monochromator and control console in an integrated unit, which for convenience we call a "spectraclave".

PRELIMINARY RESULTS

Since November we have conducted over thirty experiments with the high pressure cells and associated equipment using a small prism spectrometer (Perkin-Elmer 137) acquired several years ago as government surplus. In view of the limited resolving power of this instrument we have concentrated on systems exhibiting relatively small numbers of relatively widely spaced $\nu(\text{CO})$ frequencies and which therefore do not demand high resolving power to obtain definitive and significant chemical information. For this reason these initial studies have concentrated on cyclopentadienylmetal carbonyl chemistry, an area of chemistry which, although very extensive, has received relatively little attention in catalysis. After we get our new Perkin-Elmer 281 spectrometer in operation in the spectraclave, we will no longer have such limited resolving power and therefore will be able to study systems more directly related to those currently significant in catalysis.

Our preliminary results with cyclopentadienylmetal carbonyl chemistry can conveniently be summarized according to the central metal atom. All reactions cited below were run in tetradecane as a solvent.

(1) Chromium: The pentamethylcyclopentadienyl derivative $[(\text{CH}_3)_5\text{C}_5\text{Cr}(\text{CO})_2]_2$ (I: $\text{M} = \text{Cr}$) was studied in order to determine the conditions where carbon monoxide might add

to the chromium-chromium triple bond.¹ The compound I ($M = Cr$) was stable under 300 atmospheres CO until 90°. Above this temperature it formed a product A with infrared bands at 2025 (s), 1945 (s), and 1915 (vs). This pattern does not correspond to the expected CO-addition product $[(CH_3)_5C_5Cr(CO)_3]_2$. Species A was stable to 168° at 300 atmospheres CO and persisted upon cooling to room temperature and removal of CO pressure. Upon opening the cell a pink air-sensitive solution was obtained. We plan to attempt to synthesize this product A in bulk in an attempt to identify it by usual analytical methods.

(2) Molybdenum: A variety of cyclopentadienylmolybdenum derivatives were available for this preliminary investigation. A characteristic feature of many of these cyclopentadienylmolybdenum derivatives at CO pressures of ~320 atmospheres and temperatures in the range 175-200° was their instability with respect to removal of the cyclopentadienyl ring with the resulting formation of $Mo(CO)_6$. However, under milder conditions, interesting intermediates could be identified in some cases.

The most stable cyclopentadienylmolybdenum carbonyl derivative was $C_5H_5Mo(CO)_2NO$. This compound survived temperatures up to 200° at 330 atmospheres CO without any change detectable in the infrared $\nu(CO)$ region.

The analogous p-tolylazomolybdenum derivative $CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ ² was considerably less stable towards CO under pressure. Above 150° at 320 atmospheres CO

pressure $\text{Mo}(\text{CO})_6$ was produced. However, upon cooling under CO pressure the $\text{Mo}(\text{CO})_6$ reacted partially with a cyclopentadiene derivative concurrently produced in the original carbonylation to produce $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ or a ring-substituted derivative thereof.

The oximatomolybdenum derivative³ $(\text{CH}_3)_2\text{C}=\text{NOMo}(\text{CO})_2\text{C}_5\text{H}_5$ (II) is still more reactive towards carbon monoxide. At 70° and 70 atmospheres CO new infrared $\nu(\text{CO})$ frequencies appeared which could be due to a tricarbonyl $(\text{CH}_3)_2\text{CNOMo}(\text{CO})_3\text{C}_5\text{H}_5$. At temperatures above 120° and 70 atmospheres CO a mixture of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ and $\text{Mo}(\text{CO})_6$ appeared with decay of the oximato species.

Some alkylmolybdenum derivatives were also studied. Reaction of $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ with 320 atmospheres CO at 125° formed an apparent acetyl derivative which on treatment with 300 atmospheres of H_2 at 138° gave some $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_3]_2$. Reaction of $\text{C}_6\text{H}_5\text{CH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ with 320 atmospheres CO began at 100° and led to $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ and $\text{Mo}(\text{CO})_6$ as the only products identifiable by their $\nu(\text{CO})$ frequencies.

The compound $[(\text{CH}_3)_5\text{C}_5\text{Mo}(\text{CO})_2]_2$ (I: $\text{M} = \text{Mo}$) containing a molybdenum-molybdenum triple bond began to react with 310 atmospheres of CO at 90° . However, before this reaction was complete, formation of $\text{Mo}(\text{CO})_6$ began so that the spectrum of this intermediate was not sufficiently clear for unambiguous identification.

Azulene forms a molybdenum carbonyl complex $\text{C}_{10}\text{H}_8\text{Mo}_2(\text{CO})_6$ (III) in which the five-membered ring is bonded to the molybdenum similar to a cyclopentadienyl ligand.⁴ This azulene-molybdenum derivative III was much more reactive towards carbon monoxide than any of the cyclopentadienylmolybdenum derivatives listed above since it rapidly formed $\text{Mo}(\text{CO})_6$ upon reaction with CO at either 320 atmospheres and only 50° or only 7 atmospheres and 150° .

(3) Iron: Cyclopentadienyliron carbonyl derivatives were relatively unreactive towards CO under pressure. No change was observed on heating either $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ or $[(\text{CH}_3)_5\text{C}_5\text{Fe}(\text{CO})_2]_2$ under 320 atmospheres CO up to 150° .

The methyliron derivative $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ reacted with 320 atmospheres CO at 125° to form the corresponding acetyliron derivative $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ in a typical CO insertion (i.e. methyl migration) reaction as indicated by the appearance of a new infrared band at 1660 cm^{-1} arising from an acyl carbonyl. Further treatment of this acetyliron derivative with a mixture of 340 atmospheres of CO and 140 atmospheres of H_2 gave no infrared evidence for the formation of $\text{HFe}(\text{CO})_2\text{C}_5\text{H}_5$ or acetaldehyde.

Some studies were also done on benzoferrocene, $\text{C}_5\text{H}_5\text{FeC}_9\text{H}_7$ (IV),⁵ in order to compare the relative ease of cleavage of the two ring systems. Treatment of $\text{C}_5\text{H}_5\text{FeC}_9\text{H}_7$ (IV) with 300 atmospheres of CO ultimately led to $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ through other still unidentified $[(\text{dienyl})\text{Fe}(\text{CO})_2]_2$ products as intermediates. Further work including isolation of the unidentified intermediates on a preparative scale is required before this system is fully understood.

Despite the limited resolution capabilities of our present set-up using the surplus Perkin-Elmer 137 spectrometer, we have done some preliminary studies on $\text{RMn}(\text{CO})_5$ derivatives. In accord with expectations based on a relatively old (1958) report⁶ $\text{CH}_3\text{Mn}(\text{CO})_5$ reacted with 320 atmospheres CO at 67° to form the acetyl derivative $\text{CH}_3\text{COMn}(\text{CO})_5$, identified by a new band at $\sim 1663\text{ cm}^{-1}$. Treatment of this $\text{CH}_3\text{COMn}(\text{CO})_5$ with 320 atmospheres H_2 at 95° resulted in the disappearance of this 1663 cm^{-1} band with the production of a new band at 1725 cm^{-1} characteristic of acetaldehyde. After removal of the CO pressure, an infrared spectrum of the resulting yellow solution indicated the presence of $\text{Mn}_2(\text{CO})_{10}$. The resulting sequence of three reactions thus was performed in the high pressure cell with each step identified by infrared spectroscopy:

The oxygen required from the last step came from inadvertent exposure to air during removal of the final solution from the infrared cell.

The analogous trifluoromethyl derivative $\text{CF}_3\text{Mn}(\text{CO})_5$ was found to behave differently under CO pressure in accord with the stronger bonds of transition metals to fluorocarbons relative to corresponding hydrocarbons.⁷ Thus treatment of $\text{CF}_3\text{Mn}(\text{CO})_5$ with 340 atmospheres CO at 200° led directly to $\text{Mn}_2(\text{CO})_{10}$ without any evidence for the formation of $\text{CF}_3\text{COMn}(\text{CO})_5$.

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FIGURE 1

Solenoid

3.000"

1.750"

FIGURE 2

FIGURE 3

FIGURE 4