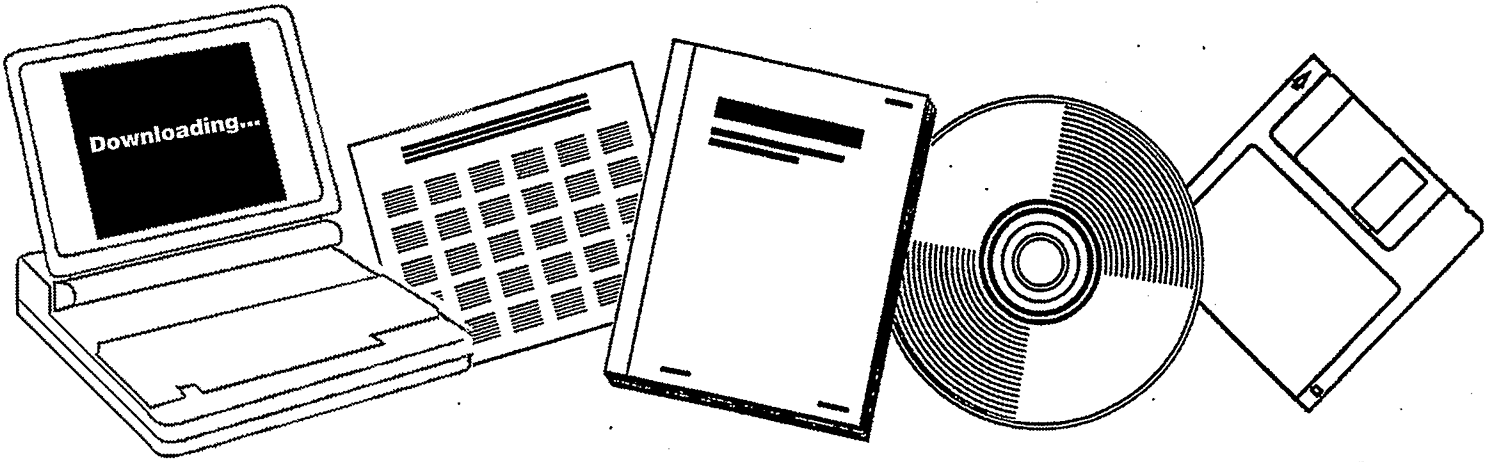
DE87005181

CHEMICAL TRAPPING OF CO/H SUB 2 SURFACE SPECIES: QUARTERLY REPORT

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL AND PETROLEUM ENGINEERING

JAN 1987



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DOE/PC/80526-T6.

DOE/PC/80526--T6
DE87 005181

Chemical Trapping of CO/H_2 Surface Species

Quarterly Report

January 1987

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Prepared for the U.S. Department of Energy
under Grant No. DE-FG22-85PC80526

I. INTRODUCTION

The work on the project during the last quarter has focused on the design and construction of a system that will allow us to better investigate how a model organometallic complex may serve as a system analogous to that of the metal catalyst-adsorbate bond. We have also made considerable modifications to the reaction system for performing in-situ trapping reactions concurrent with the catalytic CO + H_2 reaction. Both of these thrusts were suggested by the positive preliminary results we have obtained in both the organometallic complex and in-situ catalytic reaction parts of the project.

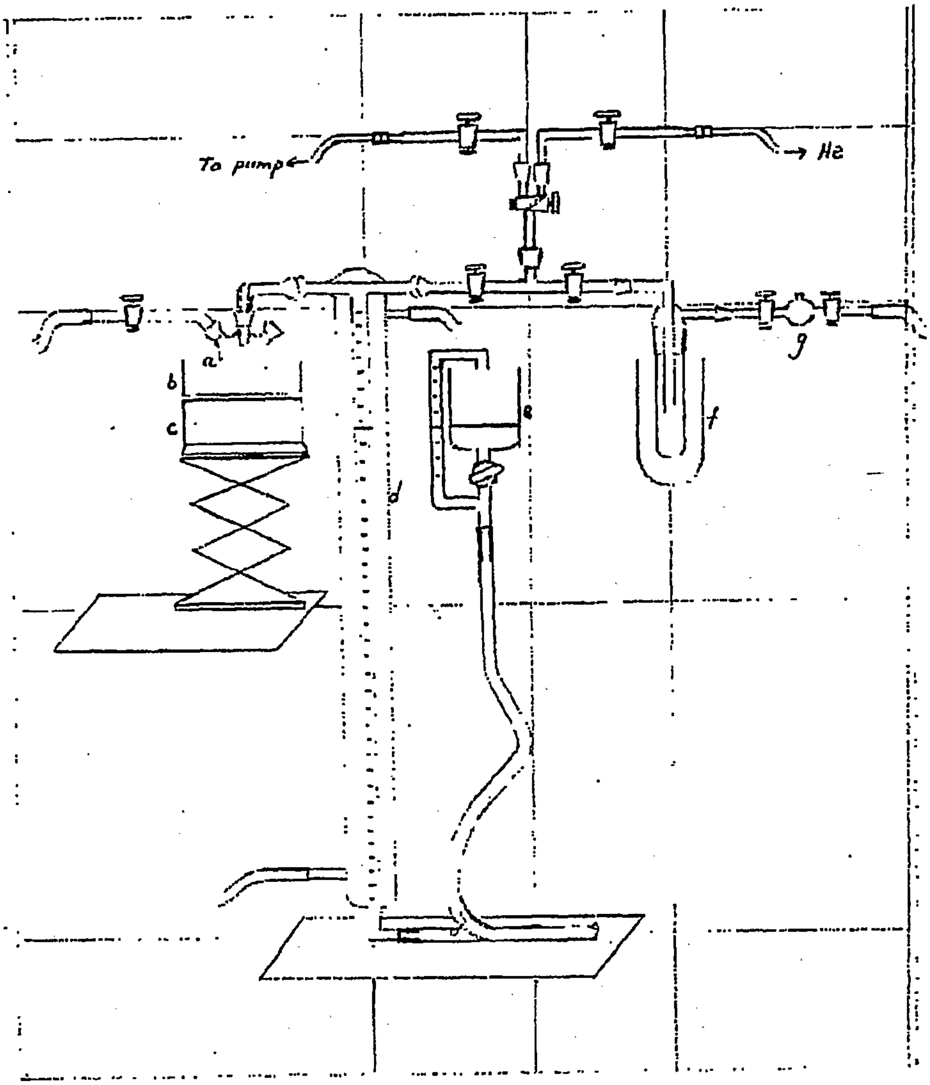
II. SYSTEM FOR STUDYING TRAPPING OF ORGANOMETALLIC COMPLEXES

A sketch of the experimental apparatus to be used in the chemical trapping studies of model organometallic complexes is given in Figure 1. The apparatus is constructed of pyrex glass and will allow the volumetric measurement and sampling of the gases evolved during the chemical trapping reaction and is similar to those used by Orchin and Wender (1) and Joshel (2) for quantitative catalytic hydrogenation, dehydrogenation and Zerewitinoff determination. It consists of:

- a three-neck reaction flask with a septum for the injection of the trapping reagent;
- a 100 cc buret and a mercury reservoir system for gas collection and measurement;
- a cold trap and sampling system
- helium and vacuum lines for flushing and evacuating

FIGURE 1

EXPERIMENTAL SYSTEM FOR CHEMICAL TRAPPING
OF MODEL ORGANOMETTALLIC COMPOUNDS



After the model complex is weighed into the reaction flask in a suitable solvent, air can be displaced from the apparatus by opening the appropriate stopcocks and sweeping with helium at the beginning of each run. Successive flushing and evacuation can also be accomplished in this system.

Stirring is accomplished by a magnetic stirrer and heating by an oil bath when desired. A known amount of the trapping agent can be injected through the septum on the reaction flask by means of a syringe, after the isolation of the reaction flask and the buret system.

a critical dimension is the height of the buret, in order that the system may be subjected to either a vacuum or to higher pressure without forcing the mercury out of the manometer. Following injection of the trapping agent, the mercury level may be lowered so that a slight negative pressure can be maintained within the system while the gas is being generated.

Before the volumetric reading is taken, the height of the mercury in the buret may be adjusted so that the pressure inside the system is equal to the atmospheric pressure, as evidenced by the same level in both arms of the manometer.

A cathetometer will be used to adjust and read the mercury levels in the buret and the thinner sidetube of the mercury reservoir. The stopcock to the main mercury reservoir may be closed after a rough leveling of the reservoir and the thinner sidetube may be used for more sensitive readings.

The apparatus lends itself very easily to correction for changes in barometric pressure and/or temperature during experiment since with the aid of the mercuryt reservoir, a measured differential between the internal and atmospheric pressures can be created at will before making the final volumetric reading.

Because the nature of the evolved gas will be of interest, samples will be taken by evacuating the sampling system, closing the stopcock to the pump and slowly opening the stopcock to the buret.

The rate of flow through the cold trap may be reduced by placing a negative pressure in the buret before the system is opened to the evacuated gas sampling bulb.

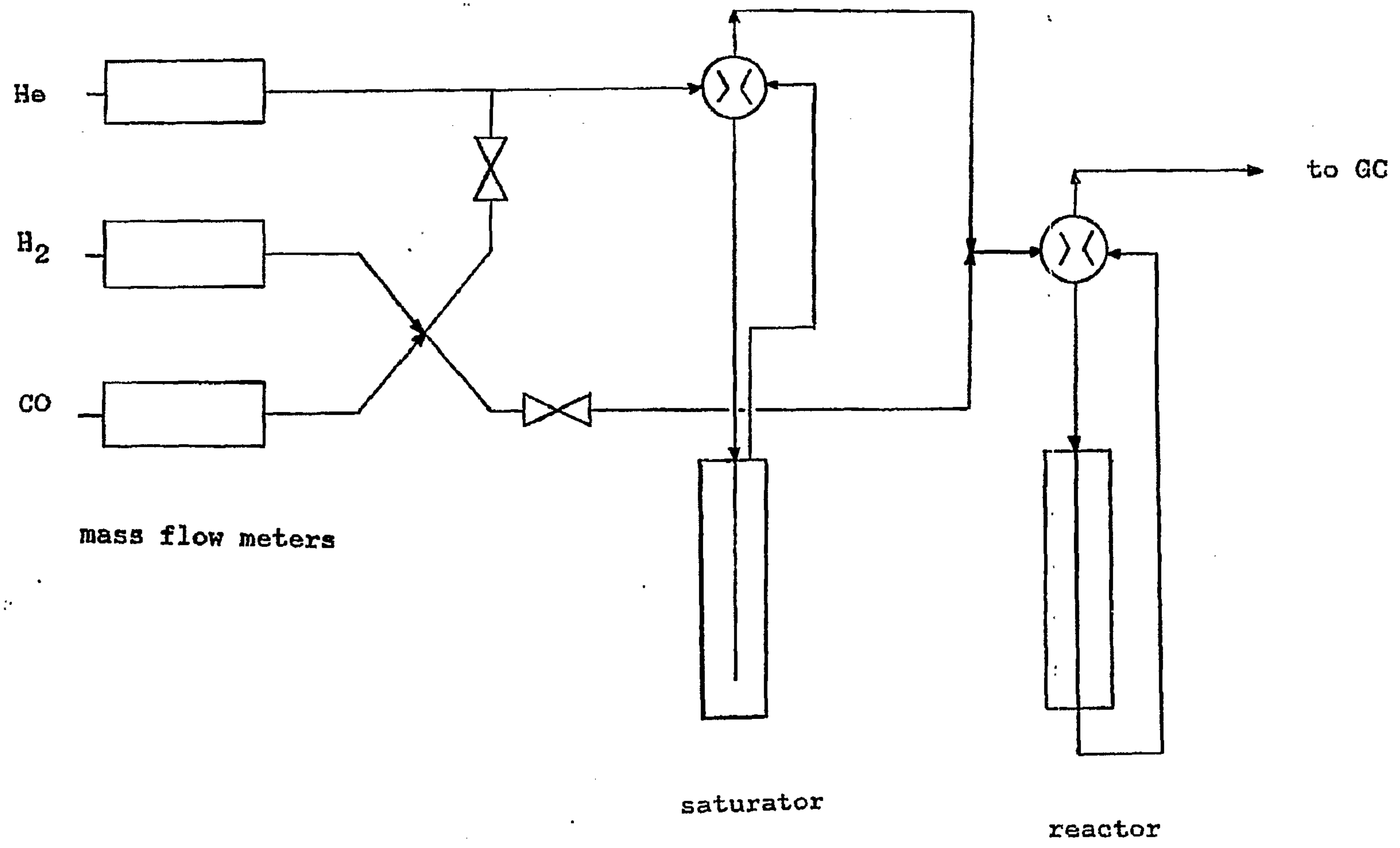
II. EXPERIMENTAL SYSTEM FOR CO HYDROGENATION/CHEMICAL TRAPPING

The experimental system for the CO hydrogenation/chemical trapping experiments has been modified to allow better control of the concentration of the trapping reagent in the reaction mixture. The new configurationis shown in Figure 2. The concentration of the trapping reagent in this new system is determined not only by the temperature of the saturator, but also on the amount of helium used to dilute the stream exiting the saturator. This allows a greater range of trapping agent concentrations to be examined, which is particularly important for regents with high vapor pressures.

The desired concentration of the trapping reagent is obtained by flowing helium through a saturator which is kept in an isothermal bath. This mixture is then mixed with the CO/H_2 stream. Provisions have also been made to allow isolation of the

FIGURE 2

EXPERIMENTAL SYSTEM FOR CO HYDROGENATION AND CHEMICAL TRAPPING STUDIES



saturator and reactor separately. This enables analysis to be made of the stream being fed to the reactor both with and without the trapping reagent.

III. ONGOING WORK

Positive preliminary results involving chemical trapping of RuY zeolites in situ during CO hydrogenation have led to further exploration of Ru on other supports. The action of the trapping reagent appears to be complex in nature, involving a number of processes in addition to the alkylation of surface-carbon or surface-oxygen bonds. The presence of I in CH_3I suppresses hydrogenation. Large amounts of the reagent effectively poisons the catalyst surface, but very small amounts (<0.1%) may actually enhance hydrogenation. Ru on other supports seems to deactivate much more quickly than RuY zeolite under trapping conditions. The new experimental system for trapping reactions promises to allow us to expand this work greatly to other catalyst systems.

IV. PERSONNEL

In addition to the two co-principal investigators, Prof. D.G. Blackmond and Prof. I. Wender, three other scientists have now assumed active roles in this project. They are Dr. R. Oukaci (Research Associate), Dr. A. Senatalar (Research Associate), and Mr. F. Cavalcanti (Ph.D. student).

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