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CHEMISTRY OF VARIOUS COMPOUNDS CONTAINING A
CARBON-OXYGEN DOUBLE BOND

by

JOHN PAYNE BELL

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

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MAY, 1984
ABSTRACT

STUDIES OF THE EFFECT OF PHOTOLYSIS ON THE METAL VAPOR CHEMISTRY OF VARIOUS COMPOUNDS CONTAINING A CARBON-OXYGEN DOUBLE BOND

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JOHN PAYNE BELL

In the last decade metal vapor synthesis has become an important method for producing organometallic species that have been unattainable or difficult to make by other routes. However, many important reactions lie just outside the reach of the procedure because the energy of activation for the process is too high. Matrix isolation experiments indicate that direct photolysis of a metal-organic cocondensate is an excellent method for introducing energy into a metal vapor reaction system so that new chemical processes can be accessed.

A metal vapor reactor was built in which one could irradiate with U.V.-visible light the deposition surface during co-deposition of the reactants. The reactor was designed so that the reaction surface was a rotating drum placed between the furnace and the photolysis well. This design minimized the accumulation of a metal coating on the photolysis lamp but introduced a time lag between deposition and photolysis.
The reactions of transition metal vapors with acetone produced both pinacol by a metal atom process and aldol condensation products formed by a metal particle catalyzed process. Photolysis of the co-deposited layers of some transition metals with acetone produced an increase in the amount of pinacol formed (from 1.0 to 6% for iron, 0.8 to 3.7% for cobalt and 0.0 to 1.1% for nickel). No such reductive coupling products were observed for the reaction of iron and nickel with cyclohexanone under photochemical conditions.

Nickel was the only transition metal (of Cr, Mn, Fe and Ni) that reacted with ethyl acetate without photolysis. This reaction produced products which were apparently formed from the decomposition of oxidative insertion products of nickel and ethyl acetate: Et-O-Ni-Ac and Et-Ni-O-Ac. Chromium and manganese reacted via a photolytically induced oxidative insertion to produce acetaldehyde and other products which were derived from a similar R-O-M-Ac complex. The yield of acetaldehyde in this reaction was dependent on the R-group in the ester and the deposition ratio of the metal and organic.
ACKNOWLEDGMENT

First, I wish to acknowledge and thank Dr. John Margrave and Dr. W. E. Billups for the contributions they made to this work and for starting me on my scientific career.

I especially wish to thank Robert Hauge for suggesting the design of the photochemical reactor and for many discussions we had about it. Many other graduate students and post-docs provided friendship and aid during this period. Mark Konarski, Monte Douglas, Ram Badachhappe, Leif Fredin and Zakya Kafafi, I wish to give my thanks for your help and interest.

Also, I wish to acknowledge the friendship and help of the madman from Arkansas. Wesley Moorehead, I probably learned a lot more from you than you did from me.

The suggestions of Joe Hightower on the preparation of this manuscript are gratefully acknowledged.

The generosity of the N.S.F., for providing a pre-doctorial fellowship, and 3M, for providing research funding, is also acknowledged.

Finally, I wish to express my appreciation to Catherine Alberte, who's love and friendship during the last two years probably kept me sane and made it all the more worthwhile.
To my sister, Karen, without whom this would have probably never been.
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CHAPTER 1

INTRODUCTION

Metal Vapor Synthesis

In the last decade metal vapor synthesis has become an important method for producing organometallic species that have been unattainable or difficult to make by other routes.\(^1\) This technique involves the co-deposition of metal vapor with a reactive material at low pressure. Often, the reactant is cocondensed with the metal on a cryogenically cooled surface. The coldest conveniently attained temperature for macroscale reactions is \(-196^\circ\text{C}\), which is obtained with liquid nitrogen baths. However, microscale reactions can be done at \(~10\ \text{K}\) with liquid helium cooling.

Cryogenic experiments involving the reaction of a high temperature species on a cold surface are not limited to the use of metal atoms as the high temperature species. The first macroscale cryogenic cocondensation experiments were the Skell and Westcott studies of the reactions of organic molecules with carbon vapor (which contains \(\text{C}_1\), \(\text{C}_2\) and \(\text{C}_3\) species) from a carbon arc.\(^2\) Soon after, Timms and Margrave studied the reaction of the unstable species \(\text{SiF}_2\) with a number of organic and inorganic materials.\(^3,4\) A few years
later, Timms reported the first studies of the reactions of metal vapors with organic compounds.\textsuperscript{5}

By its very nature, metal vapor chemistry is the cleanest and simplest method of producing zero-valent transition metal organometallic species. An early example of this attribute was the direct synthesis of bisarene chromium compounds by cocondensation of chromium with the respective arene.\textsuperscript{5-8} This reaction produces in a single step moderate to low yields of these compounds. Earlier syntheses required a two-step process\textsuperscript{9} which often produced more than one product and whose conditions greatly limited the functional groups on the arene. The metal vapor technique does not generally have such limitations.\textsuperscript{10} Many zero-valent transition metal complexes have been made with this method using alkenes, dienes and larger polyenes, phosphines and other pi-bonding species.\textsuperscript{11-18} No macroscale preparations of metal-carbon monoxide species have been made by direct cocondensation because carbon monoxide cannot be condensed at liquid nitrogen temperatures. The technique is not limited to making zero-valent pi-bonded species. The first paper published on transition metal vapor synthesis showed that ferrocene is produced in high yield by the cocondensation of iron and cyclopentadiene.\textsuperscript{5} Cyclopentadienyl complexes of other metals are similarly made.\textsuperscript{16,7}
One overwhelming advantage of this technique is that the reactive species, e.g. the metal atom, is sterically unhindered. Thus, a major driving force in these reactions is the need to fulfill the valence needs of this species. This explains the ready reactivity of metal atoms with systems which have available pi electrons.

Another reaction that fulfills the valence needs of a metal atom is the oxidative insertion of a metal atom into a chemical bond. The oxidative insertion of the nickel triad metals with organic halides has been extensively studied by Klabunde. In many cases the initial insertion product could be trapped by adding additional ligands.

\[
M + R-X \xrightarrow{-196^\circ C} R-M-X \xrightarrow{\text{warm}} R-M-X^L
\]

\[
M = \text{Ni, Pd, Pt}
\]

Outside of the nickel triad, few reports have been made of such oxidative insertion reactions for other transition metals, although there has been extensive work on oxidative insertion reactions with main group metals such as calcium, magnesium, aluminum and boron.

In addition, there is a variety of additional reactions that metal atoms can undergo with other compounds. Among these are electron transfer, extraction, substitution and disproportionation. Of these, electron transfer processes require more than a passing mention in this introduction.
Very few reports have appeared on electron transfer in macroscale metal vapor reactions. Most have dealt with the reaction of a metal with an electron-demanding material such as tetracyanoquinodimethane (TCNQ). For example, TCNQ forms a bis radical-anion salt with nickel:\(^{32}\)

\[
\text{Ni} + \text{TCNQ} \quad \xrightarrow{-196^\circ\text{C}} \quad \text{Ni}^{2+} \cdot \text{(TCNQ)}_2
\]

Another electron transfer process is the reductive coupling of ketones to form pinacols by lanthanides, actinides and early transition metals:\(^{33,34}\)

\[
\text{M} + \text{R-C-R} \quad \begin{array}{c}
1) \xrightarrow{-196^\circ\text{C}} \\
2) \text{R.T.} \\
3) \text{H}^+
\end{array} \quad \text{HO} - \text{OH} \quad \begin{array}{c}
\text{R} \quad \text{C-C} \quad \text{R} \\
\text{R} \quad \text{R}
\end{array}
\]

**Metal Clustering in Metal Vapor Chemistry**

In all metal vapor experiments there is a secondary reaction -- clustering of the metal atoms -- which competes with any other reaction. Klubunde has studied the behavior of the metal clusters that form by condensing metals into organic materials that undergo no other reactions; i.e., alkanes and ethers like pentane and THF.

The cluster experiments began with studies dealing with "active" metal slurries formed by cocondensing metals like magnesium, cadmium and zinc with alkanes or THF. Addition
of alkyl halides to the slurries lead to the formation of the expected organometallic species; e.g., magnesium formed Grignard reagents while cadmium and zinc formed the dialkyl compounds.\textsuperscript{35,36} All of these metals were unusually reactive in this metal slurry form; the magnesium slurry readily formed Grignard reagents even with normally sluggish or unreactive organic halides.

Next, because of the importance of metallic nickel in catalysis, Klabunde studied the cocondensation of nickel into alkanes, THF, and other "inert" materials. The nickel-toluene reaction was studied by adding strong ligands to the reaction mixture at various temperatures during its warm-up.\textsuperscript{37} If triethylphosphite were condensed onto the cocondensate before it was allowed to melt, a 40\% yield of the nickel tetraphosphite complex was formed. If the cocondensate were allowed to melt upon the ligand, a similar yield of the complex was found. No (<1\%) metal complex was observed when the condensate was warmed to room temperature before adding the ligand. Since the phosphite complex could only be formed by displacing weaker ligands around a nickel atom, these results show that solvated nickel atoms were present during the deposition of the reactants. After the condensation was ended these solvated atoms survived when the deposition melted, but upon further warming the nickel atoms formed clusters. Klabunde concluded that the interaction of a metal atom with an inert solvent followed
several distinct steps: (I) a metal-organic sigma or pi complex formed on cocondensation, (II) a metal atom or telomer solution resulted upon meltdown, (III) metal particles formed as the temperature was raised, (IV) removal of the solvent left a black crystalline material which (V) evolved organics on pyrolysis (see Figure 1-1).

Klabunde speculated that the organics which were formed upon pyrolysis of the metallic residues isolated in these reactions came from a metal-solvent adduct in the material that was cracked in the heating process. Skell\textsuperscript{38} reported similar results when he cocondensed zirconium with neopentane and isobutane, and then hydrolyzed the materials formed in these reactions. He found that 0.547 mmol of lower hydrocarbons were evolved, per mmole of metal deposited, for the material formed in the zirconium-isobutane reaction. Hydrogen was also evolved. Skell attributed these products to zirconium atom insertions into the C-C and C-H bonds of the alkane.

Later, Klabunde found that two different types of nickel powder could be formed in the nickel-pentane reaction by using different deposition ratios of metal and organic.\textsuperscript{39,40} At a metal/organic ratio of less than 1/300, a ferromagnetic black powder was formed which had a low organic content (Ni:C:H was 5:1:2). If an over 300 fold excess of pentane was used, then a black non-ferromagnetic powder was formed that had a smaller particle size and a
FIGURE 1-1

REACTION OF METAL ATOMS WITH INERT SOLVENTS

\[ -196^\circ C \]

M vapor + solvent vapor \( \rightarrow \) M-solvent complex

cocondense \( \rightarrow \) (colored) I

melt

vaporized excess

(M)\textsubscript{n} -solvent slurry \( \leftarrow \) further warming M-solution

solvent 25\(^{\circ} \)C

(b) IV (M)\textsubscript{n} -solvent adduct \( \rightarrow \) (M)\textsubscript{n} + organics

(black, small crystallites)

b) pyrolysis

IV

a) Based on the experiments involving nickel atoms and toluene.
b) Later work suggested that this stage is better formulated as a "pseudo-organometallic" material
greater organic content (Ni:C:H was 2:1:2) than the other form. But most importantly, he found that the low organic ferromagnetic material could be converted to the high organic non-ferromagnetic form by warming the former material to -130°C after deposition and keeping it at this temperature for 2 hours before further work-up. Taking this fact into account along with the pyrolysis, hydrolysis, and hydrogenation studies done on the samples, Klabunde concluded that instead of a nickel-alkane adduct being formed which survived at room temperature, nickel particles were reacting with pentane to form a "pseudo-Ni-organometallic" material. At low temperatures, there is a competition between the material's particle growth and its reaction with pentane.

Klabunde considered that the nickel particles were simply cracking the alkane at low temperature and suggested that the organic species evolved from the resulting material were fragments of the original starting materials. However, experiments done in the Margrave group showed that a more complex reaction was taking place. In these experiments first row transition metals were cocondensed with dimethyl ether and with trimethyl-, diethyl-, and triethyl- amines. 41-45 Even though these organic compounds are C1 and C2 carbon species, hydrolysis of the materials formed in these reactions produced hydrocarbons with up to eight carbon atoms. Studies of the interaction of pentane and
cyclopropane with transition metals showed that this more complex reaction also occurred with alkanes as well.\textsuperscript{46}

Klabunde also showed that the powders formed by cocondensing nickel into alkanes, THF, or toluene were quite active catalysts, with catalytic activities specific to the organic substrate used.\textsuperscript{47} For example, the nickel-pentane powder was an active hydrogenation catalyst; the nickel-toluene powder was also an active hydrogenation catalyst with a higher selectivity for particular alkenes; but the nickel-THF powder was fairly unreactive as a hydrogenation catalyst. Shevlin showed that the still frozen molybdenum-THF cocondensate could hydrogenate alkenes added to the deposition.\textsuperscript{48} In our own laboratories, it was shown that the metal powders formed from the reactions of transition metals with a variety of organic substrates could also hydrogenate alkenes without added hydrogen.\textsuperscript{46}

The catalytic and stoichiometric reactivity of the metal particles formed in metal vapor reactions make it possible that in any such reaction the products formed from the reaction may actually be the result of a metal particle reaction and not a metal atom reaction. Therefore, to say conclusively that a certain product arises from a metal atom reaction, it must first be shown that the product did not arise from a metal particle reaction.

Researchers in the field often attempt to show that the products observed in a cocondensation experiment did not
arise from reaction of the organic with bulk metal by doing a blank experiment where a metallic film is first deposited and then the organic material is condensed on to it. Since Klabunde has shown that depositing metal atoms into an organic material produces metal particles with properties dependent on the nature of the substrate, such experiments cannot be considered definitive. More conclusive evidence can often be obtained through studies of the reaction with the micro-scale version of the metal vapor technique, matrix isolation spectroscopy.

Matrix Isolation Spectroscopy

Matrix isolation began as a technique which allowed spectroscopic investigation of unstable chemical species frozen at very low temperatures in a film of some inert material (the matrix).49 Pimentel is considered the creator of the modern technique. In 1954 he studied the infrared spectra of several small molecules frozen in noble gas matrices.50 However, G.N. Lewis studied the phosphorescence of aromatic molecules in low temperature glassy media in 194151 and as early as 1924 Vegard detected the emissions from atomic species generated in low temperature noble gas matrices.52

An extremely fruitful sub-branch of matrix isolation chemistry has been the study of metal atoms that are
deposited in an inert gas matrix with a potentially reactive species. Shown in Figure 1-2 is a schematic diagram of the matrix isolation apparatus built and used at Rice University for such studies. The apparatus has: cryogenically cooled surfaces (c) on which the matrices are to be deposited; a closed cycle He refrigerator (d); an inert gas inlet (a); and sources of both reactive species — a metal furnace (e), and a reactant gas inlet (b). Not shown in the diagram is a window in the apparatus that allows the matrices to be photolyzed by a high-pressure mercury arc lamp. The thin film matrices formed in this apparatus are examined by I.R. reflection spectroscopy. However, other spectroscopic techniques; such as Raman, U.V./visible, Mossbauer, ESR, and Magnetic Circular Dichromism, have been used in matrix isolation work.

Andrews and Pimentel provided the first examples of matrix isolation work using metal atoms as a reactive chemical species. They studied by I.R. spectroscopy radical species produced through the abstraction of halides by alkali metals. An example is the formation of the methyl radical:

\[
\text{CH}_3\text{I} + \text{M} \rightarrow \text{CH}_3 + \text{MI}
\]

\[\text{M} = \text{Li, Na, K}\]

Other species that have been produced by this type of reaction are \text{CCl}_3, \text{HCF}_2, \text{HCCl}_2, \text{HCCl}_2, \text{HCBr}_2, \text{etc.}
FIGURE 1-2 MATRIX ISOLATION APPARATUS
Another reaction that has been studied in a matrix is electron transfer by alkali metals. The first example of this reaction was also observed by Andrews and Pimentel.\textsuperscript{59}

\[
\text{Li} + \text{NO} \rightarrow \text{Li}(\overset{\text{N}}{-}) \xrightarrow{\text{h}\nu} \text{Li}(\overset{\text{O}}{-})
\]

Some other molecules that can act as electron acceptors are \(\text{O}_2\), \(\text{O}_3\), \(\text{N}_2\), \(\text{F}_2\), \(\text{Cl}_2\), \(\text{Br}_2\), \(\text{I}_2\), \(\text{NO}_2\), \(\text{CO}\), \(\text{CO}_2\), etc. Little, if any, work has been done on electron transfer reactions involving transition metals in a matrix isolation experiment.

For the last few years the Margrave group has been studying the spectra of adducts and reaction products formed by cocondensing first row transition metals with a reactive species in an inert gas matrix. When water was used as the reactive species all the transition metals studied, with the exception of nickel, formed adducts upon cocondensation.\textsuperscript{71}

In the case of scandium, titanium and vanadium; there was a spontaneous insertion of the metal into the OH bond of water to form an HMOH species. For most other metal-water adducts, photolysis with 300 - 600 nm light induced a metal atom insertion to form the same HMOH species.

\[
\text{M} + \text{H-O-H} \rightarrow \text{M}<\overset{\text{H}}{-}\overset{\text{O}}{\text{H}} \xrightarrow{\text{h}\nu} \text{H-M-O-H}
\]

In some cases, further photolysis caused bond cleavage in the insertion compound to form MOH or MO species. Metal
dimers also gave adducts with water. Photolysis gave an insertion product, either $\text{HM}_2\text{OH}$ or $\text{HMOMH}$, for these species. Interaction of one metal atom with two water molecules was also seen. Similar adduct formation and photolytic insertion occurred when transition metals were cocondensed with molecules isoelectronic to water; e.g., methane, ammonia, and hydrogen fluoride.$^{71}$

The reactions of manganese atoms with dimethyl ether and methanol have also been studied.$^{42}$ In both cases, an adduct was formed upon cocondensation of the reactants in an argon matrix. Photolysis of the adduct gave insertion of manganese into the C-O bond of the ether and the O-H bond of the alcohol. Similar results were seen for calcium$^{42}$ and silicon.$^{75}$
NATURE OF THE RESEARCH PROBLEM

Many potential reactions that one would like to perform via metal vapor chemistry lie just beyond reach of the procedure because the activation energy of the process is too high. In some cases, such a reaction can be made to go by raising the temperature of the system. However, in a M.V.S. experiment there is always a competing reaction which reduces the viability of this approach: metal clustering. This process severely limits the potential reactivity of a metal atom.

In most metal atom reactions, the metal is first complexed or solvated by the ligand species, and then a further reaction occurs. If the metal atom is only weakly complexed and there is not enough energy to react further, the metal atom will start to cluster as the temperature is raised. Ideally, unrealized atom reaction channels could be accessed by putting energy into the system in some form that does not induce clustering.

Lagow has done this indirectly by cocondensing main group metals with methyl or trifluoromethyl radicals to form homo-alkyl organometallic species\textsuperscript{72,73} The radicals were generated by R.F. discharges through ethane or hexafluoroethane.
M + n CH₃ (or CF₃) \rightarrow M(CH₃)ₙ or M(CF₃)ₙ
-196°C

M = Hg, Te (n = 2); Bi (n = 3); Ge, Sn (n = 4).

The matrix isolation experiments done at Rice University indicate that direct photolysis is an excellent method for introducing energy into a metal vapor experiment. Therefore, it was decided that a metal vapor reactor should be built that could photolyze a macroscale deposition with U.V./visible light.

The final design of the reactor and course of study for the various sets of experiments described in this thesis were shaped by the following concepts and preliminary requirements:

1. The number of photons of light emitted in unit time by the photolysis source is the limiting reagent in the system. Therefore, deposition rates and quantities must be scaled to match the lamp output. Data for the output of a Hanovia 450 watt medium pressure Hg lamp were used to calculate the photons available in certain spectral ranges from this lamp (see Table 1-I). The calculations indicated that at least 100 to 300 mmol (millieinstines) are available in each of the ranges considered. Therefore, a deposition rate of one mmol per hour of metal should provide a very good chance of undergoing a photochemical reaction under this flux of radiation.

2. The reactor must be constructed so that the photolysis unit does not become coated with a metal film.

Two approaches were used to try to reduce the amount of metal clustering that would occur:
1. High ratios of reactant to metal were used. At a minimum, ratios of 50/1 were used. Many experiments used higher ratios. These ratios tended to be much larger than normal for metal vapor synthesis; and had the effect of making product work-up more difficult, since products were diluted in a great amount of starting material. Also, reactions with rarer compounds were more impractical because of the amounts needed for each experiment. The large substrate condensation rates together with the need for a clean reaction system (free of moisture and air) required that a high capacity, high vacuum system was used for pumping the reactor.

2. The substrates used were chosen to have an available π electron system which could help stabilize atomic metal species, yet did not form highly stable metal-π bonding interactions. The π electron system chosen for this task was the carbonyl group (-(C=O)-).

Finally, it is important to consider mechanistic details in metal vapor reactions. If a stable metal-containing species is not isolated, but a transformation of the substrate occurs, there exists the possibility that a metal cluster particle is the actual reactive species. It is usually far easier to prove that a reaction is caused by a metal cluster particle than not. Particle reactions will tend to produce products with yields dependent on the warm-up conditions; i.e., how long and to what temperature a reaction is warmed before the products and substrate are removed from the metallic residue. Often, longer the warm-up period, the more extensively a reaction will occur. However, as Klabunde's work has shown, particle reactions can also be temperature sensitive. In the reaction of nickel particles with alkanes, the reaction
mixture had to be kept at a low enough temperature so that the reaction of the clusters with the solvent could compete with further particle growth.

Since matrix experiments have shown that metal dimers and telomers have an extensive reaction chemistry, it is not possible to state unequivocally that the reactive species is a metal atom, and not a dimer or telomer, in a reaction that does not give a metal containing product molecule.

The yield of a product resulting from a metal atom or telomer reaction should depend on the reaction conditions in the following ways:

1. The yield of the product is not dependent on warm-up conditions. If it is, the yield should decrease as the warm-up period is lengthened because the product is being destroyed by the metal cluster particles.

2. The yield of product should increase as a greater excess of substrate is used. However, depending on the vacuum system of the reactor, this principle cannot always be taken as evidence for or against metal atom or telomer involvement. In the vacuum systems found in the more common types of metal vapor reactors, the pumping speed of the system is not often great enough to keep the pressure of the system below $10^{-3}$ torr when a great excesses of substrate is being condensed. Above this pressure, gas phase reactions are possible and pyrolysis on the furnace begins to occur. Such pyrolysis can lead to product destroying radical species. The products most affected by these processes seem to be metal-containing complexes.

In the work to be described, reactions not attributable to metal cluster/particle reactions are considered to be metal atom reactions. Thus, the mechanisms devised for
these reactions were written as involving metal atoms. However, the possibility of a dimer or telomer being involved in the reaction is not excluded.
TABLE 1-I

PHOTON OUTPUT OF A 450 WATT MEDIUM PRESSURE MERCURY ARC LAMP

<table>
<thead>
<tr>
<th>RANGE Å</th>
<th>WATT OUTPUT</th>
<th>EINSTEINS/HR</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000-2800</td>
<td>27.0</td>
<td>0.2</td>
</tr>
<tr>
<td>2800-3200</td>
<td>28.7</td>
<td>0.3</td>
</tr>
<tr>
<td>3200-4000</td>
<td>28.0</td>
<td>0.3</td>
</tr>
<tr>
<td>4000-6000</td>
<td>75.7</td>
<td>1.1</td>
</tr>
<tr>
<td>10,000-40,000</td>
<td>16.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>


b) Photon output is calculated using either the averaged wavelength for a range or the wavelength in the range with more than 50% of the energy of that range.
REFERENCES AND NOTES


30. Reference 1b, pp. 153-159.

31. See reference 1d, p. 6 for examples of each.


46. Unpublished work.


49. For background on matrix isolation spectroscopy see: Reference 1a, pp. 9 to 61 and 195 to 524.


52. L. Vegard, Nature 114, 357 (1924).


71. J. W. Kauffmann, Ph.D. thesis, Rice University (1981). Group II, III and IV main group metals and metalloids were also studied.
74. See references 1c and 1h for discussions of product yields in metal vapor reactions.
CHAPTER 2

APPARATUS CONSTRUCTION AND GENERAL EXPERIMENTAL PROCEDURES

APPARATUS CONSTRUCTION

The Photochemical Metal Vapor Reactor

A metal vapor reactor was specially built to allow photolysis with U.V.-visible light during deposition of the reactants. A diagram of the reactor is shown in Figure 2-1 and a photograph of the apparatus is shown in Figure 2-2. The reactor was contained in a six inch diameter glass cross which was connected to a high vacuum (below $1 \times 10^{-6}$ torr) system with high capacity pumps. Depositions were made on the surface of an axially rotating drum which was filled with liquid nitrogen for cryogenic cooling of the surface. A resistively-heated furnace, surrounded by a water-cooled heat shield, was pointed at just below the center of one side of the drum. Two substrate inlets, one on either side of the furnace, also pointed at the same position on the drum. On the other side of the drum, protected from metal over-coating by the furnace, was a quartz photochemical well with a 450 watt medium pressure mercury arc lamp. Below the
FIGURE 2-1

DIAGRAM OF THE PHOTOCHEMICAL METAL VAPOR REACTOR

A) THE REACTION DRUM
B) THE METAL FURNACE AND COOLING SHIELD
C) SUBSTRATE INLETS
D) MERCURY LAMP, PHOTOLYSIS WELL AND REFLECTING SHIELD
E) COLLECTION FUNNEL
F) COLLECTION FLASK
G) SIEVE FOR MOTOR DRIVE
H) MECHANICAL VACUUM GAUGE
FIGURE 2-2  PHOTOGRAPH OF THE PHOTOCHEMICAL REACTOR
drum assembly was a glass collection funnel for collecting the depositions after a reaction was ended and the drum was warmed. The funnel drained into a Schlenk flask which could then be removed for work-up of the reaction. A drip tube (not shown) allowed the drum to be washed with solvents to dissolve depositions made with substrates with high melting points.

The reactor and its vacuum system were mounted on a cart, made from Unistrut framing, that was 33 inches wide by 60 inches long by 28 inches tall. A piece of 3/4 inch thick plywood board was fitted to the top of the cart. The supports for the glass cross and the vacuum pumps of the reactor were mounted on this surface.

The main vacuum pump for the reactor was a NRC (now Varian) Model VHS-6 high capacity diffusion pump backed with a Welch Duo-Seal RL397 rotary oil pump. The system was rough pumped by a Precision Scientific Model 150 rotary oil pump. A Freon cryo-pump, which was not used, was attached the top of the diffusion pump. Above the Freon cryo-pump was an up-right liquid nitrogen cryo-trap. This trap was used more as a pump than as a trap since it could not be isolated from the diffusion pump. The LN2 trap was made of stainless steel and was modified from an existing structure. It was 19 inches high and had an outside diameter of 5 1/2 inches. The inner trap that held the coolant was a cylindrical drum 12 1/2 inches long and 4 inches in diameter
made from of 30 mil stainless steel. The coolant inlet to the drum was a 2 1/2 inch long, 1 inch diameter, 20 mil stainless steel tube which was welded in the center of a 1/2 inch thick, 7 1/2 inch diameter stainless steel flange that bolted to the top of the cryo-trap. The vacuum seal between the flange and the rest of the trap was made with an o-ring (6 1/2 inch O.D. by 1/4 inch wall). O-rings were used throughout the vacuum system and the reactor as seals between metal flanges and between metal flanges and beaded glass surfaces.

A 3 inch long by 4 inch O.D. horizontal tube extended from the middle of the LN2 trap. The reactor was connected to the vacuum system through this tube. On the tube were the fittings for a Veeco DV-1M thermal conductivity gauge tube and an ionization gauge tube. The ionization tube fitting was angled upward so that back-streaming diffusion pump oil did not collect in the tube. Both the T.C. tube and the ionization tube were wired to a Veeco RG31X thermal conductivity and ionization gauge unit. The unit could support two T.C. tubes, the one here was identified as tube #2. The unit also had a high pressure relay which was attached to a vacuum pump protection device which turned off the current to the diffusion pump heater if the pressure in the system was beyond the range of the ionization gauge. This mechanism protected the pump and the
pump oil from oxidation if a leak occurred. The protection unit had an override switch.

Between the vacuum system and the reactor was an Airco Temescal 4 inch Fig. 3010 vacuum valve which was the main isolation (gate) valve. The high pressure side of the valve was, of course, on the reactor side of the interface.

Between the gate valve and the beaded glass surface of the reactor housing was a 3 inch long by 6 inch O.D. aluminum tube with the appropriate flanges welded to either side. The rough pump was connected to the reactor through a Veeco Model FL62P vacuum valve which was attached by a series of reducing Cajon fittings to a 3 1/2 inch by one inch O.D. tube that came out of the side of this connection tube.

The reactor itself was housed in a six inch by six inch glass cross from Kimax. Three flat metal flanges were attached to the glass cross, each having a sub-assembly of the reactor attached to it. The fourth side of the cross was attached to the vacuum system. The beaded glass surfaces required a 6 3/8 inch I.D. by 3/8 inch wall o-ring for making a vacuum seal to the metal flanges. This was not a standard o-ring size and a 6 1/4 inch I.D. o-ring had to be stretched to fit. The metal flanges fitted to these glass surfaces had half-depth o-ring grooves in them to improve ease of assembly. Kimax Model 7151-6000 pipe collar flanges were used to hold the attached metal flanges in
place when the reactor was not under vacuum. The attached flanges had a circular diameter of 10 1/4 inches and had a 9 1/2 inch diameter, 8 bolt hole circle (3/8 inch diameter holes) drilled in them to match the bolt hole pattern in the collar flanges.

The top flange of the reactor was made of 1/2 inch thick aluminum and had the rotating drum assembly, the photolysis unit, the solvent inlet and a mechanical pressure gauge attached to it. A cross-section of the flange and its attachments is shown in Figure 2-3.

The rotating reaction drum was essentially a cold finger. The deposition surface was a 6 inch long by 2 1/3 inch diameter cylinder made of 20 mil stainless steel. The bottom of the cylinder was capped with a conical end piece. The top of the cylinder had a similar conical endpiece, but with a 12 inch long by 1/2 inch diameter piece of 20 mil stainless steel tubing (the neck tube) coming out of its center. A second larger (3/4 inch O.D.) tube, also made of 20 mil steel, surrounded the top 10 inches of this tube; both pieces were welded together at their top end. At the lower end of the 3/4 inch tube there were two 1/2 inch long semi-circular Teflon spacers that were inserted between the larger and the smaller tubes to keep both tubes centered with respect to each other. The neck-tube on the drum was open at the top and the drum was filled with liquid nitrogen from this point. Since only the bottom half of the drum was
FIGURE 2-3

CROSS-SECTION OF THE TOP FLANGE ASSEMBLY

A) TOP FLANGE
B) REACTION DRUM
C) TEFILON CENTERING SPACERS
D) DRUM SUPPORT FLANGE AND FITTING
E) CAJON 3/4 INCH FITTING CAP
F) CAJON O-RING COMPRESSION WASHER
G) O-RING FOR FITTING-DRUM SEAL
H) O-RING SPACER
I) DRUM SUPPORT BEARING
J) BEARING COLLAR
K) O-RING FOR FLANGE TO FLANGE SEAL
L) LN2 SPLASH FUNNEL
M) MOTOR DRIVE SIEVE
N) QUARTZ PHOTOLYSIS WELL
O) 450 WATT MEDIUM PRESSURE MERCURY LAMP
P) PHOTOLYSIS WELL SUPPORT FLANGE AND FITTING
Q) CAJON-TYPE FITTING CAP
R) CAJON-TYPE O-RING COMPRESSION WASHER
S) O-RING FOR FITTING-WELL SEAL
T) PHOTOLYSIS WELL SUPPORT DISC
U) PHOTOLYSIS WELL SUPPORT O-RING
V) FLANGE CONNECTING RODS FOR WELL SUPPORT DISC
used for deposition, if the liquid nitrogen in the drum became low there was a safety margin for keeping the deposition at cryogenic temperatures. Lastly, after a reaction was completed, the conical nature of the bottom end piece allowed the melted cocondensate to drip off the drum at one point during work-up.

The neck-tube was held in place in the reactor by a modified 3/4 inch Cajon-type brass fitting set in a 3 inch square by 3/8 inch thick brass flange which was bolted to the top flange. The fitting for the neck-tube was built as a modification of a normal Cajon fitting because it had to keep a vacuum seal while the neck-tube would be rotating. It had two 3/4 inch I.D. by 1/8 inch wall o-rings surrounding the neck-tube with the lower o-ring making the vacuum seal for the system. There was a 5/8 inch long brass spacer between the o-rings with a groove around the midpoint of its outside wall. Two 1/8 inch O.D. by 1/2 inch long open tubes were on opposite sides of the outside wall of the fitting at a height corresponding to the position of this groove. These tubes allowed oil to be injected between the o-rings for lubrication.

The neck-tube was positioned so that about 5 inches of the tube extended above the top of the fitting. The bottom of the brass flange had a 1 1/2 inch diameter by 1/4 inch deep cut-out for a grease-less bearing. The bearing actually supported the neck-tube in the fitting and was
permanently placed on the neck-tube approximately 5 inches above the top end of the deposition cylinder. A 2 1/4 inch diameter by 3/8 inch thick brass collar held the bearing to the bottom of the brass flange by four 6-32 screws placed in a 2 15/16 inch diameter bolt circle. The bearing had been fitted on the neck-tube by cooling the neck-tube to \(-196^\circ\text{C}\) and positioning the collar and the bearing on the neck-tube was it was still cold.

The drum was filled from a line made of copper tubing attached to a 160 liter tank of liquid nitrogen. A Hoke 2215P4M throttling valve in the line controlled the flow rate of liquid nitrogen. To prevent liquid nitrogen from spilling on the lower parts of the reactor, an eight inch diameter polyethylene funnel was fitted over the top of the drum's neck-tube. The stem of the funnel was shortened to the point where its inner diameter was large enough to fit around the neck-tube, but it was prevented from slipping down the neck-tube by a brass ring held in place with set screws on the tube. A steady rate of liquid nitrogen flow into the drum had to be maintained during a reaction; from nine to ten hours of use was obtained from a single 160 liter tank.

The drum was rotated by a sheave and belt attached to a variable speed Dayton 4Z132 gear motor drive with a 6X165B DC motor controller. On the shaft of the motor was a BK72H Browning sheave (6.95 inch O.D.) and bushing which were
connected by a 33 by 1/2 inch v-belt to a BK34 Browning sheave (3.55 inch O.D.) positioned about 3 1/2 inches from the top of the reaction drum neck-tube. The gear motor was mounted on a piece of Equipto L-framing which was attached to the top flange by the bolts that held the flange collar in place. The piece of framing upon which the motor was mounted was stabilized by bolting to it two vertically positioned pieces of the same material. These pieces rested on the reactor frame mounts. Normally, the drum rotated counter-clockwise (looking down from above) at about 112 RPM. The direction of rotation was arbitrary, but because of competing clustering reactions and other factors mentioned before, the fastest rotational speed was used for most experiments.

The photolysis lamp was a Canrad-Hanovia medium pressure mercury-vapor 450 watt lamp, powered by an Ace Glass 7830-60 power supply. The length of the lamp was 109.5 mm; the total length of the unit -- lamp and electrical connections -- was 236.5 mm. The quartz photolysis well in which the lamp was placed was fabricated in the departmental glass shop. It was identical to the Ace Glass 7874-35 quartz immersion well except that it was 50 mm longer. The well was attached to the top flange by a large Cajon-type brass fitting set in the center of a 2 5/8 inch square by 3/8 inch thick brass flange. The fitting was originally for a 1 7/8 inch diameter object, but the bore
had to be increased somewhat for the photolysis well because of irregularities in the diameter of the quartz tubing used in making the well. The bottom of the well rested on 1 inch O.D. by 1/4 inch thick o-ring set in a circular depression in a 2 3/4 inch diameter by 1/4 inch thick brass disc. The disc was attached to the top flange by four 12 inch long 6-32 threaded steel rods. This disc supported the well and prevented it from being pressed further into the reactor by the pressure differential under which the reactor operated. Aluminum foil was wrapped around the support rods on three sides with the side facing the drum being open. The foil acted as a reflector for the lamp so that all the light emitted was directed to the drum.

The solvent inlet, not shown in Figure 2-3, was a long piece of 1/4 inch copper tubing bent in such a way that one end was in the reactor pointed toward the deposition zone and the other was outside the reactor connected to the solvent reservoir. The solvent reservoir was a 200 ml Schlenk dropping funnel, placed on an adaptor made of a female 24/40 tapered joint attached to a 1/4 inch Kovar-glass seal. The Kovar end was connected to the solvent inlet tube by a Swagelok fitting with Teflon ferrules. The inlet tube entered the reactor through a bored-through 1/4 inch Cajon to 1/4 inch male pipe fitting which was screwed into a hole in the top flange that was located 2 inches in front of the center point of the drum flange. The threads of the fitting
were wrapped with Teflon tape in order to make the connection vacuum tight. Throughout the reactor, any fitting that was screwed into a flange was wrapped with Teflon tape before it was attached to the system.

A mechanical vacuum gauge (shown in Figure 2-1) was added to the reactor for monitoring the pressure in the system during the time the reactor was being filled with an inert gas during product work-up. The gauge, a U.S. Gauge Model 1212-1 vacuum gauge that read pressures from 0 to (-)30 inches of mercury, was screwed into a hole with 1/4 inch pipe threads in the top flange that was located 2 inches in front of the center point of the photolysis well flange.

The side flange of the reactor was made of 1/2 inch thick aluminum and contained the furnace, furnace cooling shield, substrate inlets, inert gas inlet and a T.C. vacuum tube. A face-on view of the flange and its attachments is shown in Figure 2-4.

A co-axial resistive furnace, designed by Dr. Robert Hauge for the new F.T.I.R. matrix isolation unit built in the Margrave group, was used in the reactor. The furnace was designed for cylindrical crucibles that would be some distance (about six inches or more) from where the furnace would be attached to the system. Thus, the furnace leads were two co-axial tubes, one longer than the other, with the heating element between them. This design allowed the
FIGURE 2-4
FACE-ON VIEW OF SIDE FLANGE

A) SIDE FLANGE
B) SUBSTRATE INLET TUBE FITTINGS
C) FURNACE SHIELD COOLING WATER FITTINGS
D) FURNACE ANGLING FLANGE
E) FURNACE
F) THERMOCOUPLE GAUGE TUBE
G) INERT GAS INLET VALVE
H) UNUSED 1/4 PIPE FITTING HOLE WITH PLUG
furnace to be somewhat self heat-shielding. The furnace hearth, which incorporated the water-cooling system and the electrical contacts, was constructed at the Rice University Research Machine Shop according to Dr. Hauge's design. The nature of the furnace leads placed on the hearth depend on the usage of the furnace. On the photochemical reactor, the leads were made of two tubes of 20 mil tantalum — the outer one 4 7/8 inches long by 3/4 inch O.D. and the inner one 4 inches long by 1/2 inch O.D. On the furnace, the outer lead extended about 1 1/2 inches beyond the inner one. The heating element was of 1 mil tantalum foil, rolled into a cylinder and attached by spot welding to the furnace leads.

The voltage to the furnace was reduced from 110 volts by a 1:8 G.E. Model 9T21Y58 step-down transformer. A Powerstat variac was connected between the stepdown transformer and the wall to provide fine control on the voltage.

The alumina crucibles used for the experiments were purchased from Coors Porcelain (Catalog No. CN-2). The temperature of the crucible was measured with a Pt-6% Rh vs. Pt-30% Rh thermocouple placed just behind the crucible. The T.C. junction was covered with a short piece of closed-end 1/2 inch O.D. alumina tubing. The end of the crucible rested on this piece of tubing. The T.C. wires were encased in a ceramic T.C. tube and exited at the opposite end of the
furnace hearth. The thermocouple emf was measured with a Leeds and Northrup millivolt potentiometer.

The furnace hearth was bolted to an angling block attached to the side flange. This block was made of brass and was 3 inches square with a depth varying from 1 to 3/32 inches. It gave the furnace unit a 15° upward tilt which prevented molten metal from spilling out of the crucible.

The furnace was surrounded by a water-cooled heat shield made from 2 1/8 inch O.D. by 3/32 inch thick copper tube. One end of the shield had a 15° bevel and the other end had a 2 1/8 inch diameter by 1/8 inch flat copper plate with a 3/4 inch hole in its center through which metal vapor from the furnace passed. An angled oval hole was cut in the side flange that allowed the heat shield to be inserted so that the beveled end of the shield rested against the furnace angling block. Thus, the shield also had a 15° upward tilt. One fourth inch O.D. copper tubing, for carrying cooling water, was wound around and soft-soldered to the shield.

On the horizontal center line of the side flange were four 1/4 inch pipe holes, one inch apart from each other, which had bored-through 1/4 inch Cajon fittings screwed into them. The cooling water lines for the heat shield entered and exited through the inner two fittings. The outer two fittings had the substrate inlet tubes running through them.
The substrate inlets were made from 1/4 O.D. copper tubing with one on either side of the furnace, placed so that they ended about one inch from the drum surface. The ends were bent so that they faced toward the drum, with one end pointing a little above and the other pointing a little below the center of the deposition area. The ends of the tubes were also flared. These modifications produced a more even deposition pattern on the drum. On the outside of the reactor the inlet tubes were connected by a Swagelok tee union to form one inlet line which was connected to the substrate reservoir. A Nupro SS-4BMW metering valve was placed in the inlet line to control the rate of substrate introduction. The substrate reservoir was connected by a glass/metal adaptor directly to the metering valve. The rate of introduction was monitored by a Hasting Mass Flow Tranductor (Type F 300M, Model LF-300) in the line between the metering valve and the reactor. The rate was read on the flow meter, which was calibrated from 0 to 300 SCCM. However, the meter readings were not accurate mass flows, and the meter had to be calibrated for absolute measurements.

There were two different types of substrate reservoirs. If the substrate was a volatile liquid (acetone or an acetate ester) then a flask with a glass vacuum adaptor was used. The vacuum adaptor consisted of a 24/40 male tapered joint attached to a 0-4 mm high vacuum valve which was
itself attached to an 18/9 female ball joint. The tapered joint was attached to the orifice end of the valve since this end makes a better vacuum seal. By use of a vacuum adaptor, a flask could be attached to any vacuum system in the lab. Liquids had to be degassed before using in this reactor. Degassing was done either by cooling the liquid down to a low enough temperature so that its vapor pressure was negligible and pulling a vacuum on it or by repetitive freeze-pump-thaw cycles.

If the substrate was a liquid with a low volatility (cyclohexanone or acetophenone) then a different substrate inlet system was used. The metering valve and all pieces beyond the tee in the inlet system were removed. An 18/9 female glass/metal adaptor was placed, pointing upward, in the tee and the exposed parts of the substrate inlet system were wrapped with heating tape. The substrate reservoir, a graduated dropping funnel with a 0-3 mm high vacuum valve and an 18/9 male ball joint at the lower end, was attached to the glass/metal adaptor. The substrate was dripped into the heated system where it was vaporized into the reactor. The rate of introduction was controlled by the 0-3 mm valve. Better control of the rate could be achieved if the orifice sealing o-ring was removed and only the Teflon stem was used for the orifice seal. The substrate also had to be degassed before using. The design of the reactor made it impossible to use non-volatile liquids or solids as a substrate.
A 1/4 inch pipe tee fitting was attached to the side flange by a 1/4 inch male pipe nipple that was to the lower left of the Cajon fitting for the left inlet tube. The other two ends of this fitting had the other T.C. gauge tube and a Nupro B-4H bellows valve attached to them. This T.C. gauge tube was used primarily to monitor the pressure in the reactor during the time the reactor was being rough pumped. The Nupro Valve was used to control the introduction of inert gas into the reactor during warm-up. The valve was connected by copper tubing to a tank of Big-3 Chromatographic Grade nitrogen.

The bottom flange of the reactor was made of 3/4 inch thick aluminum and had the product collection system attached to it. The flange had a 6 inch diameter cut-out in its center so that there was clearance for moving the collection funnel in and out of the reactor.

The funnel had a 5 3/4 inch diameter and was modified from a commercially available 5 inch glass funnel by carefully flaring its top edge and shorting its stem to 2 inches long. The funnel rested up-right on a 7 1/2 inch diameter by 1/4 inch thick round brass flange with a one inch Cajon fitting pointing downward in its center. A short piece of one inch glass tubing with a 24/40 male tapered joint was set in this fitting. The stem of the funnel was placed in the glass tube so that when material melted off the drum, it ran down the funnel, through the 24/40 joint and was
collected in a flask connected to the joint. Usually a 100 to 250 ml Schlenk flask was used for collection. The whole system was designed so that the brass flange could be easily bolted and unbolted from the bottom reactor flange.

Other Metal Vapor Reactors

Two static metal vapor reactors were used in routine experiments that did not require photolysis. Their designs were very similar to those of Timms, so only one will be described here. The other reactor differed slightly in its dimensions, had a different type of step-down transformer, and was a mirror image of the one described.

A diagram of the first reactor with its supporting vacuum line is shown in Figure 2-5. The reactor itself was a test tube like cylinder about 12 inches long with an inner diameter of 3 inches and had a perpendicular glass tube, ending in a female ball joint which attached to the vacuum system, about 3 inches from the top open end. The reactor was capped with a 3/8 inch thick by 6 1/4 inch diameter flange through which all connections with furnace leads, substrate inlets and vacuum gauges were made. In the reactor, a resistance-heated furnace was held in place about 9 inches below the top flange by two water-cooled 3/8 inch copper leads placed 2 1/2 inches apart. Between the furnace leads, ending about 1 1/2 inches above the furnace, was the
FIGURE 2-5

DIAGRAM OF A STATIC METAL VAPOR REACTOR

A) REACTOR

B) REACTOR TOP FLANGE

C) FURNACE

D) FURNACE LEADS

E) SUBSTRATE INLET TUBE AND FLANGE FITTING

F) FURNACE LEAD FLANGE FITTINGS

G) FLANGE FITTING FOR THERMOCOUPLE GAUGE TUBE AND
   INERT GAS INLET VALVE

H) THERMOCOUPLE GAUGE TUBE

I) INERT GAS INLET VALVE

J) SUBSTRATE RESERVOIR CONNECTING TUBE

K) ACCESSORY CONNECTION MANIFOLD

L) STABILIZING LIGAND RESERVOIR AND/OR
   CRYOTRAP FOR REMOVING VOLATILES

M) MAIN LN2 VACUUM TRAP

N) ROUGH PUMP CONNECTION MANIFOLD

O) VALVE TO DIFFUSION PUMP
substrate inlet tube. The last inch of this 1/4 inch copper tube was drilled with holes for producing a deposition pattern of the substrate that was similar to that of the metal.

Sylvania Emissive Products CS-1008 integral alumina coated tungsten furnaces were used in the reactor. To help provide heat shielding, they were wrapped with a layer of 1 mil tantalum foil and a second layer of 5 mil tantalum foil was placed around that. Power to the furnace was supplied by a 110 V G. E. Model 9T12V58 8:1 step-down transformer. A Powerstat variac was placed between the wall plug and the transformer for fine control.

Nylon Swagelok fittings were used for making the vacuum seal between the top flange and the furnace leads. These fittings also insulated the leads from the top flange and from each other. Between these fittings was the fitting for the substrate inlet. Behind this fitting was a tee fitting that had an inert gas inlet which was a 1/4 inch Nupon valve and a thermocouple vacuum gauge tube, Model Number GTC-004 from CVC Products Inc. In front of the substrate inlet fitting was an opening, threaded for a 1/4 inch pipe plug, which was used in the removal of products.

The inlet flange fitting was a 1/4 inch Swagelok to 1/4 inch male pipe connector. The pipe fitting on this connector had been drilled out and the substrate inlet tube was soldered directly into it. A 1/4 inch copper tube ran
from the top of the inlet fitting to a Hoke 1315G4B metering valve which controlled the rate of introduction of the substrate. Like the photochemical reactor, if the substrate was a volatile liquid the substrate reservoir was attached to the valve through an 18/9 male glass/metal adaptor on the valve and a vacuum adaptor on the flask. If the substrate was a liquid with low volatility like acetophenone, then a different inlet system was used. The substrate inlet tube was replaced with one made of glass with a gas dispersion frit on one end and a 1/4 inch Kovar seal on the other. The Kovar end was soldered into the inlet flange fitting. An 18/9 female glass/metal adaptor was insert into the top of the fitting. A dropping funnel, like that used in the photochemical reactor for similar purposes, was connected to the glass/metal adaptor. The substrate was introduced into the reactor by dripping it into the inlet tube from the funnel. As long as the rate of addition was not too great, radiative heating from the furnace kept the gas dispersion frit hot enough to vaporize the substrate that dropped onto it.

The reactor was evacuated by a CVC MCF-60 2 inch diffusion pump, backed by a Welch Duo-Seal Model 1402 rotary oil pump. The reactor and its supporting vacuum system was connected to the diffusion pump by a Pyrex right-angle V-15 high vacuum valve situated above the pump. The supporting vacuum system of the reactor consisted of the rough pump
connection manifold, the main vacuum trap and the accessory connection manifold. The rough pump connection manifold, which was a short length of vacuum line with a 0-10 mm high vacuum valve attached to it, was connected to the diffusion pump valve. The glass valve on the manifold was connected to the rotary oil pump by thick-walled rubber tubing and was used when rough pumping the reactor. Next to this manifold was the main vacuum trap, which was cooled by immersion in a liquid nitrogen bath. Next to the trap was the accessory manifold, which was a length of vacuum line about six inches long that had a connection pointing upward for a manometer and two other side tubes pointing downward to which other items could be connected. Connections between pieces in the vacuum manifold itself were made by 28/15 high vacuum ball joints. The connections to the manometer and other items added to the line were made via 18/9 ball joints. The ball joints on the system were male. The side tube for the manometer had a 0-10 high vacuum valve in it; the other side tubes had to be capped when not in use. The two extra connections were used for attaching cryo-traps for removing volatiles or storage flasks containing volatile stabilizing ligands which were used after completion of a reaction.
**Gas Measurement and Chemical Vacuum Line**

A gas handling and measuring system was added to a pre-existing glass vacuum line.² A diagram of the entire vacuum line is shown in Figure 2-6.

The diffusion and rough pumps used on the system were the same as those used on the static metal vapor reactors. The line consisted of a vacuum pump connection manifold; a liquid nitrogen vacuum trap; a tee-piece where a CVC thermocouple tube was connected; and the main vacuum line which was built from four identical sub-manifolds, each of which served as a connection to an U-trap. A 0-10 mm high vacuum valve was placed in each sub-manifold so that pumping of the line was done either straight through the sub-manifold (valve open) or through the U-trap (valve closed). Each U-trap had two 0-10 mm high vacuum valves which allowed the U-trap to be sealed and removed from the rest of the vacuum system. The sub-manifolds were connected to each other by 35/20 high vacuum ball joints; the U-traps were connected to the manifolds by 18/9 high vacuum ball joints. On top of each sub-manifold there was an extra 18/9 ball joint for connecting extra pieces to the line. The top joint on the third sub-manifold was connected to a pre-purified nitrogen line. All the 18/9 joints on the line were male.

A bubbler-manometer similar in design that described in Schriver's book (reference 2, p. 35) was attached to the
FIGURE 2-6

DIAGRAM OF THE VACUUM LINE

A) VACUUM PUMP CONNECTION MANIFOLD
B) MAIN LN2 VACUUM TRAP
C) CONNECTION TO THERMOCOUPLE GAUGE TUBE
D) THERMOCOUPLE GAUGE TUBE
E) U-TRAP CONNECTION MANIFOLDS
F) U-TRAPS
G) INERT GAS VALVE AND CONNECTION
H) BUBBLER-MANOMETER
I) TOEPLER PUMP CONNECTION MANIFOLD
J) TOEPLER PUMP
K) TOEPLER PUMP SAMPLING FLASK
L) TOEPLER PUMP CONSTANT VOLUME MANOMETER
fourth sub-manifold. Each arm of the manometer had a glass vacuum valve to increase the versatility of the unit. The non-bubbler side of the manometer had a side arm to which flasks could be attached for pressure measurement. In those cases, the bubbler arm served as the high vacuum comparison side. The unit was a gift from Dr. Kenton Whitmire of the Rice University Chemistry Department.

A Toepler pump and constant volume manometer was added to the end of the original vacuum line for the measurement of permanent gases. The Urry type pump, purchased from Kontes-Martin\(^3\), had a 500 ml mercury capacity. The design of the pump-manometer unit was similar to one described in Schriver's book (reference 2, P. 14), with the only deviation being an extra vacuum valve placed between the manometer and pump.

**Schlenk Line and Equipment**

A double manifold glass Schlenk line was built for work with air sensitive materials.\(^4,5\) It consisted of a vacuum manifold and an inert gas manifold interconnected by five three-way, oblique bore stopcocks. The stopcocks were connected to other apparatus with 1/4 inch I.D. by 3/16 inch wall rubber tubing. The inert gas and vacuum manifolds were also interconnected by a 0-10 mm valve so that the entire system could be evacuated.
The vacuum line was pumped by a Welch Duo-Seal Model 1400 rotary oil pump. A vacuum trap, for protecting the pump from solvent vapors, was between the manifold and the pump. The pressure in the vacuum manifold was monitored with a tilting McLeod gauge which was attached to the manifold by a length of rubber tubing. The gauge could be isolated from the manifold by a stopcock.

The inert gas used in the other manifold was purified by passing it first through a 2 inch by 24 inch glass column containing 2 inches of 4X molecular sieves, 12 inches of a de-oxygenation catalyst\(^6\), and another 2 inches of molecular sieves; then through a second column filled with Drierite. The manifold could be isolated from the inert gas line by a 0-4 mm high vacuum valve. One end of the manifold was connected to a mercury bubbler made from a gas washing bottle and connected to the manifold by Tygon tubing. A stopcock on the manifold allowed isolation of the manifold from the bubbler. Control of the gas flow into the manifold was accomplished with the flow control valve on the pressure regulator of the inert gas source.

The de-oxygenation column was wrapped with insulated heating wire and was designed with stopcocks so that it could be isolated from the manifold and inert gas tank. Regeneration of the catalyst was done by heating it to about 180°C under a slow flow of inert gas and then passing a 10% hydrogen in nitrogen mixture through it for about 2 hours.
A stopcock was provided on top of the column for attaching a line to the regeneration mixture. A second stopcock on the bottom of the column was provided for attaching a bubbler to the column during regeneration. Regeneration of the column produced fairly large amounts of water which drained from the column through the bubbler. After regeneration, the bubbler was replaced with a vacuum line and the column was allowed to cool under vacuum overnight.

A set of Schlenk glassware was produced from conventional glassware to give a set equivalent to ones available commercially.
Analysis and Physical Measurements

Routine gas chromatographic analyses were done on a Hewlett-Packard F&M 700 gas chromatograph with a thermal conductivity detector using either a six foot by 1/8 inch O.D. nickel column packed with 20% SE-30 on 80/100 Chromosorb W-A.W., a six foot by 1/8 inch O.D. stainless steel column packed with 10% Carbowax 20-M on 80/100 Chromosorb W-H.P., or a six foot by 1/8 inch O.D. nickel column packed with 100/120 Porapak QS. Peak areas were measured with a planimeter and are uncorrected. Permanent or light gas analyses were done using a 3 foot by 1/8 inch O.D. nickel column packed with 80/100 Spherocarb on an Aerograph 200 gas chromatograph fitted with a 6-port Valco GC Valve with a sampling loop to allow airless sample introduction, and a Gow-Mac 11-625 gas density balance detector. Mass spectrometry was done on a Finnigan 3300 spectrometer using a SE-30 column for routine G.C.-mass spectrometric studies and a Porapak QS column for light gas studies. Proton and carbon-13 N.M.R. spectra were obtained on a JEOL FX90Q F.T.-N.M.R. spectrometer.
General Procedure for the Photochemical Metal Vapor Reactor

The day before a reaction was to be done, about one gram of the metal to be studied was placed in a crucible and the filled metal crucible and the substrate reservoir were weighed. The crucible was slipped into the furnace; then the furnace, the substrate reservoir and a clean collection flask (250 ml Schlenk flask) were attached to the reactor. The rough pump valve was opened and when the pressure in the system was below 50 microns (as measured by T.C. #1) the rough pump valve was closed and the diffusion pump gate valve was opened. The system was pumped overnight with the vacuum pump protection unit activated.

By the next day the pressure in the system was usually less than $5 \times 10^{-6}$ torr and by filling the cryo-trap with liquid nitrogen the pressure could be reduced to $1 \times 10^{-6}$ torr or below. Next, the furnace was connected to the cooling water lines and electrical leads and the crucible was outgassed by heating to about $1000^\circ$C (about $400^\circ$C for manganese). When the pressure returned to below $10^{-6}$ the reaction drum could be filled with liquid nitrogen and the motor rotation drive activated. At this point the vacuum pump protection unit was adjusted to the override position.

With the substrate control valve closed, the substrate reservoir valve was opened and an appropriate rate of introduction into the reactor was established by slowly opening the control valve and watching the mass flow meter.
The proper rate for a particular compound had to be ascertained before-hand by a blank experiment (no metal or photolysis). If a compound with a low volatility was being used, then the special inlet set-up was used and the rate of introduction of the substrate into the reactor was established by observing how fast the liquid level dropped in the graduated funnel.

Once a thin film of substrate had been condensed on the drum, the furnace was brought up to the proper temperature. If the experiment was to be run under photochemical conditions, the photolysis lamp and its cooling water system was turned on at the same time. At this point the experiment was considered to have begun.

In most of the experiments that were done, about 0.05 grams of metal was vaporized per hour with a 50 to 100 molar excess of the substrate. The experiments usually lasted from three to five hours.

When an experiment was terminated, the reservoir valve was first closed and the furnace variac was slowly lowered until the furnace was off. Then the lamp was turned off and the reactor was isolated from the vacuum system by closing the gate valve. Next, the reactor was pressurized to half an atmosphere with prepurified nitrogen. The residual liquid nitrogen in the drum was removed by blowing it out with a hose connected to a compressed air outlet. At this point, if a substrate had been used that melted at or near
room temperature, the cocondensate was washed off the drum with a low melting solvent like diethyl ether. In any case, the cocondensate on the drum either melted or was dissolved off the drum and was collected in the Schlenk flask under the reactor. The reactor was brought up to atmospheric pressure with nitrogen and the flask was quickly removed and stoppered for further work-up.

Lastly, the metal crucible and substrate reservoir were removed and reweighed; and the surfaces in the reactor with built-up layers of metal deposited were cleaned by wiping them with 10% hydrochloric acid and then rinsing with de-ionized water.

**General Procedure for the Static Metal Vapor Reactors**

To begin a reaction, the filled furnace and the substrate reservoir were first weighed. The reactor was assembled and pumped down, first by rough pumping to less then 50 microns and then to less than 1 micron with the diffusion pump. The minimum time needed to get a one micron vacuum was usually about two hours, although longer pump-down times were usually used since they resulted in cleaner systems. After attaining the necessary vacuum, the furnace was outgassed by heating it to a bright red glow, just below the vaporization temperature, and keeping it at this temperature until the pressure in the system fell to
below 1 micron. The vacuum trap was then cooled to \(-196^\circ\text{C}\) with liquid nitrogen and the furnace was slowly cooled. The setting of the variac was the only indication of the temperature of the furnace. Increasing or decreasing the furnace temperature had to be done in increments since sudden large temperature changes could shorten the life of a furnace drastically.

After the glass of the reactor had cooled to near room temperature, the reactor was immersed in a liquid nitrogen bath, the valve to the substrate reservoir was opened and the desired rate of condensation of substrate into the reactor was set with the metering valve in the inlet line. The correct setting for the metering valve had to be known either from experience or by doing a blank experiment. A layer of substrate was first allowed to condense in the reactor for a few minutes before heating of the furnace was begun. Pre-condensing a layer of substrate on the reactor reduced the tendency for the cocondensate to stick to the walls of the reactor after the reaction was finished. When the metal was being heated for vaporization, it was useful to overheat the metal to melt it and then quickly bring the temperature back down to the proper level. This made the metal bead up in the furnace, which improved the efficiency of the vaporization. For metals like chromium, which do not melt just above their vaporization point, this procedure
could not be used. Once vaporization began, the reaction was considered to have started.

Typically, from 3 to 7 mmols of metal was condensed with a 50 to 100 fold molar excess of substrate over a one to a one and a half hour period. The amount of substrate used was larger than most previous workers have used (usually a 10- to 15-fold excess); but since the results from the static reactors were to be used as comparisons to the photochemical reactor, similar deposition ratios were used in both.

After the reaction, the reactor was isolated from the diffusion pump and allowed to warm to room temperature. Often at this point, all volatile material was bulb-to-bulb distilled into a flask attached to the system. The non-volatile residue left in the flask was worked up in several ways. If an air and water stable product was thought to be in the residue, then the reactor was pressurized with argon, opened to the air and several milliliters of water was added to neutralize the pyrophoric metallic residue. This was followed by an organic solvent. If the product was resistant to acid, then diluted acid was added, instead of water, to dissolve the residual metallic residues.

If the metallic residue was to be examined, it had to be removed in such a way that it was not exposed to air or water. To do this, the reactor was pressurized as before
and the pipe plug in the top flange was removed so that there was a fast stream of inert gas coming out of the hole. About 20 to 30 ml of a dried, de-oxygenated organic liquid, preferably freshly distilled from a ketyl still, was syringed into the reactor. Alternatively, instead of collecting the substrate by bulb-to-bulb distillation from the reactor, it was often left in the reactor and used as the slurry medium for the metallic residues. The metallic residue slurry was then siphoned out of the reactor using a Schlenk flask with a special glass adaptor that had been dried in a 160°C oven for a few hours and purged with inert gas. The adaptor consisted of a 24/40 male joint with a long 1/4 inch glass tube that went through the sealed top of the joint. One end of the tube was thus in the flask and the rest of the tube curved around so that the other end could be inserted in the pipe hole and placed at the bottom of the inside of the reactor. The stopcock on the Schlenk flask was connected by rubber tubing to a three-way valve that was connected to both a vacuum and an inert gas line. By manipulating the three-way valve, the metallic residue slurry was sucked into the Schlenk flask by pulling a partial vacuum on the flask for a few seconds. The flask was then stoppered and removed for further work-up.

The reactor was disassembled and the furnace and substrate reservoir were reweighed. The outer glass piece of the reactor was cleaned with 10 to 20 ml of 10%
hydrochloric acid or, if necessary, 10% hydrofluoric acid. The piece was then rinsed with acetone and deionized water. The furnace leads and inlets in the reactor were cleaned by rubbing off metallic residues with steel wool.
REFERENCES AND NOTES

1. These reactors and their supporting vacuum systems are equivalent to the one described in: Inorganic Synthesis 19 (D. F. Schriver, ed.), pp. 59 to 65 (1979).


3. Kontes catalog no. KM-924900-0500 pump and KM-924902 pump control


5. The Schlenk double manifold unit and its gas purification train is similar in design to one made by Ace Glass Company (the Ace-Burlitch Inert Atmosphere System).

6. Chemalog's Catalyst R3-11, catalog no. 18-3000-00.

7. Reference 1 has an excellent discussion of the procedure involved in doing a metal vapor reaction in this type of reactor and the problems that are encountered.
CHAPTER 3

REACTIONS OF TRANSITION METALS WITH ALDEHYDES AND KETONES

BACKGROUND

Recently Shevlin reported cocondensing cobalt with acetaldehyde. The only volatile product observed from this reaction was a trace of methane which was evolved during the warm-up of the reaction. More methane (4.1%) was evolved when the non-volatile residue formed in the reaction was hydrolyzed. He also cocondensed cobalt with ethylene and added an aldehyde (acetaldehyde or formaldehyde) to the deposition at 196°C. A complex mixture of products was obtained from these reactions. In the acetaldehyde reaction, methane (3.3%), ethanol (13.4%), 2-butanone (7.3%), 2-butanol (3.6%) and ethyl acetate (4.2%) were seen. From these experiments and others using deuterium-labeled reactants, he postulated that addition of the aldehyde to the cobalt-ethylene complex formed upon initial cocondensation lead to the oxidative insertion of the complex into the aldehydic C-H bond to form a cobalt acyl hydride. Then, insertion of an ethylene into the
cobalt-acyl bond produced butanone and butanol, while reduction of the acetyl group by the hydride produced methane, ethanol and ethyl acetate.

The only other report of a metal vapor experiment using an aldehyde was a footnote in a paper by Gladysz. He reported that the coupled diol was produced in the reaction between titanium and decanal, but no products were seen using chromium. The reaction of iron and decanal produced a 12.5% yield of the alcohol.

The earliest report of a reaction between a metal and a ketone was by Westcott and Klabunde which concerned the reaction between magnesium and cyclic ketones such as cyclohexanone and cycloheptanone. These reactions produced the reductively coupled pinacol as well as aldol products and other products which were interpreted to have come from a carbene or carbenoid intermediate. For example, reacting magnesium with cycloheptane produced a 13% yield of the pinacol, 22% aldol products, 12% cycloheptene and about 1/2% each norcarane and cycloheptane.

DeKock vaporized a series of transition and inner transition metals with cyclohexanone and reported that most metals gave both pinacol and aldol products, while nickel and cobalt gave only aldol products. Gladysz reported similar results in his metal atom de-oxygenation studies. However, he reported that both cobalt and nickel gave very small yields of pinacol and pinacol-derived products from
both cyclohexanone and cycloheptanone. The yield of the reductively coupled products found in these metal vapor experiments was no more than 20%. These yields can be contrasted to those found in ketone coupling reactions using zero-valent transition metal complexes, such as the McMurry reaction. In the McMurry reaction a titanium (II) or (III) complex is first reduced to a titanium (0) species that couples and often also de-oxygenates the ketone.

\[
\begin{align*}
\text{TiCl}_3 + 2 \text{R-C-R'} & \rightarrow \text{R} = \text{C} = \text{C} \text{R} \text{R'} \\
3 \text{K} & \text{or} \\
1/2 \text{LAH} & \\
\end{align*}
\]

The yields in these reactions are often high, up to 90%. Ledon, et al. found that cocondensing titanium with arenes formed a bis-arene complex which also coupled ketones to form alkenes in nearly 100% yield.\(^7\) The titanium slurry formed in this reaction also coupled ketones, but at a slower rate than the complex. It is significant that aldol products were never seen as side products in these zero-valent metal coupling reactions.\(^7\)
RESULTS AND DISCUSSION

The Reactions of Iron and Chromium with Aldehydes

Iron and chromium were cocondensed with acetaldehyde and iron was cocondensed with isobutyraldehyde in the static reactors. In all cases, after warm-up and removal of volatiles, an intractable solid was left in the reactor. Iron left a brown material while chromium left a green solid. A clear, gelatinous, and soluble material was left after excess acetaldehyde evaporated from the volatile portion of the reaction products. Proton N.M.R. and mass spectral data showed this material to be polyacetaldehyde.\[11\]

\[
\begin{array}{c}
\text{Me} \\
\text{Me} \\
\text{Me}
\end{array}
\]

\[
\begin{array}{c}
\text{\textbf{-C-O-C-O-C-}} \\
\text{x}
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

No attempt was made to analyze the intractable materials formed. Over a period of a week the iron material became more crystalline in appearance, while the chromium-acetaldehyde product turned to a green liquid within 24 hours. It seems likely that these materials were all polyaldehydes with a sufficient molecular weight to make them non-volatile and insoluble.

With the exception of paraformaldehyde, linear polyaldehydes are unstable with respect to the unpolymerized
material at room temperature, unless the polymer chain is suitably "end capped" with some other group. Apparently, in the iron-aldehyde reactions the solid polyaldehyde formed had a suitable capping group, while the chromium product was not suitably stabilized. However, a second N.M.R., taken 24 hours after the first, of the volatile fraction formed in the iron-acetaldehyde reaction showed that it almost totally reverted back to acetaldehyde. So, although the non-volatile portion of the iron-acetaldehyde product was thermally stable, the volatile portion was not.

Because of the intractable nature of the materials formed in these reactions, it was decided to do no further experimentation on them.

The Reaction of First Row Transition Metals with Acetone

Several first row transition metals -- chromium, manganese, iron, cobalt, nickel and copper -- were cocondensed with acetone in a static metal vapor reactor. The conditions for each experiment and the products isolated are given in Table 3-I. In the general, the trend for the formation of pinacol in these reactions followed the results of DeKock for the reaction of metals with cyclohexanone. The early transition metals, chromium and manganese, gave roughly a 20% yield of pinacol. Copper, which DeKock did not study, formed about 7% pinacol. Iron, cobalt and nickel
### TABLE 3-I

**REACTIONS OF TRANSITION METALS WITH ACETONE:**

**STATIC METAL VAPOR REACTORS**

<table>
<thead>
<tr>
<th>METAL mmol</th>
<th>ACETONE mol</th>
<th>RATIO</th>
<th>TIME min.</th>
<th>PINACOL % (mmol)</th>
<th>ALDOL % (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-7.37</td>
<td>0.319</td>
<td>1/43</td>
<td>90</td>
<td>14 (1.01)</td>
<td>9 (0.65)</td>
</tr>
<tr>
<td>Mn-5.46</td>
<td>0.690</td>
<td>1/124</td>
<td>90</td>
<td>20 (1.09)</td>
<td>29 (1.61)</td>
</tr>
<tr>
<td>Fe-5.41</td>
<td>0.384</td>
<td>1/71</td>
<td>90</td>
<td>0.2 (0.01)</td>
<td>2.0 (0.11)</td>
</tr>
<tr>
<td>Co-3.72</td>
<td>0.426</td>
<td>1/115</td>
<td>90</td>
<td>0.8 (0.03)</td>
<td>2.7 (0.10)</td>
</tr>
<tr>
<td>Ni-7.60</td>
<td>0.376</td>
<td>1/49</td>
<td>90</td>
<td>-</td>
<td>39 (2.94)</td>
</tr>
<tr>
<td>Cu-5.16</td>
<td>0.502</td>
<td>1/97</td>
<td>90</td>
<td>7 (0.37)</td>
<td>6 (0.32)</td>
</tr>
</tbody>
</table>

*a) Percent yield based on mmol product/mmol metal vaporized.*

*b) Diacetone alcohol, except for manganese which gave: Mesityl oxide (22%), diacetone alcohol (7%).*
produced only trace amounts of pinacol (1% or less.) All the metals formed aldol condensation compounds and some produced isopropanol as secondary products. However, other experiments showed these materials were not reproducibly produced. If it is assumed that formation of the pinacol was due to an interaction between metal atoms and acetone molecules, then the following synthetic scheme can be written:

\[
\begin{align*}
\text{M + Me-C-Me} & \xrightarrow{196^\circ C} M(\text{O=C-Me}) & & M(\text{O-C-Me}) \\
\text{H+} & \xrightarrow{\text{HO-OH}} \text{C-C-Me} & & \text{M}
\end{align*}
\]

In this scheme, a metal atom is first solvated by acetone molecules and then electron transfer takes place to form a pinacolate species. This mechanism is equivalent to that proposed for the reduction step in the coupling reaction of transition metal complexes with ketones. However, the formation of aldol products in these metal vapor experiments is not explained by this mechanism.
**Metal-Acetone Metallic Residues**

The non-volatile residues formed in the transition metal-acetone reactions have the following visual characteristics: chromium forms a greenish solid; manganese forms a yellowish white solid; iron, cobalt and nickel yield blackish powders and copper forms a black material with small metallic copper particles in it. The chromium residue tended to retain about half of the total pinacol formed in the reaction, while manganese retained almost all that was formed.

Samples of the residue formed in iron-acetone and chromium-acetone reactions were subjected to hydrolysis and the gases produced were collected, measured and identified. The amounts of gases evolved and the percentages of each species found are presented in Table 3-II. In addition to the species listed in Table 3-II, a significant amount of hydrogen was evolved in both cases. Even though the acetone molecule has only three carbons, both materials gave off trace amounts of hydrocarbons with seven and eight carbon atoms. This suggests that these materials are similar to those formed by the cocondensation of transition metals into alkanes and simple ethers and supports the concept that if metal atoms do not interact with other species upon cocondensation, they instead form metal-metal aggregates which attack any organics present to produce an "organometallic" powder. It is probable that the iron-,
<table>
<thead>
<tr>
<th>SOLID</th>
<th>Cr-Acetone</th>
<th>Fe-Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>METAL/ORGANIC RATIO</td>
<td>1/113</td>
<td>1/65</td>
</tr>
<tr>
<td>SAMPLE MASS gm</td>
<td>0.053</td>
<td>0.088</td>
</tr>
<tr>
<td>TOTAL GAS mmol/gm</td>
<td>(5 \times 10^{-2})</td>
<td>(2 \times 10^{-2})</td>
</tr>
<tr>
<td>PERCENT OF:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>1.8%</td>
<td>6.6%</td>
</tr>
<tr>
<td>C-3 species</td>
<td>8.4</td>
<td>31.5</td>
</tr>
<tr>
<td>C-4 species</td>
<td>3.9</td>
<td>26.3</td>
</tr>
<tr>
<td>C-5 species</td>
<td>11.2</td>
<td>20.1</td>
</tr>
<tr>
<td>C-6 species</td>
<td>28.0</td>
<td>8.1</td>
</tr>
<tr>
<td>C-7 species</td>
<td>21.4</td>
<td>5.5</td>
</tr>
<tr>
<td>C-8 species</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>Acetone and isopropanol</td>
<td>21.4</td>
<td>1.8</td>
</tr>
</tbody>
</table>
cobalt- and nickel-acetone residues are identical to those formed in metal-alkane reactions. The residues formed by manganese and chromium are more complex, since they obviously contain significant amounts of metal-alkoxide species.

Since these "organometallic" powders have significant catalytic ability, an attempt was made to investigate whether they may account for any of the products seen in the metal vapor experiments with acetone. A vacuum-dried sample of a chromium-acetone powder was added to fresh acetone and the reaction was monitored by gas chromatography. The results of this experiment are shown in Figure 3-1. In five hours observable amounts of diacetone alcohol appeared. After thirty hours some of the original aldol product had dehydrated to mesityl oxide. The reaction gave a steady increase in total aldol products over the entire observed period. Presumably the water formed in the aldol dehydration was slowly poisoning the catalyst, explaining why a drop in the rate of aldol formation was noted after 100 hours. Secondly, the water liberated the bound pinacol dianion and the presence of pinacol could be noted after 50 hours in measurable amounts. This amount was essentially constant over the course of the reaction. The amount formed (~3%) was well under what one would expect for being in the original sample. The final yield for all aldol condensation products was 151% after 200 hours. An
FIGURE 3-1
REACTION OF THE CHROMIUM–ACETONE POWDER WITH ACETONE

YIELD MMOLS
3.0

○ TOTAL ALDOL
□ DIACETONE ALCOHOL
△ MESITYL OXIDE
• PINACOL

HOURS
100
200
experiment done with the iron-acetone powder gave quite similar results with a yield of 305% of aldol products after 175 hours and a barely detectable trace of pinacol.

Although the presence of isopropanol was not established in these experiments, it is probable that the powder forms this product also. The yield of this product was not consistent from experiment to experiment but its presence correlated to the presence of larger amounts of aldol products.

The results indicate that the products formed in these metal vapor reactions probably arise from an initial reaction of a metal atom with acetone molecules to form a reductively coupled pinacolate species and a later catalytic reaction between the metal cluster particles and the excess ketone to form the aldol products. Thus the following scheme can be written for this reaction:

\[
\text{M} + \text{Me-C-Me} \rightarrow \xrightarrow{\text{excess acetone}} \text{"carbonaceous metal cluster"} \rightarrow \text{Aldol Products}
\]
The Effect of Photolysis on the Metal-Acetone Reactor

Table 3-III presents the results of experiments where the metal-acetone cocondensate was photolyzed during deposition in the photochemical reactor. The reactions of chromium, manganese, iron, cobalt, nickel and copper with acetone were studied. For comparison, experiments without photolysis were done with manganese, iron, cobalt and nickel in the reactor; the results are also presented in Table 3-III.

A comparison of the reactions done in the static reactor with the reactions done in the photochemical reactor would at first imply that photolysis decreased the yield of pinacol for chromium, manganese and copper. However, experiments in which manganese was vaporized into pentane or diethyl ether in both reactors, recovered under an inert atmosphere and weighed in a dry-box, indicated that 75% of the metal vaporized in the static reactor could be recovered while only 50% was recovered in the photochemical reactor. Thus, less metal was deposited on the reaction surface of the photochemical reactor than in the static reactors. In both cases, the missing metal was intercepted by cooling shields and furnace leads before it encountered the deposition area. When this is taken into account, the differences in yields of pinacol for chromium, manganese and copper with and without photolysis disappear. The data for manganese also show that identical yields of pinacol were
<table>
<thead>
<tr>
<th>METAL</th>
<th>ACETONE</th>
<th>RATIO</th>
<th>TIME</th>
<th>PINACOL</th>
<th>ALDOL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mmol</td>
<td>mol</td>
<td>min</td>
<td>% (mmol)</td>
<td>% (mmol)</td>
</tr>
<tr>
<td>Cr-4.40</td>
<td>0.441</td>
<td>1/100</td>
<td>300</td>
<td>8 (0.36)</td>
<td>5 (0.20)</td>
</tr>
<tr>
<td>Mn-5.72</td>
<td>0.245</td>
<td>1/43</td>
<td>180</td>
<td>7 (0.38)</td>
<td>20 (1.15)</td>
</tr>
<tr>
<td>Mn-5.92</td>
<td>0.259</td>
<td>1/43</td>
<td>180</td>
<td>7 (0.41)</td>
<td>7 (0.39)</td>
</tr>
<tr>
<td>Mn-3.69</td>
<td>0.405</td>
<td>1/110</td>
<td>300</td>
<td>11 (0.39)</td>
<td>88 (3.25)</td>
</tr>
<tr>
<td>Fe-10.48</td>
<td>0.260</td>
<td>1/25</td>
<td>180</td>
<td>1.0 (0.10)</td>
<td>-</td>
</tr>
<tr>
<td>Fe-7.92</td>
<td>0.416</td>
<td>1/52</td>
<td>300</td>
<td>6 (0.48)</td>
<td>11 (0.90)</td>
</tr>
<tr>
<td>Co-3.65</td>
<td>0.268</td>
<td>1/74</td>
<td>180</td>
<td>0.8 (0.03)</td>
<td>0.3 (0.01)</td>
</tr>
<tr>
<td>Co-2.99</td>
<td>0.226</td>
<td>1/76</td>
<td>150</td>
<td>3.7 (0.11)</td>
<td>10 (0.31)</td>
</tr>
<tr>
<td>Ni-5.20</td>
<td>0.293</td>
<td>1/56</td>
<td>180</td>
<td>-</td>
<td>5 (0.27)</td>
</tr>
<tr>
<td>Ni-8.31</td>
<td>0.476</td>
<td>1/57</td>
<td>300</td>
<td>1.1 (0.09)</td>
<td>13 (1.09)</td>
</tr>
<tr>
<td>Ni-2.16</td>
<td>0.574</td>
<td>1/266</td>
<td>420</td>
<td>1.8 (0.04)</td>
<td>1.4 (0.03)</td>
</tr>
<tr>
<td>Cu-3.49</td>
<td>0.343</td>
<td>1/99</td>
<td>255</td>
<td>3.4 (0.12)</td>
<td>0.3 (0.01)</td>
</tr>
</tbody>
</table>

a) Reactions without photolysis are marked by *.  
b) Percent yield based on mmol product/mmol metal vaporized.  
c) All diacetone alcohol.
obtained with and without photolysis in the photochemical reactor; decreasing the metal concentration of the cocondensate increased the yield of pinacol, an effect that would be expected for the mechanism of pinacol formation proposed above.

Photolysis of iron-, cobalt-, and nickel-acetone cocondensates during deposition produced a small but significant increase in the yield of pinacol for these metals — from 1.0 to 6% for iron, from 0.8 to 3.7% for cobalt and from zero to 1.1% for nickel. An attempt was made with nickel to see if an increase in the yield of pinacol could be observed by decreasing the metal concentration of the cocondensate and slowing the rate of deposition. At a metal/organic molar ratio of 1/266 and and 5X reduction in the rate of metal deposition an insignificant increase in yield occurred, from 1.1 to 1.8%. This implies that, at least for the nickel-acetone experiment, the yield of pinacol was not being significantly limited by the photon flux.

It is probable that a metal-to-ligand charge transfer bond between a metal atom and its coordinated acetone molecule(s) was being excited by the photolysis to form a diradical species such as $M^\cdot -O-C^\cdot$. This species would attack an adjacent coordinated acetone molecule to form the pinacolate dianion.
The Effect of Photolysis on the Reaction of Nickel and Iron with Cyclohexanone

Iron and nickel were cocondensed with cyclohexanone under photochemical conditions. The reaction conditions and results are presented in Table 3-IV. In both cases the major product was 2-(1-cyclohexene-1-yl)cyclohexanone which resulted from an aldol condensation. Other products were formed in less than one percent yield in both cases and were not analyzed.

The lack of a significant yield of pinacol in these two reactions is puzzling, but may be due to the inability of the larger ketone to form a complex which survives long enough for the drum to rotate enough and allow the metal-ketone complex to be exposed to the photolysis unit.

The Reactions of Transition Metals with Acetophenone

Acetophenone was cocondensed with several transition metals in both the static and photochemical reactors. The results of these experiments are presented in Table 3-IV.
In all cases the only product found was the pinacol of acetophenone: 2,3-diphenyl-2,3-butanediol. In the case of chromium, very good yields of the pinacol are formed without photolysis (~50%). It is doubtful that any of the bis-arene complex, which is the expected product from the reaction of chromium and an aryl compound, would survive the work-up procedure. Also, the yield of such a compound would be expected to be low since similar oxygenated phenyl derivatives, such as methyl benzoate, give very low yields of sandwich compounds.16

Iron also gave good yields of the pinacol without photolysis, but nickel gave a very low yield without photolysis (~3%). With photolysis iron gave a 10% yield of the pinacol, while nickel did not produce any observable amounts. Since the warm-up procedure was much more rapid for the photochemical reactor than for the static reactor in these experiments, the differences in yield seem to imply that the formation of pinacols for a mono-aryl ketone is a process dependent on the warm-up period and suggests a cluster process and not a metal atom process.
### TABLE 3-IV

**REACTIONS OF TRANSITION METALS WITH CYCLOHEXANONE AND ACETO anusone**

<table>
<thead>
<tr>
<th>METAL mmol</th>
<th>KETONE mol</th>
<th>RATIO</th>
<th>TIME min</th>
<th>REACTOR</th>
<th>PRODUCT % (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-1.85</td>
<td>CyHx-0.191</td>
<td>1/103</td>
<td>180</td>
<td>P.C.</td>
<td>82 (1.52)</td>
</tr>
<tr>
<td>Ni-1.53</td>
<td>CyHx-0.189</td>
<td>1/123</td>
<td>180</td>
<td>P.C.</td>
<td>15 (0.22)</td>
</tr>
<tr>
<td>Cr-3.90</td>
<td>PhAc-0.101</td>
<td>1/26</td>
<td>60</td>
<td>N.P.C.</td>
<td>64 (2.51)</td>
</tr>
<tr>
<td>Fe-8.32</td>
<td>PhAc-0.129</td>
<td>1/16</td>
<td>90</td>
<td>N.P.C.</td>
<td>51 (4.27)</td>
</tr>
<tr>
<td>Fe-1.87</td>
<td>PhAc-0.148</td>
<td>1/79</td>
<td>180</td>
<td>P.C.</td>
<td>10 (0.18)</td>
</tr>
<tr>
<td>Ni-5.40</td>
<td>PhAc-0.122</td>
<td>1/23</td>
<td>90</td>
<td>N.P.C.</td>
<td>3 (0.15)</td>
</tr>
<tr>
<td>Ni-1.49</td>
<td>PhAc-0.126</td>
<td>1/85</td>
<td>180</td>
<td>P.C.</td>
<td>-</td>
</tr>
</tbody>
</table>

a) CyHx - cyclohexanone; PhAc - acetophenone

b) P.C. - photochemical reactor; N.P.C. - static reactors

c) 2-(1-cyclohexen-1-yl)cyclohexanone for cyclohexanone  
2,3 diphenyl-2,3-butanediol for acetophenone

d) Percent yield based on mmol product/mmol metal vaporized.
EXPERIMENTAL SECTION

All of the metals used were received as powders from the following sources: chromium - ROC/RIC 99.9%; manganese - Fairmount 99.5%; iron - Curtin-Scientific; nickel - ROC/RIC; copper - B&A Acetone (Baker "Photrex" grade) was distilled from Drierite under pre-purified nitrogen and degassed by repetitive freeze-thaw cycles before use. Cyclohexanone was the Aldrich "gold label" grade and acetophenone was the Fisher certified grade. Both were distilled from molecular sieves and degassed by high vacuum pumping before use. Mesitylene was the Aldrich "gold label" grade and cyclooctane was from City Services Corporation. Both were used as received. Water used in the hydrolysis studies was HPLC grade from Mallinckrodt and was degassed by repetitive freeze-thaw cycles.

Spectral Data

polyacetaldehyde: $^1$H N.M.R. (CCl$_3$D, int. TMS) $\delta$ 1.37 (d, 3H, CH$_3$), 5.06 (m, 1H, O-CH-O); mass spectrum (70 e.v.) m/e 44 (M+, 52%), 43 (M-1, 32%) 29 (M-15, 95%), 18 (M-26, 100%).

2,3-dimethyl-2,3-butandiol (pinacol): $^1$H N.M.R. (acetone-d$_6$, int. TMS) $\delta$ 1.18 (s, 6H, CH$_3$), 3.4 (varies, s, 1H, OH); mass spectrum (70 e.v.) m/e 103 (M-15, 5%), 85 (M-31, 38%), 60 (M-58, 100%).
4-methyl-4-hydroxyl-2-pentanone (diacetone alcohol): $^1$H N.M.R. (acetone-$d_6$, int. TMS) $\delta$ 1.21 (s, 6H, CH$_3$), 2.22 (s, 3H, CH$_3$), 2.60 (s, 2H, CH$_2$), 3.9 (varies, s, 1H, OH); mass spectrum (70 e.v.) m/e 101 (M-15, 11%), 85 (M-33, 22%), 59 (M-62, 68%), 43 (M-73, 100%).

4-methyl-3-penten-2-one (mesityl oxide): $^1$H N.M.R. (acetone-$d_6$, int. TMS) $\delta$ 1.88 (s, 3H, CH$_3$), 2.10 (s, 6H, CH$_3$), 6.12 (s, 1H, vinyl); mass spectrum (70 e.v.) m/e 98 (M+, 25%), 83 (M-15, 71%), 55 (M-43, 100%), 43 (M-55, 50%).

2-(1-cyclohexen-1-yl)cyclohexanone: $^1$H N.M.R. (CDCl$_3$, int. TMS) $\delta$ 1.60, 1.89, 2.34, 2.80 (all m, CH$_2$), 5.42 (s, vinyl); $^{13}$C N.M.R. (CDCl$_3$, int. TMS) 22.07, 22.47, 24.42, 24.91, 26.89, 27.21, 41.65, 58.28, 123.10, 135.45.

2,3-diphenyl-2,3-butanediol: $^1$H N.M.R. (acetone-$d_6$, int. TMS) $\delta$ 1.52, 150 (both s, 3H total, CH$_3$), 3.97, 4.11 (both s, 1H total, OH), 7.18, 7.29 (s, m, 5H total, aromatic H); $^{13}$C N.M.R. (acetone-$d_6$, int. TMS) 25.11, 25.54, 78.91, 127.01, 127.20, 128.34, 145.9; mass spectrum (70 e.v.) m/e 242 (M+, less than 1%), 121 (M-121, 100%), 105 (M-137, 65%), 77 (M-165, 91%), 44 (M-198, 89%).

Reaction of Iron with Acetaldehyde. In a static reactor 6.98 mmol of iron was cocondensed with 0.498 mol of acetaldehyde at -196°C over a 60 minute period. After the condensation was ended, the reactor was isolated from the vacuum system and allowed to warm to room temperature while
all volatiles were collected in a trap cooled to -196°C. An intractable brown solid was left in the reactor which was not analyzed further.

The volatiles were warmed to room temperature to drive off excess acetaldehyde. This left a viscous clear liquid which $^1$H N.M.R. showed to be a mixture of acetaldehyde and higher polymeric polyacetals. A second N.M.R. on the same sample 24 hours later showed that it had almost completely depolymerized even though the sample tube had been refrigerated.

Reactions of Transition Metals with Acetone

The following are typical procedures for reactions done both in the static reactor and the photochemical reactor. 

**Reaction of Chromium and Acetone.** In the static reactor 7.37 mmol of chromium was cocondensed with 0.319 mol of acetone at -196°C over a 90 minute period. After the condensation was ended the reactor was isolated from the vacuum system and allowed to warm nearly to room temperature. At this point the reactor was vented with pre-purified argon and opened to the atmosphere via a small pipe fitting. Under a fast stream of argon the metal-acetone slurry was siphoned into a schlenk flask.

The liquid was filtered off the solid under vacuum into another flask cooled with liquid nitrogen. Using this set-up, the solid was kept under vacuum for one hour to
assure complete transfer of all volatiles and drying of the solid.

The liquid was then exposed to the atmosphere and the acetone was carefully distilled off. The residue was analyzed by $^1$H N.M.R. and G.C.-mass spectrometry using mesitylene as an internal standard.

The recovered acetone was analyzed by gas chromatography for low boiling products. Isopropanol was seen, but 2,3-dimethyl-2-butene was not.

The solid was hydrolyzed under pre-purified nitrogen with about 35 ml of 3N hydrochloric acid and then extracted with three 20 ml portions of ether. These were combined, dried over anhydrous magnesium sulfate and the ether was stripped off. The residue was analyzed in a fashion similar to the residue from the liquid. The final yields were combined for the residues from the liquid and solid.

**Reaction of Iron and Acetone with Photolysis.** In a 300 minute period, 7.92 mmol of iron and 0.415 mol of acetone were cocondensed under photochemical conditions. After the reaction was ended, the reactor was isolated from the vacuum system and pressurized to one-half an atmosphere with pre-purified nitrogen. After the drum was emptied of liquid nitrogen with a stream of compressed air, the condensate melted off the drum and ran into the collection flask. The reactor was then fully pressurized and the flask was removed
under nitrogen. The cocondensate was worked-up by the method described earlier.

Experiments with the Metal-Acetone Metallic Solid

The reaction was done as described above in the static reactor but, instead of hydrolyzing the solid during work-up, the solid was taken into the dry-box for further experimentation. The following experiments that are described are typical.

Vacuum Hydrolysis of the Iron-Acetone Solid. In the dry-box, 0.088 gm of the solid recovered from the reaction of iron with acetone was placed in a vacuum hydrolysis flask. The flask was removed from the dry-box, pumped to below $10^{-3}$ torr and cooled to $-196^\circ$C. About 1 ml of water was condensed into the flask, the flask was isolated from the vacuum line and allowed to warm to room temperature.

The quantity of gas given off was measured by a typical gas-measurement vacuum line. Identification of the species given off and their percentages were done by G.C.-mass spectrometry.

Reaction of the Chromium-Acetone Solid with Acetone. In the dry-box, 0.097 gm of the solid recovered from the reaction of chromium with acetone was placed in a 10 ml flask equipped with a stirbar with 5.103 gm of acetone. The flask was capped with a septum, removed from the box and 0.33 mmol of
cyclooctane was syringed in as an internal standard. The course of the reaction was followed by gas chromatography.

Reactions of Iron and Nickel with Cyclohexanone

The following procedure was used for both metals.

Reaction of Iron and Cyclohexanone with Photolysis. Over a 180 minute period 1.85 mmol of iron was condensed with 0.191 mol of cyclohexanone under photochemical conditions. After ending the experiment, the reactor was isolated from the vacuum system, filled with one-half atmosphere of pre-purified nitrogen and the coolant was blown out of the drum. After the cocondensate melted off the drum and ran into the collection flask, the system was fully pressurized and the flask was removed. Then 25 ml of 10% sulfuric acid was added and the mixture was extracted with three 25 ml portions of ether. These were combined, washed with saturated salt solution and dried over anhydrous sodium sulfate. Volatiles were removed in vacuo and the residue was dissolved in ether, filtered through a short cellulose column and the solvent was removed. Gas chromatography showed one major product and two minor ones. The major product was identified with $^1$H and $^{13}$C N.M.R. The minor ones were not identified.
Reactions of Transition Metals with Acetophenone

The following experiments are typical of those carried out in both the static and photochemical metal vapor reactors.

Reaction of Chromium and Acetophenone. Over a 60 minute period, 3.90 mmol of chromium was condensed with 0.100 mol of acetophenone at -196°C. After ending the reaction, the reactor was isolated from the vacuum system, warmed to room temperature with a tepid water bath so that the acetophenone would melt and vented with pre-purified argon. Then 25 ml of 10% sulfuric acid was added to dissolve the residual metal. The mixture was extracted with three 20 ml portions of ether. These were combined, washed with saturated salt solution and dried over anhydrous sodium sulfate. All volatiles were removed in vacuo and the residue was taken up in ether and filtered through a short cellulose column. The ether was stripped off to give white crystals, which \(^{1}\)H N.M.R. showed to be a dl-meso mixture of the pinacol.

Reaction of Nickel and Acetophenone with Photolysis. Over a 180 minute period, 1.49 mmol of nickel was condensed with 0.126 mol of acetophenone under photochemical conditions. After ending the experiment, the reactor was isolated from the vacuum system, the drum was emptied of liquid nitrogen and the system was pressurized to one half atmosphere with pre-purified argon. After five minutes the drum was washed down with anhydrous ether. The reactor was then fully
pressurized with argon, the collection flask was removed and the collected mixture was subjected to the work-up described above.
REFERENCES AND NOTES


2. Unless stated otherwise, yields for metal vapor experiments are based on metal vaporized.


4. Unpublished results provided by J. A. Gladysz.


6. The word "pinacol" is a common name for 2,3-dimethyl-2,3-butanol, which is the reductively coupled dimer of acetone. The word is also used as a generic term for this type of compound (α,β-diols).


12. O. Vogel, in Polyaldehydes, pp. 43 to 66.

13. See chapter one of this thesis, p. 9.

14. Peak areas are uncorrected.

15. Yields for the catalysis experiments are based on assuming a formula weight of 52 for the chromium powder.
and 55.8 for the iron powder. The stated yields are thus the lower limits of actual yields.

CHAPTER 4

REACTIONS OF TRANSITION METALS WITH ACETATE ESTERS

BACKGROUND

Of all the organic compounds that have been studied in metal vapor experiments, simple alkyl esters have apparently never been examined as substrates. The only examples found in the literature of any ester being used in such an experiment were those in which benzoic acid esters were cocondensed with chromium to give the expected sandwich compounds.\(^1\) The reason for this lack of interest in these compounds is probably very simple. Esters are considered to be fairly inert compounds which would not be expected to give rise to stable organometallic compounds. Yet at the same time, esters have enough functionalities that they would probably not be considered enough an "inert" solvent for the creation of active metal slurries.

It could be anticipated that esters would display a reactivity similar to acyl halides, since in a broad sense, the alkoxide group in an ester could be considered equivalent to a halide.
The reaction of acyl halides with transition metals has been studied by Klabunde and others. Cocondensation of acyl halides with nickel or palladium leads to a low yield (about 10%) oxidative insertion of the metal into the carbon-halogen bond.²,³ These divalent species tend to decompose far below room temperature, with the liberation of carbon monoxide. The palladium compounds are more thermally stable than the nickel; for example, the insertion compound with perfluorobutyric chloride is stable above -80°C.

The impetus for studying the effect of photolyzing a metal-alkyl ester deposit is that these organic compounds could undergo a photo-assisted metal insertion chemistry similar to that elucidated by matrix isolation spectroscopy for the reactions of transition metals with water and ethers. In a sense, an ester is an ether linkage with a carbonyl group next to it. The presence of this extra functionality -- the -(C=O)- group -- should heighten the stability of any metal-organic adduct formed upon deposition and increase the possibility that it could undergo a photo-reaction.
EXPERIMENTS USING A STATIC REACTOR

Ethyl acetate was used to make a survey of the reactivity of transition metal vapors with alkyl esters. Chromium, manganese, iron, and nickel were cocondensed with ethyl acetate in the static reactors with metal/organic molar ratios from 1/30 to 1/70. The reaction conditions and volatile products found are presented in Table 4-I. Except for nickel, only trace amounts of ethanol were occasionally seen in the recovered ester. Nickel gave small (about 10% each) yields of acetaldehyde and ethanol. The metallic residues formed in these reactions were hydrolyzed with dilute acid and the solution was immediately extracted with dibutyl ether in order to analyze for low boiling compounds. Trace quantities of low molecular weight hydrocarbons could be seen via G.C.-mass spectrometry in the ether, but no other compounds, except starting material, were seen that could be attributed to the reaction.

The small quantities of hydrocarbons seen in the ether used to extract the hydrolyzed solid could be expected as the result of "carbonaceous metal particles" in the residue similar to those found in the reaction of transition metals with alkanes or ethers.
TABLE 4-1  
REACTIONS OF TRANSITION METALS WITH ETHYL ACETATE:
STATIC METAL VAPOR REACTORS

<table>
<thead>
<tr>
<th>METAL mmol</th>
<th>EtOAc mol</th>
<th>RATIO</th>
<th>TIME min</th>
<th>PRODUCTS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ACETALDEHYDE</td>
</tr>
<tr>
<td>Cr-7.42</td>
<td>0.285</td>
<td>1/38</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>Mn-3.25</td>
<td>0.236</td>
<td>1/73</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>Fe-2.82</td>
<td>0.153</td>
<td>1/54</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>Ni-4.09</td>
<td>0.251</td>
<td>1/61</td>
<td>60</td>
<td>9 (0.38)</td>
</tr>
</tbody>
</table>

a) Percent yield based on mmol product/mmol metal vaporized.
The G.C. trace for the nickel-ethyl acetate reaction also showed the presence of ethylene. Repeated with a more careful analysis for volatile gases and a more exacting analysis of the solid, the experiment gave a 7% yield of acetaldehyde with no ethanol, along with a 28% yield of ethylene and a 17% yield of acetic acid. Small amounts of ethane and methane were also seen.

Cocondensing nickel and ethyl acetate with a high metal to organic deposition ratio (1/7) resulted in a 16% yield of acetic acid, but only trace amounts of acetaldehyde and ethanol. Gaseous products from this reaction were methane (>9%)\(^4\) and ethane (6%). Since attack by the residual metal on any initially formed products would be the greatest at high metal concentrations, this experiment indicates that methane and ethane are secondary products in this reaction.

These products can be rationalized as deriving from two divalent nickel intermediates formed by oxidative addition of nickel atoms into either of the ester's carbon-oxygen single bonds. Either intermediate could eliminate ethylene by an inter- or intramolecular process to form a metal hydride that would attack the acetyl-ethoxonickel species to form free aldehyde:

\[
\text{Ni} + \text{Et-O-C-Me} \xrightarrow{-196^\circ C} \text{Et-O-Ni-C-Me} + \text{Et-Ni(C-Me)}
\]
Elimination of aldehydes by acyl metal complexes in the presence of metal hydrides is well known. The acetic acid formed in this reaction arises from the decomposition of the oxidative insertion product formed by the insertion of nickel into the ethyl-oxygen bond of the ester. The ethanol formed in this reaction may arise from the decomposition of the acetyl-ethoxonickel species. However, some ethanol was the sole observed product in the reactions with other transition metals. This suggests that some, if not all, of the ethanol seen in the reaction of ethyl acetate with nickel may arise from some other reaction, common to other transition metals, in which the other fragment of the ester is not observed.

The exact mechanisms through which these oxidative additions occurred are not obvious from these experiments. Nickel also gives oxidative insertion products with acetyl halides. However, the insertion products eliminates carbon monoxide at low temperatures (< -100°C). To see if this elimination occurred with nickel and ethyl acetate, an experiment was done in which the nickel-ethyl acetate cocondensate was warmed to -78°C after deposition and kept at that temperature for one hour. The reactor was then
recooled to −196°C and the pressure in the system was measured. There was no (<1/2 mm Hg) pressure in the reactor, thus no permanent gases had been evolved during the warm-up period. The amount of acetaldehyde (9%) observed for this reaction was quite comparable to that seen in other nickel-ethyl acetate reactions. Thus the acetyl-ethoxonickel insertion product has a decomposition path — acetaldehyde elimination — occurring below −78°C; without this path the insertion product would eliminate carbon monoxide like the insertion products formed from acetyl halides.

**Experiments using the photochemical reactor**

Nickel was cocondensed with ethyl acetate under photolytic conditions in the photochemical reactor. Yields of acetaldehyde and ethanol for this reaction were similar to, although lower than, the yields found using a static metal vapor reactor. The lower yields of the photochemical reactor versus the static reactors reflects a trend seen for the metal-acetone work of the previous chapter and can be attributed to a smaller amount of vaporized metal actually encountering the reaction surface in the photochemical reactor than in the static reactors. Ethylene was seen in the product mix, but no special analysis was done to
ascertain its yield or the yield of acetic acid that the presence of ethylene would imply.

Iron was cocondensed with ethyl acetate under photochemical conditions using deposition ratios from 1/33 to 1/236 (metal/organic). Ethanol was observed in low yield (2%) at a deposition ratio of 1/33 and in trace (>1/2%) yields at higher ratios. At a deposition ratio of 1/236 a trace of acetaldehyde was seen in the recovered ethyl acetate via G.C./mass spectroscopy, but examination of the G.C. traces from this and the other iron-ethyl acetate experiments suggest that such trace amounts may be in other experiments as well and thus did not result from photolysis. The data for the reactions of both iron and nickel with ethyl acetate in the photochemical reactor are summarized in Table 4-II.

A series of experiments was then carried out to study the reactions of chromium and manganese with acetate esters under photochemical conditions. The reaction conditions and products of these experiments are presented in Table 4-III.

Chromium and ethyl acetate were cocondensed under photochemical conditions with metal/organic deposition ratios from 1/39 to 1/296. At a metal/organic ratio of 1/39, no volatile products were observed for the reaction. However, at a metal/organic ratio of 1/110, a 1/2% yield of acetaldehyde and a trace of ethanol were observed. In a series of experiments with progressively more dilute metal
### TABLE 4-II

**REACTIONS OF IRON AND NICKEL WITH ETHYL ACETATE**:

**PHOTOCHEMICAL REACTOR**

<table>
<thead>
<tr>
<th>METAL mmol</th>
<th>EtOAc mol</th>
<th>RATIO</th>
<th>TIME min</th>
<th>ACETALDEHYDE % (mmol)</th>
<th>ETHANOL % (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-6.45</td>
<td>0.211</td>
<td>1/33</td>
<td>180</td>
<td>-</td>
<td>2 (0.11)</td>
</tr>
<tr>
<td>Fe-1.93</td>
<td>0.207</td>
<td>1/107</td>
<td>180</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>Fe-1.71</td>
<td>0.403</td>
<td>1/236</td>
<td>180</td>
<td>b</td>
<td>trace</td>
</tr>
<tr>
<td>Ni-1.71</td>
<td>0.199</td>
<td>1/116</td>
<td>180</td>
<td>5 (0.09)</td>
<td>3 (0.05)</td>
</tr>
</tbody>
</table>

**a**) Percent yield based on mmol product/mmol metal vaporized.

**b**) Trace amounts of acetaldehyde were seen by G.C./mass spectroscopy.
TABLE 4-III

REACTIONS OF CHROMIUM AND MANGANESE WITH ACETATE ESTERS:

PHOTOCHEMICAL REACTOR

| METAL mmol | ORGANIC mol | RATIO | TIME min | PRODUCTS ACETALDEHYDE % (mmol) | OTHER |%
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>*Cr-1.30 MeOAc-0.272 1/209 180 -</td>
<td>MF 1.5 (0.02)</td>
<td>M trace</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*Cr-1.42 EtOAc-0.200 1/141 180 -</td>
<td>E 6 (0.09)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*Cr-1.62 PrOAc-0.230 1/142 180 -</td>
<td>P 2.5 (0.04)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr-2.38 MeOAc-0.247 1/104 180 2 (0.05)</td>
<td>MF trace</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr-0.73 MeOAc-0.269 1/367 180 30 (0.22)</td>
<td>M 10 (0.07)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>MF 4 (0.03)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr-5.27 EtOAc-0.205 1/39 180 -</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr-1.86 EtOAc-0.209 1/112 180 .5 (0.01)</td>
<td>E trace</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr-1.14 EtOAc-0.247 1/217 180 5 (0.06)</td>
<td>E trace</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr-0.79 EtOAc-0.210 1/266 180 7 (0.06)</td>
<td>E trace</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr-0.90 EtOAc-0.266 1/296 180 10 (0.09)</td>
<td>E 8 (0.07)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr-1.47 PrOAc-0.178 1/121 150 -</td>
<td>P 4 (0.06)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-3.56 EtOAc-0.198 1/56 180 -</td>
<td>E 3 (0.10)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn-0.29 EtOAc-0.256 1/882 180 28 (0.08)</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Reactions without photolysis are marked by *.
b) Percent yield based on mmol product/mmol metal vaporized.
c) E - ethanol, P - formaldehyde, M - methanol, MF - methyl formate, P - propene.
concentrations (1/217, 1/266, 1/296) larger yields of acetaldehyde were seen (5%, 7%, and 10%). A blank experiment was done (without photolysis) in the reactor using a deposition ratio of 1/141. Ethanol (6%), but no acetaldehyde, was observed.

Chromium was cocondensed with methyl acetate under photochemical conditions with a deposition ratio of 1/104. A 2% yield of acetaldehyde was observed along with trace yields of methyl formate and methanol. At a ratio of 1/367, a 30% yield of acetaldehyde, 10% yield of methanol, 4% yield of methyl formate and a trace of formaldehyde was produced. To determine which of these products were photochemically generated, a blank (without photolysis) experiment was done. At a deposition ratio of 1/209, the reaction of chromium and methyl acetate produced a 1.5% yield of methyl acetate and a trace of methanol. Again, no acetaldehyde was seen.

Chromium and n-propyl acetate were cocondensed with and without photolysis in the photochemical reactor. In both cases propene was the only observed product.

Manganese and ethyl acetate were also cocondensed under photochemical conditions. At a deposition ratio of 1/56 a three percent yield of ethanol was observed. At a ratio of 1/882, the reaction produced a 28% yield of acetaldehyde.

These data indicate that photolysis leads to an insertion of chromium or manganese atoms into the
carbon-oxygen single bond in the carboxyl group in the ester:

\[ M + R-O-C-CMe \rightarrow M-O-C-CMe \xrightarrow{h\nu} R-O-M-C-CMe \]

\[ M = Cr, Mn. \]

Furthermore, if the yields of acetaldehyde are compared for methyl, ethyl and propyl acetate for experiments with deposition ratios of about 1/100, then one finds that the yields increase in the order methyl > ethyl > propyl. Plotting (Figure 4-1) the yield of acetaldehyde versus moles of ester/moles of metal for the chromium experiments implies that the increase in the yield of this product is greater for methyl acetate than for ethyl acetate as the metal concentration is decreased.

This apparent dependence of photoreactivity upon the size of the alkoxyl group in the ester can have several explanations:

1. The photoreactivity of the metal-ester adduct may decrease as the size of the ester increases. This may be because as the size of the adduct grows larger, there are more non-chemical modes whereby the adduct can dump the energy it gained by absorbing a photon of light.

2. A larger ester molecule may not be able to stabilize the metal long enough or well enough to keep it from clustering before photolysis occurs. Such an inability for the larger esters to adduct to a metal atom as well as a smaller ester could be the result of either steric and/or inductive effects.
FIGURE 4-1

YIELD OF ACETALDEHYDE VS. DEPOSITION RATIO FOR THE REACTION
OF CHROMIUM AND ACETATE ESTERS WITH PHOTOLYSIS

% YIELD OF ACETALDEHYDE

- □ MeOAc
- ○ EtOAc
- △ PrOAc

ORGANIC/METAL DEPOSITION RATIO
The data obtained do not distinguish one explanation from another. However, an experiment was performed where the rotational speed of the drum was slowed to about 30 rpm. The yield of acetaldehyde was quite comparable to yields in those experiments with full rotational speed (acetaldehyde - 6% and ethanol - 5%, at a deposition ratio of 1/230). This experiment indicates the adduct that is initially formed is not rapidly decomposing and that it has a lifetime of at least one second.

Finally, the oxidative addition complex that is formed must have a decomposition path available to it that leads to the products observed in the reaction. For the reaction of ethyl acetate and chromium, the decomposition path used by nickel and ethyl acetate would also be available for this reaction. In fact, traces of ethylene are seen in this reaction for the higher dilution experiments. However, analyses for the total amounts of ethylene and the presence of acetic acid were not undertaken in the experiments done.

The decomposition path where a metal hydride is formed by the elimination of ethylene is, of course, not available in the chromium-methyl acetate reaction. One possible decomposition pathway for this reaction would be a $\beta$-hydride shift from the methoxyl group, which would then drop off as a formaldehyde group. The metal acetyl hydride would then decompose to free metal and acetaldehyde:
As this mechanism would predict, formaldehyde was found in the reaction mixture for chromium and methyl acetate.  

The chromium-methyl acetate reaction gave the largest absolute yield of a photochemically produced product — 0.21 mmol of acetaldehyde in a three hour reaction. If 2.5 moles of photons are emitted by the lamp per hour (Table 1-1), then the apparent quantum yield of this reaction is \( \sim 3 \times 10^{-5} \). However, if a quantum yield is defined as the number of product molecules produced per number of quanta absorbed by reactant molecules, then this apparent quantum yield is probably an extreme lower limit for the true quantum yield. Not only is the absorption spectrum of the photo-active metal-ester adduct unknown, but the concentration of this species in the deposition is also unknown. It is possible that the photo-active species has a very high quantum yield (\( \sim <1 \)) for undergoing an insertion reaction and the yield of acetaldehyde depends on the availability of this species, not the number of photons.
EXPERIMENTAL SECTION

All metals used were in the form of powders, except iron which was in the form of wire, and were from the following sources: chromium - ROC/RIC 99.9%, manganese - Fairmount 99.5%, iron - "Baker Analyzed" grade, nickel - ROC/RIC. Ethyl acetate obtained from Mallinckrodt (AR grade) and methyl acetate was obtained from Matheson, Coleman and Bell. Both esters were dried over Drierite, distilled from phosphorus pentoxide under pre-purified nitrogen and partially degassed by cooling to -78°C and pumping down to 50 microns before use. Final degassing was done on-line. Propyl acetate was prepared from n-propanol and acetic anhydride. The crude product was distilled using a 12-inch Vigreux column and washed first with concentrated sodium hydroxide, then with saturated salt water and finally twice with deionized water. The ester was dried over anhydrous magnesium sulfate, distilled from molecular sieves under prepurified nitrogen and degassed in the same manner as the other esters.

Gas chromatographic analysis was done using either the SE-30 column and mesitylene as an internal standard, or the Porapak QS column and benzene as an internal standard.
Reactions of Transition Metals with Ethyl Acetate: Static Reactors. Typically, in an hour 3 to 7 mmol of metal was cocondensed with 200 to 300 mmol of ethyl acetate at -196°C in a static metal vapor reactor. After the reaction, the reactor was isolated from the vacuum system and allowed to warm up to room temperature, while all volatiles were collected in a trap cooled to -196°C. The recovered ethyl acetate was analyzed by both gas chromatography and G.C.-mass spectrometry for volatile reaction products using added mesitylene as an internal standard.

Under a flow of argon about 15 to 25 ml of 4N sulfuric acid was added to the residues left in the reactor. The solution was immediately covered with with 10 to 20ml of dibutyl ether. After all the metal had dissolved, the ether was used to extract the aqueous phase. This phase was extracted twice more and the ether portions were combined and dried over anhydrous magnesium sulfate. The ether was analyzed by gas chromatography and G.C.-mass spectrometry for reaction products using added mesitylene as an internal standard.

Reactions of Nickel and Ethyl Acetate: Complete Analysis. In a 60 minute period, 5.43 mmol of nickel was cocondensed with 0.195 mol of ethyl acetate. After the reaction was finished the reactor was isolated from the vacuum system and warmed to room temperature while all volatile material was
condensed into a collection trap cooled to \(-196^\circ\)C. The reactor was then pressurized with pre-purified argon and the collection trap was removed.

The trap was placed on a vacuum line and cooled to \(-78^\circ\)C. Volatile materials were bulb-to-bulb distilled into a calibrated bulb cooled to \(-196^\circ\)C. The amount of gas collected was measured on a vacuum line and the percentage and identity of the species in the sample was found using the G.C. with the gas-density balance. The liquid sample was analyzed as before.

The residue in the reactor was dissolved with 25 ml of 2N sulfuric acid solution. This was continuously extracted with ether overnight. The organic phase was then dried over molecular sieves, filtered and the ether was stripped off. The residue was analyzed by \(^1\)H N.M.R. using mesitylene as an internal standard.

Found: Ethene - 1.53 mmol, acetaldehyde - 0.41 mmol, acetic acid - 0.938 mmol, ethane - 0.18 mmol, methane - 0.01 mmol.

Reactions of Transition Metals with Acetyl Esters: Photochemical Reactor. Typically, in a 180 minute period, about 1 to 6 mmol of metal was cocondensed with about 200 to 300 mmol of ester. After the reaction, the reactor was isolated from the vacuum system and pressurized with half an atmosphere of pre-purified nitrogen. The liquid nitrogen in
the drum was then removed with a stream of compressed air. After collecting the melted cocondensate, the flask was removed from the reactor and taken, under nitrogen, to a vacuum line where the volatile materials could be bulb-to-bulb distilled into another flask. The ester recovered was then examined by gas chromatography and G.C./mass spectroscopy for volatile products using mesitylene or benzene as an internal standard.
REFERENCES AND NOTES


4. a) J. Azran and M. Orchin, Organometallics 3, 197 (1984); and references within. b) D. Milstein, Organometallics 1, 1549 (1982).

5. Since methane has a significant vapor pressure at -196°C and much of the methane certainly escaped during work-up, the yields for methane in these experiments are a lower limit for the amount present.

6. It was found that the G.C. column used for some earlier analyses was inaccurate for measurement of very small amounts of ethanol. Since ethanol was a non-photochemically generated species and acetaldehyde was the product that appeared only in photochemical experiments for chromium and manganese, the dilution experiments that used the old column were not repeated.

7. The effect whereby increasing the size of the molecule using in making an adduct with a metal leads to a decrease in photoreactivity of the adduct has been seen with the reaction of iron atoms and alkanes in argon matrices. Z.H. Kafafi, R. H. Hauge, L. Fredin, W. E. Billups and J. L. Margrave, Chem. Commun., 1229 (1983).

8. Formaldehyde would certainly be unstable in the presence of the metallic residue in the system, so most of it could have decomposed before the volatile material in the reaction was collected.

9. One such reaction would be the metal cluster-solvent reaction described in chapter one. Some ethanol may escape this metathesis reaction before its carbon structure is incorporated into the metallic material. The acetyl group would not survive intact long enough to undergo aldehyde elimination.
CHAPTER 5

CONCLUSIONS AND FUTURE WORK

The experiments reported in this thesis show that a macroscale metal vapor experiment with photolysis during deposition can lead to new chemical reactions. Photolytically induced oxidative insertion\textsuperscript{1} and electron transfer\textsuperscript{2} have previously been observed for metal atoms in low temperature matrices at Rice and elsewhere. Now, this same type of chemistry can be done on a synthetically useful scale as well.

The data obtained for the reaction of chromium with acetate esters indicate that the photoreactivity observed decreases as the size of the ester increases. The nature of this decrease requires further study for elucidation of its cause. Furthermore, more studies are required to see if this reduction in photoreactivity for larger molecules is a general trend for most reactions. If it is, then this could be a serious limitation on the scope of this new technique.
The photochemical reactor described in this thesis had a time lag of about 0.3 seconds between the deposition of the reactants and their photolysis. Photolysis of a reaction during the deposition of the reactants might be more efficient. At a temperature of -196°C metal atom clustering is considered to be nearly instantaneous if the metal atoms are not stabilized by surrounding ligands. By photolyzing during the deposition itself, there would be a greater possibility of inducing a metal atom to react with a weakly binding substrate before it had a chance to cluster.

The photochemical reactor was designed so that the photolysis well was protected from metal over-coating by the furnace. Any metal atom reactor that would be designed for photolyzing a metal vapor reaction system during the deposition of the reactants would also have to incorporate features that prevent such over-coating. One possible design is shown in Figure 5-1. The figure presents the top view of a proposed photochemical reactor which has two photolysis wells placed behind the mouth of the furnace. This arrangement should protect the photolysis wells from metal contamination yet still give direct photolysis on the deposition surface.

This proposed reactor could be used for further studies of the reactions which have been described here. If the decrease in photoreactivity in the acetate ester reaction was due to an inability of the larger ester to stabilize a
FIGURE 5-1

TOP VIEW OF A SIMULTANEOUS PHOTOLYSIS-DEPOSITION METAL VAPOR REACTOR
metal atom, then a direct photolysis reactor may allow any size ester to undergo this reaction at higher metal concentrations than was possible for the time-lagged reactor.

Another important experiment that should be attempted with a photochemical reactor is to trap the oxidative insertion product that forms in the ester reactions by adding stabilizing ligands. Acyl metal complexes are important intermediates in many industrial processes. By careful selection of additional ligands, new acyl complexes could possibly be isolated. Furthermore, isolation of a mono-metal complex would be definitive proof of the involvement of a metal atom in this reaction.

Finally, a great number of photolytically induced reactions have been observed in matrices. Much of that chemistry has been considered by many people to be mere exotica and not "real". The application of photolysis to metal vapor synthesis has the potential to make many of those reactions very "real" and produce interesting new chemical species for practical utilization.
REFERENCES AND NOTES

1. Chapter one of this thesis, pp. 13 to 14.


3. There has been a notable tendency for workers in the area of alkane activation by metal complexes to not cite the work of Margrave and et al. on the insertion of metal atoms into alkanes in low temperature matrices. As an example see: R. G. Bergman, Science, 222, 902 (1984).