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

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
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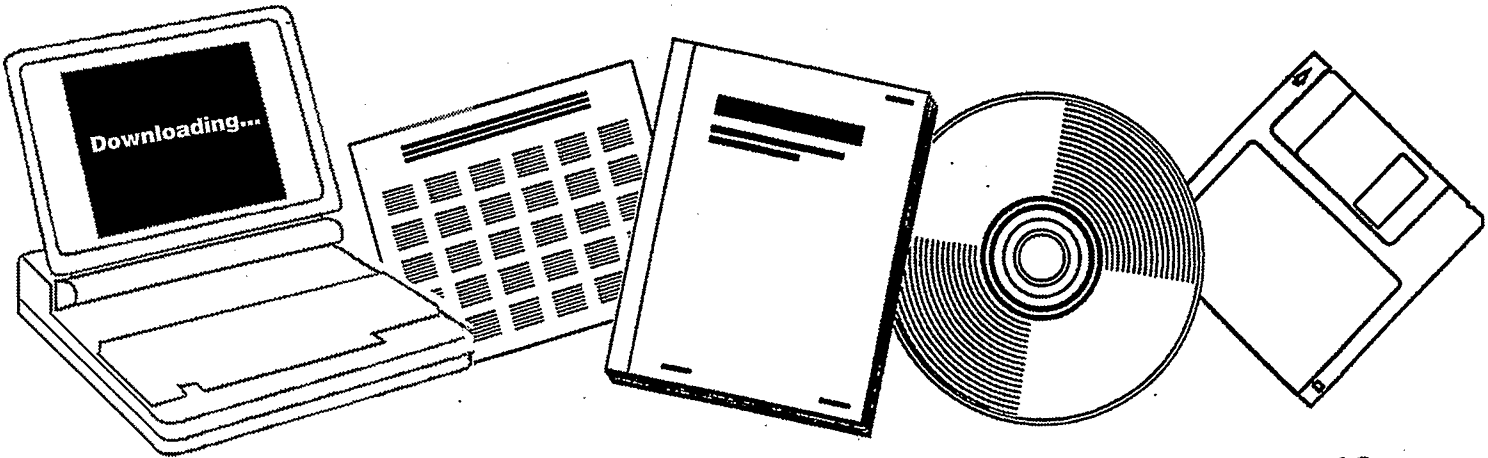

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Chemical Trapping of CO/H_2 Surface Species

Quarterly Report
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Donna G. Blackmond (Principal Investigator)
Irving Wender (Co-Principal Investigator)

Author of This Report: Michael Yusko

Department of Chemical & Petroleum Engineering
University of Pittsburgh
Pittsburgh, PA 15261

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INTRODUCTION

Model organometallic complexes provide a useful analogy to metal catalyst surfaces. Their similarities to a supported metal, absorbate atoms, and metal-absorbate bonds allow comparison of surface chemistry studies. By probing the nature and mechanisms of intermediate surface chemistry species, catalyst activity and selectivity effects can be understood. One newer such probing method, the chemical trapping technique, was introduced in Strasbourg, France by Deluzarche and coworkers [1]. Chemical trapping, shown in Figure 1, identifies surface species through the use of a trapping reagent, such as $(CH_3)_2SO_4$, which theoretically deposits an alkyl group onto the surface species at the species' previous place of attachment to the surface. However, chemical trapping complicates surface chemistry via mechanisms that we hope to better understand through this project. Chemical trapping is here importantly extended to a model organometallic complex, namely, ethylidyne tricobalt enneacarbonyl, to enjoy the mechanism-hunting advantages from a well-defined metal-absorbate complex system.

BACKGROUND

The Deluzarche group's work, although abounding with different experiments attempting to illustrate the chemical trapping theory, had some limitations:

- Frequently their experiments designed to produce formates did produce formates, but other products were not reported. Such incomplete product descriptions may actually lead to misunderstanding of the reaction mechanism.

- Some key results were reported qualitatively. The quantitative descriptions of activity and selectivity that we desire require quantitative data.

- Under dynamic conditions, some surface sites may actually be part of the reaction, whereas others remain inactive. The Deluzarche static adsorption conditions cannot provide information about such site activity and may cause misunderstanding of reaction mechanisms.

- Finally, so many catalyst systems were used that the assigning of specific reaction steps to specific catalysts is not clear-cut. Concentrating on fewer systems might better elucidate reaction steps.

The model complex used here, the methyl derivative of a class of compounds called the methinylcobalt enneacarbonyls, was specially prepared for us by Strem Chemicals and is shown in Figure 2. The chemistry of these complexes, which have a carbon atom attached to three metal atoms, has been reviewed by Seyferth [2]. Additionally, comparisons with the complex work here can be made with the large body of homogeneous catalysis literature [3,4]:

EXPERIMENTAL

The system used for the chemical trapping of the model complexes features volumetric sampling and measurement of evolved gases from the trapping reaction.

Support Preparation. Two supports were used; for a given run, either 1.52 g Davison Chemical SiO_2 gel catalyst grade 952 or 2.28 g γ-alumina Strem Chemicals were used. The chosen support was weighed into the three-neck reaction flask and flushed, by opening the appropriate stopcocks, with ultra-high purity helium (Linde) at 20 cc/min. Under helium flow the support was heated to and held at 220°C for eighteen hours using the heating mantle subject to the Omega Temperature Controller. This mantle also magnetically guides the stirring bar.

Complex Preparation. The complex, ethylidyne tricobalt enneacarbonyl, specially prepared for us by Strem Chemicals, was then added to the support. The reaction flask and buret were closed from the rest of the system at atmospheric pressure by positioning the mercury reservoir and the appropriate stopcocks. After weighing the complex (0.016 g for silica runs, 0.114 g for alumina runs) and mixing it with ≈10 cc pentane (Fisher Scientific reagent grade) as solvent, the mixture was injected through the reaction flask's septum using a syringe. The pentane is then dried off at 40°C for approximately 24 hours (until practically no pentane is left) under helium flow of 40 cc/min.

Reaction Studies. In these experiments two different trapping reagents were used:

- dimethylsulfate (Aldrich Chemical Company, 99+%, Gold Label)
- deuterated dimethylsulfate (ICN Biomedicals, d_6, 99.8%)

After the pentane had dried off, 2 cc of the trapping reagent was added at ≈30°C using a syringe through the septum. The reaction mixture was heated stepwise to 60°C, 80°C, 100°C, 120°C, 140°C, 160°C, and 180°C. However, for the special thermal decomposition runs, the complex/support was first heated stepwise to 60°C, 80°C, and 100°C, the reagent was added, and then heating continued incrementally to 180°C. At each step, 0.2 cc of any evolved gases was collected using a syringe through the septum and injected to a Varian 3300 gas chromatograph containing a Porapak Q column, 6' x 1/8", and fitted with thermal conductivity and flame ionization detectors. The TCD's signal was integrated by a Varian 4290 integrator while the FID's signal was only recorded by strip-chart. Additionally, gas evolution at each step was noted by the displacement of mercury in the buret. Samples of special interest were directly collected by manipulating stopcocks and mercury reservoir to expand gas into the GC/MS collection bulb. This bulb's gas was analysed on a Finnegan GC-MS system. Volumes of this bulb and connecting glassware were known so that buret volumetric data could continue after such sampling.

Ethylene Atmosphere. An additional experiment was performed in which ethylene (Matheson) was passed through the reaction flask in place of helium for five minutes just before DMS was added. Then the experiment continued as usual.

RESULTS

Without the complex on the silica support, the addition of DMS eventually yielded, at higher temperatures, a number of products. Methane, first evolving at 120°C, evolved more and more with increasing temperature. Methyl formate and $(CH_3O)_2CH_2$ appeared at 180°C in small amounts. However, without the complex on the alumina support, the addition of DMS yielded many products even at lower temperatures. Quantitative data for these alumina and silica blanks are shown in Table 1. Detected at 30°C were SO_2, dimethyl ether, $(CH_3O)_2CH_2$, and methyl acetate. Methyl formate, barely noticable at 30°C, at 100°C was being produced more than it was by the silica + DMS blank at 180°C. Comparing these silica and alumina + DMS blanks, we note that much more dimethyl ether and slightly more CO_2 evolved from the alumina than from the silica. However, DMS seems to yield about the same amount of SO_2 on both silica and alumina. Similarly, methane production seems the same for both supports until 160°C when methane yields increase on alumina.

When DMS was added to the silica/complex system, many new products as well as the same products as those found in the blank were observed. Very notable, as shown in the quantitative data in Table 2, was the immediate (≈30°C) production of dimethyl ether, eventually the major product. SO_2 was also made in large amounts, but appeared at 80°C, the same temperature it was seen in the silica + DMS blank. As temperatures went above 160°C, SO_2 and dimethyl ether production greatly increased. At 60°C methyl formate and methyl acetate appeared, and by 100°C methyl propionate was detected. Deuterated DMS ($(CD_3O)_2SO_2$) studies showed that these esters contain deuterated methoxy groups, as shown in Table 3. The appearance of methane by 60°C and ethane, ethylene, and propane at 100°C amounted to more hydrocarbon production than was in the blank. But above 100°C the ethane and ethylene in the gas phase decreased with increasing temperature.

Adding DMS to the alumina/complex system yielded a multitude of new and old (alumina + DMS blank) products, as shown quantitatively in Table 2. Though both SO_2 and dimethyl ether appeared immediately at 30°C on alumina, alumina yielded more dimethyl ether but less SO_2 than silica overall. Also at 30°C acetone and methane were noted. The complex on alumina yielded much more methane than the complex on silica; by 160°C methane production was greatly increasing. Deuterated DMS studies showed how DMS is incorporated into methane: the product always was CD_3H. Other hydrocarbons, namely, ethylene, propane, and 2-butene, appeared at 80°C. At 60°C C_2H_4O and methyl formate appeared as well as a product not seen in the blank--methyl acetate. Seen at 100°C was methyl propionate, also not seen in the alumina + DMS blank. These esters, as Table 3 shows, contain deuterated methoxy groups. On alumina every hydrogen in methyl acetate was deuterated. By 120°C COS evolved, but amounts of acetone, water, and C_2H_4O all appeared to be decreasing. At 120°C CO_2 evolution from the alumina/complex system was about three times that from the silica/complex system. Methyl formate and 2-butene peaks were temporarily not detected at 140°C.

When the silica/complex system was heated to 100°C before the trapping reagent was added (thermal decomposition run SC5), less ethylene and ethane were in the gas phase as compared to the gas phase composition when DMS had been added at ambient temperature. In the thermal decomposition run it was also noted that until 140°C methane evolution did not increase with temperature significantly.

Using an ethylene atmosphere instead of a helium atmosphere over the silica/complex system, and adding DMS at ambient temperature, we noted at 30°C the production of propane, SO_2, and dimethyl ether. Methyl formate evolved at 60°C, whereas methyl acetate, methyl propionate, and methane appeared at 100°C. The ethylene atmosphere was more conducive to methane and ethane production than the helium atmosphere, other conditions being similar. COS was seen at 120°C; CO_2 production was about the same in an ethylene atmosphere as in a helium atmosphere. Only at the 140°C reading did methyl alcohol appear. At temperatures above 160°C, methane, CO_2, and SO_2 production was greatly increasing.

The MS results of the deuterated DMS effects on silica and alumina complex systems are briefly summarized in Table 3.

DISCUSSION

Allowing participation of the complex in the support/DMS reactions led to some noteworthy products. A result not predictable from the chemical trapping scheme was the formation of esters. These esters' deuterated methoxy groups imply that the DMS (the "trapping agent") is adding $-OCH_3$, not $-CH_3$ as the chemical trapping theory would suggest [1]. (Refer to Table 3.) The possibility of such methoxy group insertion to surface species suggests that the oxygenated products reported by Deluzarche *et.al.* [1] may not necessarily indicate the presence of formate or methoxy surface species.

The choice of silica or alumina did not influence the amount of ester products. If the pathways to these ester products, the Co-CO ligand and Co-hydrocarbon interactions, are then independent of support, perhaps the complex interacts similarly on both supports. This possibility is interesting considering the view of the ethylidyne complex's retaining its structure on silica but rearranging on alumina [5]. However, the choice of silica or alumina did influence the degree of deuteration in the products. For example, methyl acetate: since on silica only its methoxy hydrogens were deuterated whereas on alumina all its hydrogens were deuterated (see Figure 4), the complex on silica contributes one $-CD_3$ and the DMS the other $-CD_3$. On alumina the DMS contributes both methyl groups, leading to a higher concentration of $-CD_3$ than on silica, as shown by the greater production of CD_3H on alumina than on silica. However, methyl formate production seems independent of the concentration of $-CD_3$ since both supports produce equal amounts of the ester. The methyl formate mechanism should then be similar for both supports. As shown in Figure 3's suggested mechanism for methyl formate, a carbonyl ligand on the complex, after reacting with a methoxy group, desorbs and scavenges a hydrogen from the support. One way to explain the formation of all the esters is through the restructuring of the ethylidyne complex [6,7] to a form similar to that of another Strem Chemical complex--acetylene dicobalt hexacarbonyl. During methyl propionate formation, suggested in Figure 4, the CO ligand on the right side of the Figure reacts with the methoxy group, but then the C-Co bond at a breaks and the ligand receives the complex's migrating alkyl chain. Perhaps methyl acetate derives from an alkyl migration mechanism as shown in Figure 4. If the C-C bond at b weakens after the CO ligand on either the right or left side of the Figure reacts with the methoxy group, methyl acetate may be formed. Further experiments with this complex should further the knowledge concerning the plausibility of the Figure 4 mechanism.

Although ester products seem independent of the choice of support, other products were support-dependent. Further substantiating the suggestion of DMS's interacting preference of alumina to silica was the greater formation of $(CD_3)_2O$ on alumina than on silica. Although SO_2 was detected more on silica than on alumina (when accompanied by complex), perhaps the SO_2 remained bound on alumina undetectable by vapor-phase analysis. One study has shown alumina bonds more strongly than silica to surface sulfates [8].

Some unanswered questions from this work include: what is the mechanism by which the esters are formed? The mechanisms suggested in Figures 3 and 4 need further testing before their validity can be enthusiastically endorsed. Another question: how does the complex sit on the support? Additional studies focusing on the ester mechanisms also shed light on the complex/support interaction. Methods besides vapor-phase analysis, such as IR spectroscopy, might identify support-bound species. Other future work involves using different complexes such as the Fe complexes specially prepared by J. Bradley at Exxon. We will continue to pursue the goal of understanding the activity and selectivity of metal catalysts, either as conventional metal surfaces or analogously using model complexes.

CONCLUSIONS

The mechanisms of "chemical trapping" are more complicated than mere alkyl group insertion. Esters can form not necessarily through alkylation of a formate or methoxy surface species, but through methoxy addition from DMS to ligands of the metal cluster. Further work may better show the influence of the support on ester production. How much interaction between the support and DMS exists depends on the support: the extent of participation of DMS in the observed products was shown to be greater on alumina than on silica for the methyl acetate product. A possible mechanism to explain the production of methyl acetate involves a restructuring of the complex (Figure 4) that allows for an alkyl migration. These model complex experiments are helpful analogies in evaluating already proposed chemical trapping mechanisms and may be a useful method for proposing new ones.

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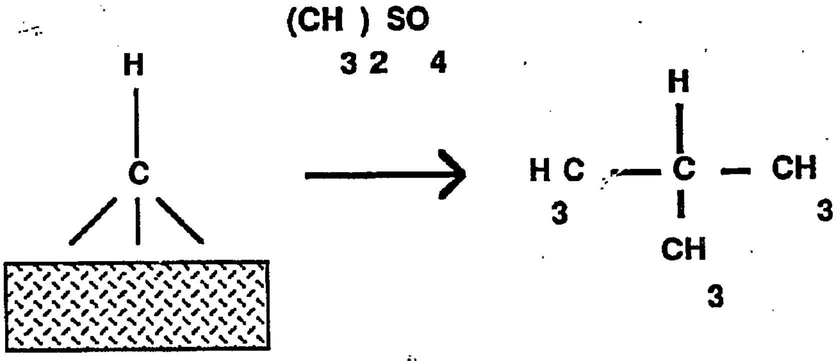

Figure 1. Chemical Trapping.

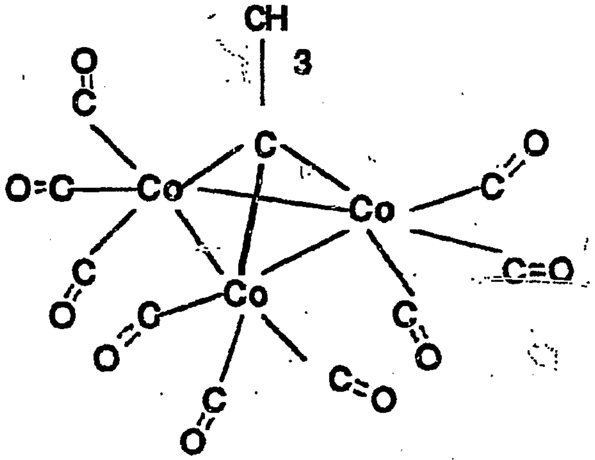

Figure 2. Ethylidyne tricobalt enneacarbonyl.

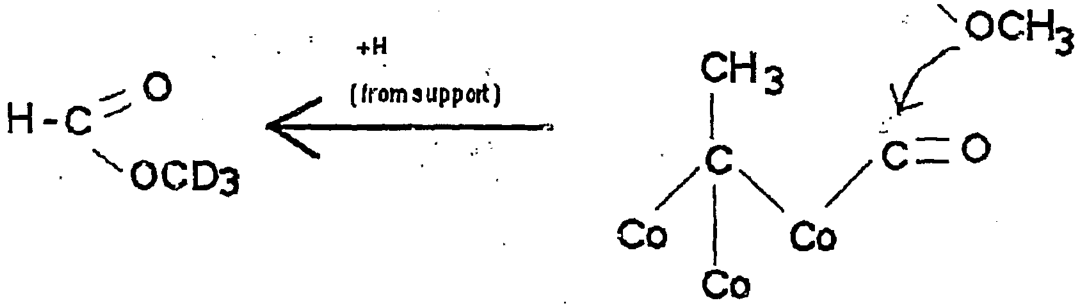

Figure 3. Possible methyl formate mechanism.

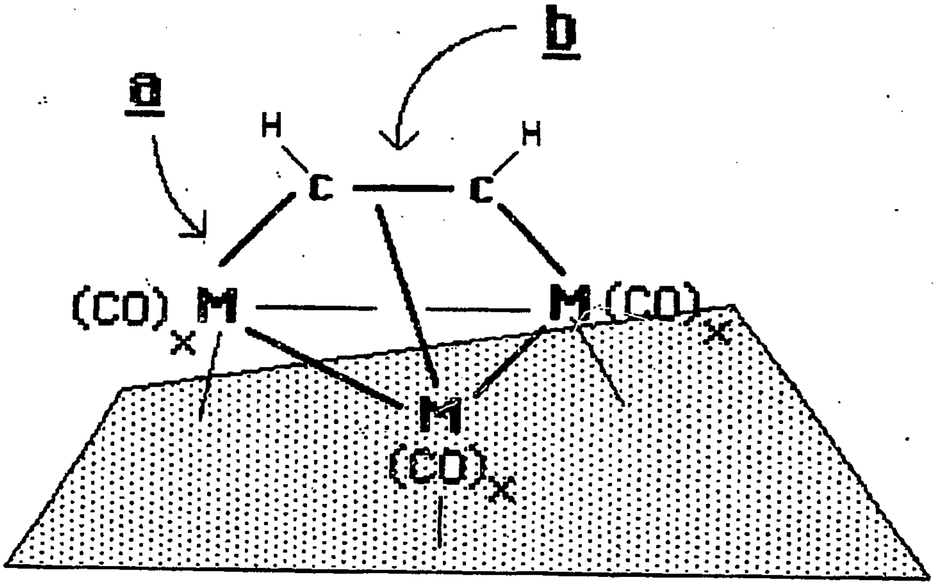

Figure 4. Possible methyl propionate and methyl acetate mechanism.

TABLE 1

Products of Support + DMS, Without Complex[a]

PRODUCT	SiO_2 (mg)[b]	Al_2O_3 (mg)[b]
CO	0.308	--
CO_2	0.006	0.002
H_2O	0.361	0.698
SO_2	--	0.221
$(CH_3)_2O$	7.600	21.100
$HCCOOCH_3$	--	0.002

---

a - reaction products analyzed after heating the support with DMS to 393 K.

b - mg moles of product per 2.28 g support used; 2 cc DMS was added to alumina, 1 cc DMS was added to silica

TABLE 2

Products from Support + DMS, With Complex

Product	SiO_2[b]	Al_2O_3[b]
CO	7.48	5.55
CO_2	0.62	2.53
C_2H_6	0.05	0.001
C_2H_4	0.06	0.002
$HCCOOCH_3$	0.05	0.04
CH_3COOCH_3	0.70	0.63
$CH_3CH_2COOCH_3$	0.14	0.25
$(CH_3)_2O$*	0.05	0.02
SO_2*	0.02	0.001
CH_4*	1.3 E-5	6.8 E-5

---

a - reaction products analyzed after heating the supported metal cluster system to 393 K in the presence of DMS.

b - moles of product per mole cluster reacted

* - moles of product per mole DMS added

TABLE 3

CD_3 Position in Deuterated DMS Products

Product	SiO_2	Al_2O_3
methane	CD_3H	CD_3H
dimethyl ether	$D_3C\text{-}O\text{-}CD_3$	$D_3C\text{-}O\text{-}CD_3$
methyl formate	$(HCO)\text{-}OCD_3$	$(HCO)\text{-}OCD_3$
methyl acetate	$(CH_3CO)\text{-}OCD_3$	$(CD_3CO)\text{-}OCD_3$
methyl propionate	$(CH_3CH_2CO)\text{-}OCD_3$	$(CH_3CH_2CO)\text{-}OCD_3$

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