

HOMOGENEOUS CATALYTIC HYDROGENATION STUDIES USING

TRANSITION METAL COMPLEXES

A thesis submitted by

ROMEU J. DARODA, B.SC., M.SC.

for the

DEGREE OF DOCTOR OF PHILOSOPHY,

UNIVERSITY OF LONDON.

Chemistry Department,
Imperial College of Science and Technology,
London, SW7 2AY.

July, 1980.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	3
ABSTRACT	5
ABBREVIATIONS	6
CHAPTER I	
Introduction	7
CHAPTER II	
The Catalytic Homogeneous Hydrogenation of Carbon Monoxide Using Transition Metal Carbonyl Catalysts: Results and Explanatory Discussion.	18
CHAPTER III	
The Nature of the Catalytic Species and the Role of the Solvent.	49
CHAPTER IV	
The Mechanism of the Homogeneous Hydrogenation of Carbon Monoxide.	72
EXPERIMENTAL SECTION	97
FIGURES (Infrared Spectra)	115
APPENDIX 1	134
REFERENCES	135

ACKNOWLEDGEMENTS

I would like to express my gratitude to Professor Sir Geoffrey Wilkinson for his continuous encouragement and enthusiasm throughout the period this work was developed, and for teaching me a real view of the organometallic and catalysis chemistry. I would also like to thank all my colleagues for their friendship and helpful advice. In particular, I am grateful to Dr. J.R. Blackborow for his encouragement and helpful discussions and Dr. Michael Hursthouse for his help in solving crystallographic problems.

Maira is thanked for typing and helping prepare this thesis and, many thanks to Colin Robinson, Roger Lincoln, Sue Johnson for their technical help. I would also like to acknowledge C.A.P.E.S. (Coordenação de Aperfeiçoamento do Pessoal de Nível Superior, for financial support) and Universidade Federal de Santa Maria (RS - Brasil) for this opportunity.

For MARCIA and ROMEUZINHO
~~~~~

## ABSTRACT

This thesis describes the homogeneous catalytic hydrogenation of carbon monoxide at syn-gas pressures below 200 atmospheres and temperatures below 200°C, using chromium, manganese, iron, cobalt, ruthenium, rhodium and osmium carbonyls as catalyst precursors.

Four main points are outlined in this work:

1. The change in the selectivity of the reduction products on changing the solvent, temperature and CO:H<sub>2</sub> ratios;
2. The reaction of the solvent (breakdown or build up) accompanying the products' formation ;
3. The isolation of the catalysts from the reaction mixtures with their identification by spectroscopic evidences;
4. The mechanistic studies of the main catalytic reactions supported by the information obtained from the isolated catalysts and organic products formed in the catalytic reactions as well as the bench experiments.

Identification of Symbols used in the Graphs.

|   |                                                                          |                      |
|---|--------------------------------------------------------------------------|----------------------|
| ◇ | $\text{CH}_3\text{CHO}$                                                  | Acetaldehyde         |
| ● | $\text{CH}_3\text{CH}_2\text{OH}$                                        | Ethanol              |
| ○ | $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_3$                        | Diethylether         |
| ▲ | $\text{CH}_3\text{COCH}_3$                                               | Acetone              |
| △ | $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}, \text{CH}_3\text{CHOHCH}_3$ | n- and iso-propanol  |
| □ | $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$                            | Methoxyethanol       |
| + | $\text{CH}_3\text{OH}$                                                   | Methanol             |
| * | $\text{HCOOCH}_2\text{CH}_3$                                             | Ethylformate         |
| ■ | $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$     | Methyldigol          |
| █ | $\text{C}_n\text{H}_{2n+2}$                                              | Paraffin             |
| ▽ | $\text{HCOOCH}_2\text{CH}_2\text{OH}$                                    | Hydroxyethyl formate |

# CHAPTER I

## INTRODUCTION

### HOMOGENEOUS HYDROGENATION

The pioneering work of Halpern<sup>1</sup> and others<sup>2,3</sup> on the homogeneous activation of molecular hydrogen on transition metal centres has led to a full and varied chemistry of homogeneous catalytic hydrogenation. The catalysts are usually solutions of Group VIII transition metal complexes. Rhodium and cobalt complexes are particularly useful and their chemistry well studied.

Interest in homogeneous hydrogenation has been mainly directed toward unsaturated hydrocarbons and their derivatives<sup>4</sup> but recently there has been a growing need to hydrogenate carbon monoxide to provide fuels and chemical feedstocks. This can be accomplished heterogeneously but is not generally a selective process for products containing more than one carbon atom.

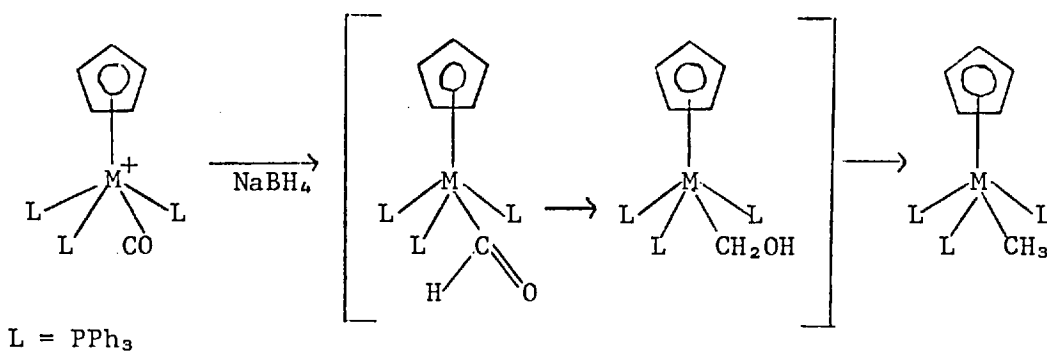
Reasonably selective homogeneous hydrogenation of carbon monoxide may be accomplished at very high pressures and temperatures using derivatives of ruthenium<sup>5</sup> or rhodium<sup>6</sup> carbonyls. The ruthenium catalyst produces methanol and methylformate and the rhodium catalyst produces methanol and poly-alcohols, including ethylene glycol, a basic chemical feedstock. Unfortunately, neither process is industrially acceptable at the moment, because the rates of reaction are too slow. The mechanism of hydrogenation in these systems is not known.

### Stoichiometric Carbon Monoxide Hydrogenation.

It has been believed that the activation of carbon monoxide and its subsequent hydrogenation may be best achieved by using polar complexes as catalysts. Thus, hydrogenation of metal carbonyl cations or carbonylation of metal hydride cations are of possible interest in catalytic studies. The carbonylation or hydrogenation of hydrogen or carbon monoxide bound to neutral electropositive metal centres, e.g., zirconium(II), has also been thought worthy of study.

There are several precedents for the viability of these ideas in stoichiometric reactions.

The hydrogenation of molybdenum carbonyl cations<sup>7</sup> with borohydride anions results in the hydrogenation of bound carbon monoxide to a methyl group.



L = PPh<sub>3</sub>

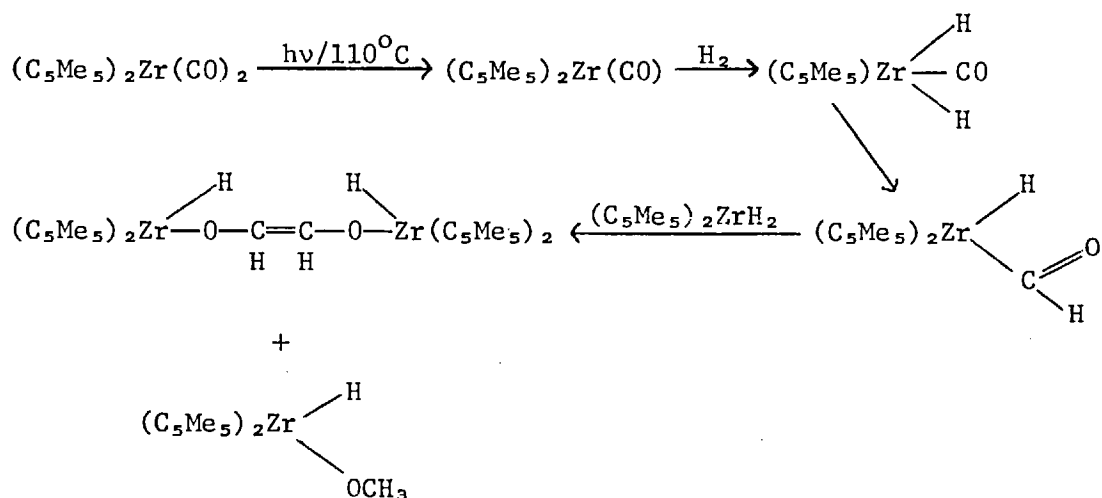
M = Mo, W

Scheme 1

(from Treichel and Shubkin<sup>7</sup>)

Bercaw<sup>8</sup> has shown that hydrogenation of bis-penta-methylcyclopentadienyl zirconium carbonyl produces complexes containing both one and two hydrogenated carbon monoxide molecules.



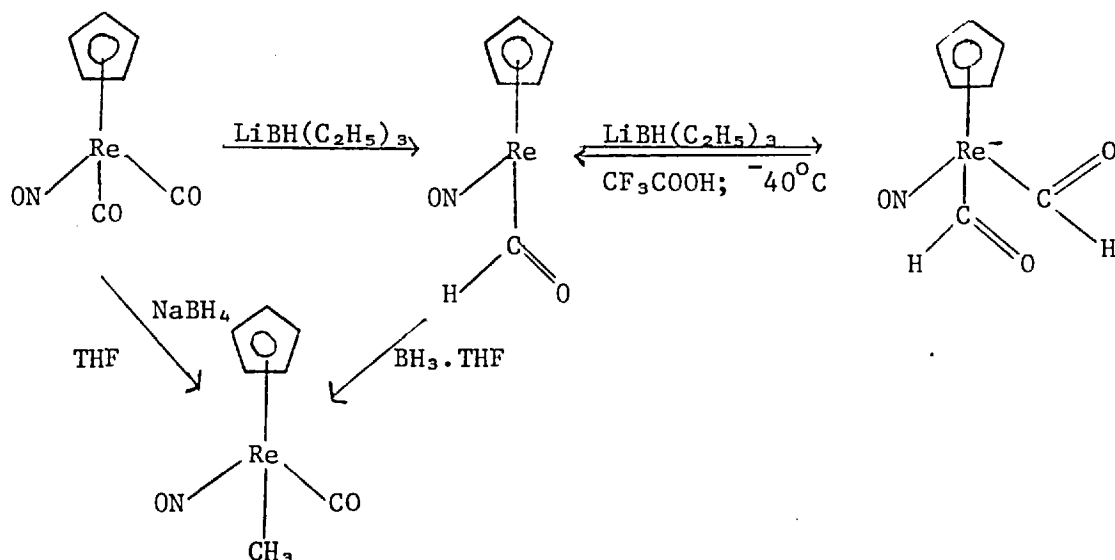


Scheme 2

(J.E. Bercaw, et al.<sup>8</sup>)

Similarly Schwartz<sup>9</sup> has been able to hydrogenate catalytically carbon monoxide bound to zirconium(II) complexes, with an acid metal hydride. The metal hydride is consumed and cannot be regenerated with molecular hydrogen. (See Scheme 3).

Manganese and rhenium carbonyls and their derivatives<sup>10a,b</sup> may be hydrogenated with hydride anions to yield formyl derivatives

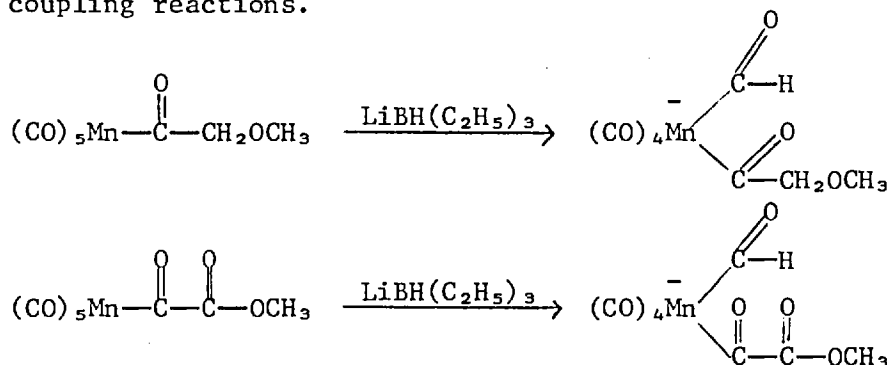


Scheme 4

(J.A. Gladysz, et al.<sup>10c</sup>)



There are few examples of stoichiometric hydrogenation reactions of bound carbon monoxide which have not been proposed to involve some sort of formyl intermediate. Particularly interesting is the observation that acyl metal carbonyl derivatives react with anionic hydrogenation reagents to yield formyl-acyl metal derivatives. The  $\pi$ -bonded carbon monoxide is therefore more reactive to hydrogenation than the  $\sigma$ -bonded carbon monoxide in the acyl group. This is the result expected for a normal base attack on a metal carbonyl derivative, and provides a route for the activation of two carbon monoxide molecules on the same metal centre which may be a step in carbon-carbon coupling reactions.



Scheme 5

(J.A. Gladysz, et al.<sup>10b</sup>)

### Homogeneous Catalytic Carbon Monoxide Hydrogenation

The catalytic hydrogenation of carbon monoxide to methanol and methyl formate with molecular hydrogen occurs with a ruthenium carbonyl catalyst<sup>5</sup> in tetrahydrofuran solution. High pressure infrared spectroscopy shows the presence of  $\text{Ru}(\text{CO})_5$  in the reactive solution and is the only detectable metal entity present. The ratio  $\text{CO}:\text{H}_2$  is

critical in determining rate and selectivity; added phosphine increases the ratio methanol: methylformate. A typical conversion rate constant for this reactions is  $8.5 \times 10^{-3}$  mole CO/gm mol Ru/sec. at 1300 atmospheres pressure in a CO/H<sub>2</sub> gas mixture of 40/60.

In contrast to this apparent monometallic catalyst, the production of poly-alcohols and methanol from Syn-gas using a rhodium carbonyl catalyst is believed to occur via a carbonyl cluster anion,<sup>6</sup> Rh<sub>12</sub>CO<sub>30</sub><sup>-</sup>. The role of the cation is important; the best appears to be caesium. Pressures of the order of 1000 atmospheres are required to produce a conversion rate of industrial interest.

#### Heterogeneous Catalytic Carbon Monoxide Hydrogenation

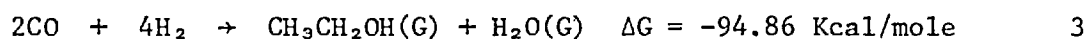
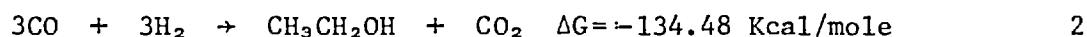
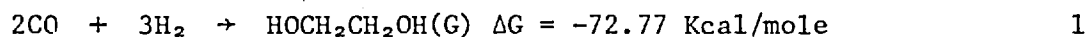
Carbon monoxide and hydrogen react readily under mild conditions over metal oxide coated surfaces of Keizelgel or Alumina to yield a series of hydrocarbons, alcohols, esters and acids. This series of reactions has become known as the Fischer-Tropsch synthesis.<sup>11</sup> The mechanism of this reaction is not known, but the essential role played by oxygen in the support and the acidity of the support has always been noted. Alkali metal or actinide metal cation activators are also important.

The metals used in the Fischer-Tropsch synthesis are usually iron, cobalt or ruthenium; iron is preferred for technical reasons. The main commercial use of the Fischer-Tropsch synthesis is the SASOL-1 plant worked in South Africa. This operates at 25 atmospheres syn-gas pressure and 220°C and produces 32% gasoline, 21% diesel and 47% higher paraffins; alcohols are not major products.<sup>12</sup>

### Thermodynamics of Carbon Monoxide Reduction

The thermodynamic parameters of the products of hydrogenation of carbon monoxide to yield mono- and bi-carbon containing compounds are given in Table I.1. It is clear that, from a thermodynamic point of view, certain products can be more easily synthesised than others. Alcohols, polyols and hydrocarbons are more easily produced than olefins, acetylenes, etc.

It should be noted that the formation of glyoxal, glycol aldehyde and ethylene glycol are amongst the most favoured processes thermodynamically. The glycols can be derived from coupling of two carbon monoxide molecules without loss of oxygen which is much less wasteful in terms of carbon monoxide or hydrogen than the formation of ethanol, or acetaldehyde which requires an extra carbon monoxide or hydrogen molecule to reductively extract oxygen. (Equations I-1,2,3)



### The Carbon Monoxide Activation Process

One of the key steps in the formation of C-2 hydrogenation products from syn-gas, (products which are the most desirable industrially) is the coupling of two carbon monoxide molecules by their carbon atoms. This can be accomplished in two ways, (Equations I-4,5).

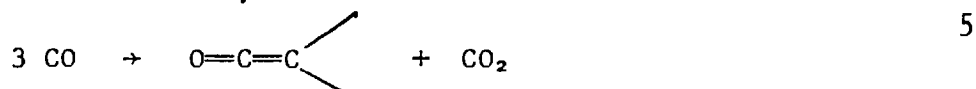


Table I.1 . Thermodynamic data for some Molecules Involved in CO

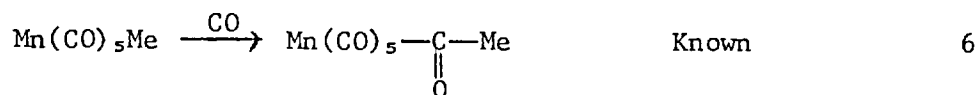
Hydrogenation Reactions.<sup>a</sup>

| Molecule                                                                             | $\Delta H_f^\circ$<br>(Kcal/mole) | $\Delta G_f^\circ$<br>(Kcal/mole) | $S^\circ$<br>(cal/mole <sup>o</sup> K) |
|--------------------------------------------------------------------------------------|-----------------------------------|-----------------------------------|----------------------------------------|
| CO                                                                                   | -26.42                            | -32.81                            | 47.30                                  |
| CO <sub>2</sub>                                                                      | -94.05                            | -94.26                            | 51.07                                  |
| H <sub>2</sub> O                                                                     | -57.80                            | -54.64                            | 45.11                                  |
| CH <sub>4</sub>                                                                      | -17.89                            | -12.15                            | 44.52                                  |
| HCHO                                                                                 | -27.70                            | -26.27                            | 52.29                                  |
| CH <sub>3</sub> OH                                                                   | -57.02                            | -39.73                            | 30.3                                   |
| CH <sub>3</sub> OCH <sub>3</sub>                                                     | -43.99                            | -26.99                            | 63.83                                  |
| CH <sub>3</sub> OCHO                                                                 | -83.6                             | -17.03                            | 72.0                                   |
| C <sub>2</sub> H <sub>2</sub>                                                        | 54.19                             | 50.00                             | 48.00                                  |
| C <sub>2</sub> H <sub>2</sub> O (Ketene)                                             | -14.60                            | -14.41                            | 57.79                                  |
| OHCCHO                                                                               | -83.7                             |                                   |                                        |
| C <sub>2</sub> H <sub>4</sub>                                                        | 12.50                             | 16.28                             | 52.45                                  |
| CH <sub>3</sub> CHO                                                                  | -39.76                            | -31.86                            | 63.15                                  |
| CH <sub>2</sub> CH <sub>2</sub> O                                                    | -18.5                             | -2.73                             | 36.76                                  |
| C <sub>2</sub> H <sub>6</sub>                                                        | -20.24                            | -7.87                             | 54.85                                  |
| CH <sub>3</sub> CH <sub>2</sub> OH                                                   | -66.20                            | -41.62                            | 38.40                                  |
| HOCH <sub>2</sub> HOCH <sub>2</sub> (l)                                              | -108.73                           | -77.29                            | 39.9                                   |
| C <sub>3</sub> H <sub>4</sub>                                                        | 44.32                             | 46.47                             | 59.30                                  |
| CH <sub>3</sub> COCHO                                                                | -73.9                             |                                   |                                        |
| C <sub>3</sub> H <sub>6</sub>                                                        | 4.88                              | 14.99                             | 63.80                                  |
| CH <sub>3</sub> COCH <sub>3</sub>                                                    | -52.00                            | -36.58                            | 70.49                                  |
| C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> (1,3-dioxolane)                         | -80.7                             |                                   |                                        |
| CH <sub>3</sub> CH <sub>2</sub> OCHO                                                 | -88.74                            |                                   |                                        |
| C <sub>3</sub> H <sub>8</sub>                                                        | -24.82                            | -5.61                             | 64.51                                  |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH (l)                               | -72.79                            | -40.79                            | 46.1                                   |
| CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OH (l)                              | -114.8                            |                                   |                                        |
| CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH | -160.8                            |                                   |                                        |
| HOCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH                | -149.7                            |                                   |                                        |

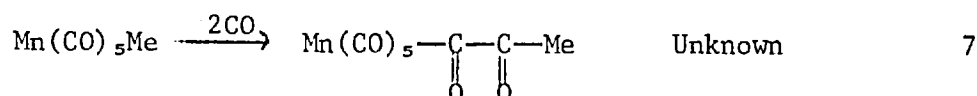
<sup>a</sup> Data obtained from "The Chemical Thermodynamics of Organic Compounds"; Daniel R. Stull, Edgar F. Westrum, Jr., and Gerard C. Sinke; John Wiley, New York, 1969.

The first process may be conceived as a double carbon monoxide insertion reaction and as such is little known under ambient pressures and temperatures. (Equations I-6,7).

#### Acylation

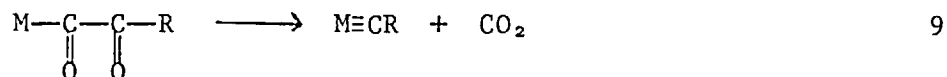
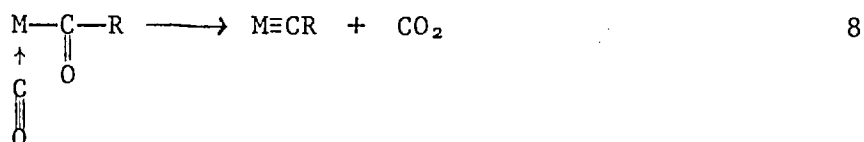


#### Double Acylation

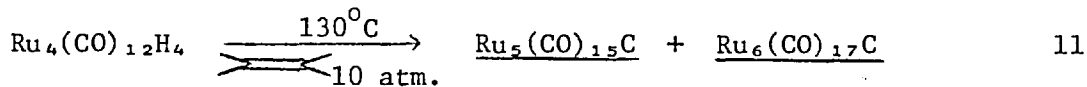
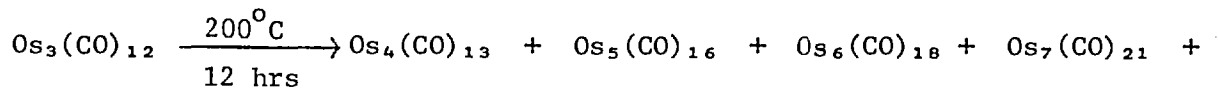


It is of great importance to note that the only stable transition metal complexes containing two adjacent ketonic carbon monoxide groups contain alkoxide substituents<sup>10b</sup>;  $(\text{CO})_5\text{Mn}-\overset{\text{O}}{\text{C}}-\overset{\text{O}}{\text{C}}-\text{OMe}$ ,  $\text{Cp}(\text{CO})_3\text{Mo}-\overset{\text{O}}{\text{C}}-\overset{\text{O}}{\text{C}}-\text{OMe}$  are two examples.

The second carbon monoxide coupling process can be conceived as a decarboxylation which may or may not involve a double carbon monoxide insertion reaction: (Equations I-8,9).



Again, there are few examples of such processes under ambient conditions, although the thermolysis of certain metal carbonyl clusters<sup>13</sup> to yield carbido-centred metal carbonyl clusters and carbon dioxide may be a reaction of this type: (Equations I-10,11).



Carbon chains of any length may be formed by repeated carbon monoxide insertion-reductive hydrogenation or by repeated insertion - decarboxylation - reductive hydrogenation.

#### Secondary Hydrogenation

Secondary hydrogenation may be defined as the hydrogenation of the activated carbon monoxide complex leading to the final hydrogenated products. Primary hydrogenation would be, for example, the conversion of a metal carbonyl to a formyl which involves the carbon monoxide activation process as well.

Secondary hydrogenation has been assumed to be a relatively facile process; this assumption is based on the relatively facile and speedy hydrogenation of unsaturated organic molecules bound to transition metal centres.

Hydroformylation with rhodium and cobalt, olefin hydrogenation with ruthenium, rhodium, cobalt, platinum, palladium, and iron, and selective ketone reduction with certain rhodium compounds can be cited as examples.



The facile reversibility of transition metal hydrogenation would imply the existence of a facile oxidative addition - reductive elimination process for hydrogen and thus, a metal with a suitable redox equilibrium  $M^n \rightleftharpoons M^{n+2}$ . The metals to the left of the periodic table, although possessing suitable redox potentials of this type are in general very electropositive and the strength of the metal oxygen bond is so high that reduced products of carbon monoxide containing oxygen remain bound to the metal centre and effectively block catalytic activity; strong acids are required to break such metal oxygen bonds and would probably produce secondary acid catalysis in reactions between the reduction products. Such systems may therefore, not be very useful in carbon monoxide hydrogenation, and our studies are limited to transition metal catalysts of Groups VI, VII and VIII.

## CHAPTER II

### THE CATALYTIC HOMOGENEOUS HYDROGENATION OF CARBON MONOXIDE USING TRANSITION METAL CARBONYL CATALYSTS: RESULTS AND EXPLANATORY DISCUSSION.

#### (i) Stoichiometric Reactions of Transition Metal Hydride Cations with Transition Metal Carbonyl Anions.

Hydride cations of tungsten and molybdenum<sup>14</sup> react with carbonyl anions of rhodium and cobalt under syn-gas pressure to yield detectable quantities of ethylene glycol (Table II-1). No catalytic activity was observed under various conditions of pressure, temperature and solvent. An accompanying side reaction was the decomposition of the methyl diphenylphosphine substituted metal hydride cation to yield benzene, no organometallic decomposition product could be identified.

The mechanism of such reactions remains obscure, nevertheless, these reactions yield the first isolable oxygen-containing hydrogenation products of two coupled carbon monoxide molecules, under ambient conditions of temperature and pressure.

The decomposition of the phosphine was unfortunate and other complexes, for example, bipyridyl hexadiene cationic complexes of rhodium<sup>15</sup> (which are known to give hydride cations under hydrogen pressure) and the bis-cyclopentadienyl tungsten and molybdenum trihydride cations,<sup>16</sup> in the presence of rhodium carbonyl anions and syn-gas were totally inactive in producing carbon monoxide reduction products.

Table II.1. Conditions and Products Obtained in the Reactions with Molybdenum and Tungsten Phosphine Hydride Cations and Rhodium and Cobalt Carbonyl Anions.

| Complexes                                                                          |                                                                                  | Solvent <sup>d</sup>               | Reaction Time (hrs) | Pressure <sup>e</sup> CO/H <sub>2</sub> (atm) (1:1) | Temp. °C <sup>e</sup> | Organic Products                     |                                      |                               |
|------------------------------------------------------------------------------------|----------------------------------------------------------------------------------|------------------------------------|---------------------|-----------------------------------------------------|-----------------------|--------------------------------------|--------------------------------------|-------------------------------|
| Metal Hydride Cation                                                               | Metal Carbonyl Anion                                                             |                                    |                     |                                                     |                       |                                      |                                      |                               |
| [MoH <sub>3</sub> (PMePh <sub>2</sub> ) <sub>3</sub> ]BF <sub>4</sub> <sup>a</sup> | [Rh <sub>12</sub> (CO) <sub>30</sub> ]Na <sub>2</sub> <sup>b</sup>               | THF                                | 12                  | 20                                                  | 150                   | CH <sub>2</sub> OHCH <sub>2</sub> OH | C <sub>6</sub> H <sub>6</sub>        |                               |
|                                                                                    |                                                                                  |                                    | 24                  | 20                                                  | 150                   | CH <sub>2</sub> OHCH <sub>2</sub> OH | C <sub>6</sub> H <sub>6</sub>        |                               |
|                                                                                    |                                                                                  |                                    | 48                  | 20                                                  | 150                   |                                      | C <sub>6</sub> H <sub>6</sub>        |                               |
|                                                                                    |                                                                                  | GLYME                              | 6                   | 20                                                  | 150                   | CH <sub>2</sub> OHCH <sub>2</sub> OH | C <sub>6</sub> H <sub>6</sub>        |                               |
|                                                                                    |                                                                                  |                                    | 12                  | 20                                                  | 150                   |                                      | C <sub>6</sub> H <sub>6</sub>        |                               |
|                                                                                    |                                                                                  |                                    | 6                   | 80                                                  | 180                   |                                      | C <sub>6</sub> H <sub>6</sub>        |                               |
|                                                                                    |                                                                                  | DIGLYME                            | 6                   | 20                                                  | 150                   |                                      | C <sub>6</sub> H <sub>6</sub>        |                               |
|                                                                                    |                                                                                  |                                    | 6                   | 100                                                 | 150                   |                                      | C <sub>6</sub> H <sub>6</sub>        |                               |
|                                                                                    |                                                                                  |                                    | 24                  | 20                                                  | 150                   |                                      | C <sub>6</sub> H <sub>6</sub>        |                               |
|                                                                                    | [W <sub>5</sub> (PMePh <sub>2</sub> ) <sub>4</sub> ]BF <sub>4</sub> <sup>a</sup> | NaCo(CO) <sub>4</sub> <sup>c</sup> | THF                 | 12                                                  | 50                    | 150                                  | CH <sub>2</sub> OHCH <sub>2</sub> OH | C <sub>6</sub> H <sub>6</sub> |
|                                                                                    |                                                                                  |                                    |                     | 12                                                  | 100                   | 150                                  | CH <sub>2</sub> OHCH <sub>2</sub> OH | C <sub>6</sub> H <sub>6</sub> |
|                                                                                    |                                                                                  |                                    | GLYME               | 6                                                   | 50                    |                                      |                                      | C <sub>6</sub> H <sub>6</sub> |
| [Rh <sub>12</sub> (CO) <sub>30</sub> ]Na <sub>2</sub>                              |                                                                                  |                                    | THF                 | 12                                                  | 6                     | 80                                   | CH <sub>2</sub> OHCH <sub>2</sub> OH | C <sub>6</sub> H <sub>6</sub> |
|                                                                                    |                                                                                  |                                    |                     | 24                                                  | 6                     | 80                                   |                                      | C <sub>6</sub> H <sub>6</sub> |
|                                                                                    |                                                                                  |                                    | DIGLYME             | 12                                                  | 50                    | 80                                   | CH <sub>2</sub> OHCH <sub>2</sub> OH | C <sub>6</sub> H <sub>6</sub> |
|                                                                                    |                                                                                  | 12                                 |                     | 50                                                  | 150                   |                                      | C <sub>6</sub> H <sub>6</sub>        |                               |
| NaCo(CO) <sub>4</sub>                                                              |                                                                                  | THF                                | 12                  | 6                                                   | 80                    | CH <sub>2</sub> OHCH <sub>2</sub> OH | C <sub>6</sub> H <sub>6</sub>        |                               |
|                                                                                    |                                                                                  |                                    | 12                  | 50                                                  | 150                   | CH <sub>2</sub> OHCH <sub>2</sub> OH | C <sub>6</sub> H <sub>6</sub>        |                               |
|                                                                                    |                                                                                  | DIGLYME                            | 12                  | 50                                                  | 80                    |                                      | C <sub>6</sub> H <sub>6</sub>        |                               |
|                                                                                    |                                                                                  |                                    | 12                  | 50                                                  | 80                    |                                      | C <sub>6</sub> H <sub>6</sub>        |                               |

Footnotes to Table II.1

- a) E. Carmona-Guzman and G. Wilkinson, J.C.S. Dalton, 1977, 1716;
- b) P. Chini and S. Martinengo, Inorg. Chim. Acta, 3, 299 (1969);
- c) Prepared from  $\text{Co}_2(\text{CO})_8$  and  $\text{Na}(\text{Hg})$  in THF;
- d) Other solvents were used, e.g., benzene, toluene, dioxane, monoethers, without result.
- e) Pressures were tested from 1 to 100 atm. and temperatures from  $25^\circ\text{C}$  to  $200^\circ\text{C}$ . These are the best conditions found.

The production of ethylene glycol stimulated our interest in the investigation of a mixed rhodium carbonyl-cobalt carbonyl-syn-gas system which might yield an active anion ( $\text{Rh}_5\text{CO}_{15}^-$ ) and an active cation  $\text{H}^+$  (from  $\text{HCoCO}_4$ ).

(ii) The Catalytic Hydrogenation of Carbon Monoxide Using Mixed Neutral Carbonyls of Rhodium and Cobalt.

The Union Carbide Corporation have a process to make polyalcohols from syn-gas which is believed to involve, under the best conditions, a catalyst consisting of a cesium cation and a  $\text{Rh}_5\text{CO}_{15}^-$  anion.<sup>17</sup> Our assumption was that this process may be speeded up by the presence of an acidic metal hydride such as  $\text{HCo}(\text{CO})_4$ , acting as a hydrogenation agent, and also yielding an active cation ( $\text{H}^+$ ). Consequently,  $\text{Rh}_4\text{CO}_{12}$  and  $\text{Co}_2(\text{CO})_8$  were mixed in THF and the mixture pressurised under syn-gas (80 atm), at 200°C. Ethanol and polyalcohols were produced. The organometallic product obtained from the reaction was found to be  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ <sup>18</sup> when the initial metal molar ratio used was unity. The solvent diglyme augmented the rate of hydrogenation and the major organic products were found to be ethanol and acetone: similarly,  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  was isolated after the reaction, for a metal molar ratio of unity. The variation of the molar ratio changed the composition of the reduction products (Table II-2): in cobalt-rich systems no organometallic product could be isolated but the presence of  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  and  $\text{Co}_3\text{Rh}(\text{CO})_{12}$  was suspected from infrared evidence.

Table II-2. Organic Product Yields (%) as a Function of Co:Rh Ratios.<sup>a</sup>

| Product      | Rhodium-rich |     |     | Cobalt-rich |     |      |      |
|--------------|--------------|-----|-----|-------------|-----|------|------|
|              | 1:5          | 1:2 | 1:1 | 2:1         | 5:1 | 10:1 | 50:1 |
| Ethanol      | 70           | 60  | 40  | 60          | 65  | 68   | 75   |
| Acetone      | 1            | 2   | 40  | 7           | 2   | 2    | 3    |
| Diethylether | 11           | 7   | 4   | 5           | 6   | 7    | 1    |
| n-Propanol   | 4            | 5   | 2   | 10          | 10  | 8    | 4    |

Note: at ratios exceeding 5Rh:1Co, rhodium precipitated as  $\text{Rh}_6(\text{CO})_{16}$ .

<sup>a</sup> Reactions conditions:  $\text{Co}_2(\text{CO})_8 + \text{Rh}_4(\text{CO})_{12}$  total weight 0.2 g;  
 10 ml of diglyme; 25 ml stainless-steel bomb; 80 atm.,  $\text{CO}/\text{H}_2$   
 (1:1); 200°C; 24 hours cycle: cold → hot → cold.

In rhodium-rich systems insoluble  $\text{Rh}_6(\text{CO})_{18}$  was isolated along with a yellow solution of cobalt containing diglyme. The rate of reaction increased with the cobalt content of the catalyst.

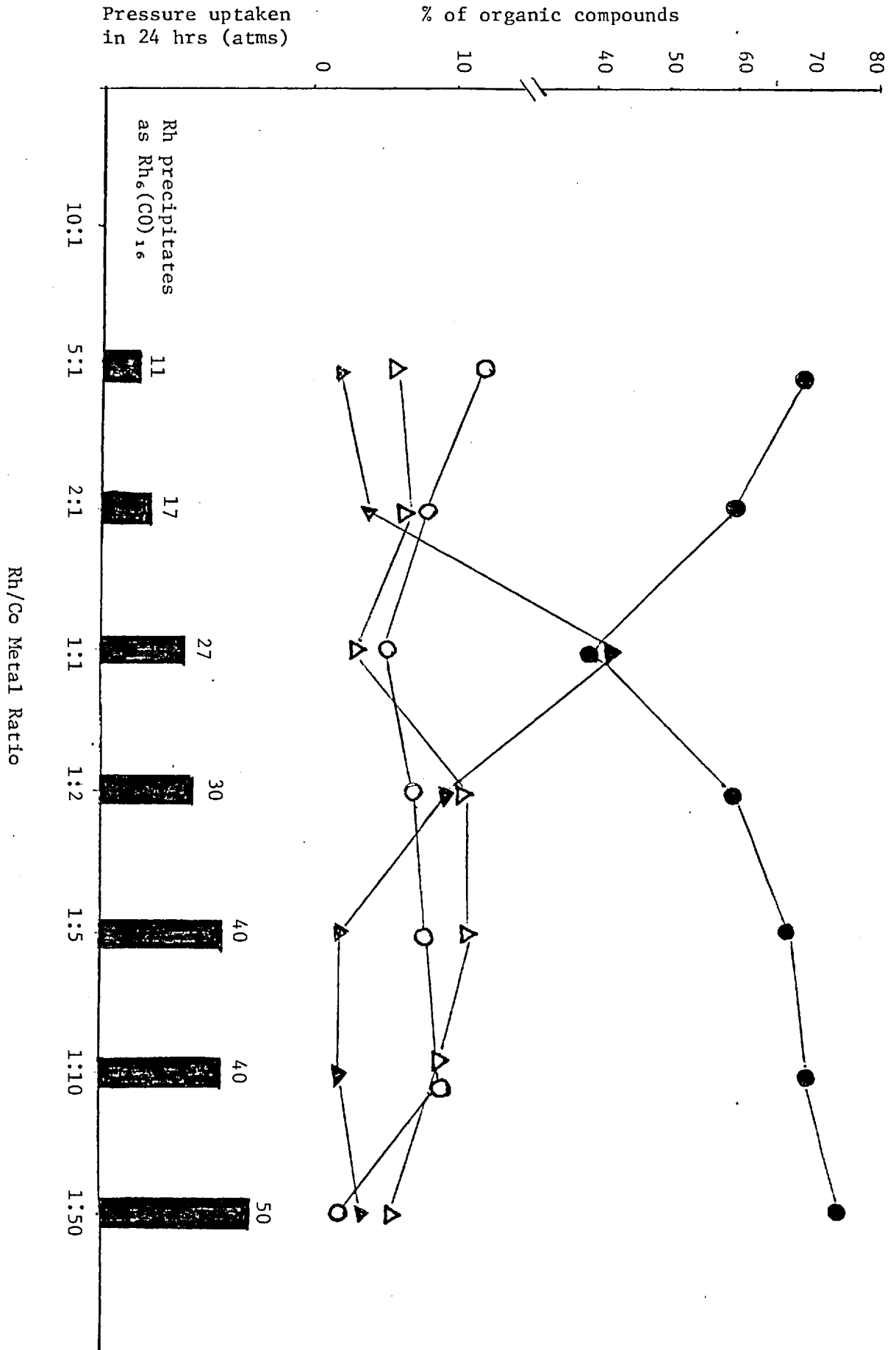
The results of these catalytic studies are best illustrated graphically for the variation in metal ratio and the gas uptake in 24 hours (Graph II-1).

The most significant observation from these systems are that, firstly the presence of cobalt carbonyl inhibits the known rhodium carbonyl clusterisation process<sup>18</sup> (to insoluble  $\text{Rh}_6\text{CO}_{18}$ ), and thus allows catalysis to be performed at much lower pressures than those used by Union Carbide,<sup>17</sup> and secondly, that cobalt carbonyl alone is the most active catalyst and, lastly, the selectivity is changed by changing the rhodium:cobalt ratio.

(iii) The Catalytic Hydrogenation of Carbon Monoxide Using a Dicobalt Octacarbonyl Catalyst.

We have shown in Graph II-1 that the rate of hydrogenation of carbon monoxide increased steadily with the cobalt content in the mixed cobalt rhodium catalyst systems. Solutions of  $\text{Co}_2\text{CO}_8$  alone, in diglyme under syn-gas pressure (100 atm) at  $200^\circ\text{C}$ , produce ethanol with greater than 85% selectivity. The selectivity and the rate of the process were investigated as a function of temperature and pressure,  $\text{H}_2/\text{CO}$  ratio, solvent, and catalyst concentration. We have expressed our results in a series of graphs and tables [Graphs II-2, -3, -4, -5, -6, and Tables II-3, -4, -5, -6].

Graph II-1: Variation of reduction products (%) as a function of Rh:Co metal ratios, and gas uptaken (atm.) in 24 hrs. or reaction (conditions as in Table II-1).





(iii-a) Selectivity as a Function of Temperature.

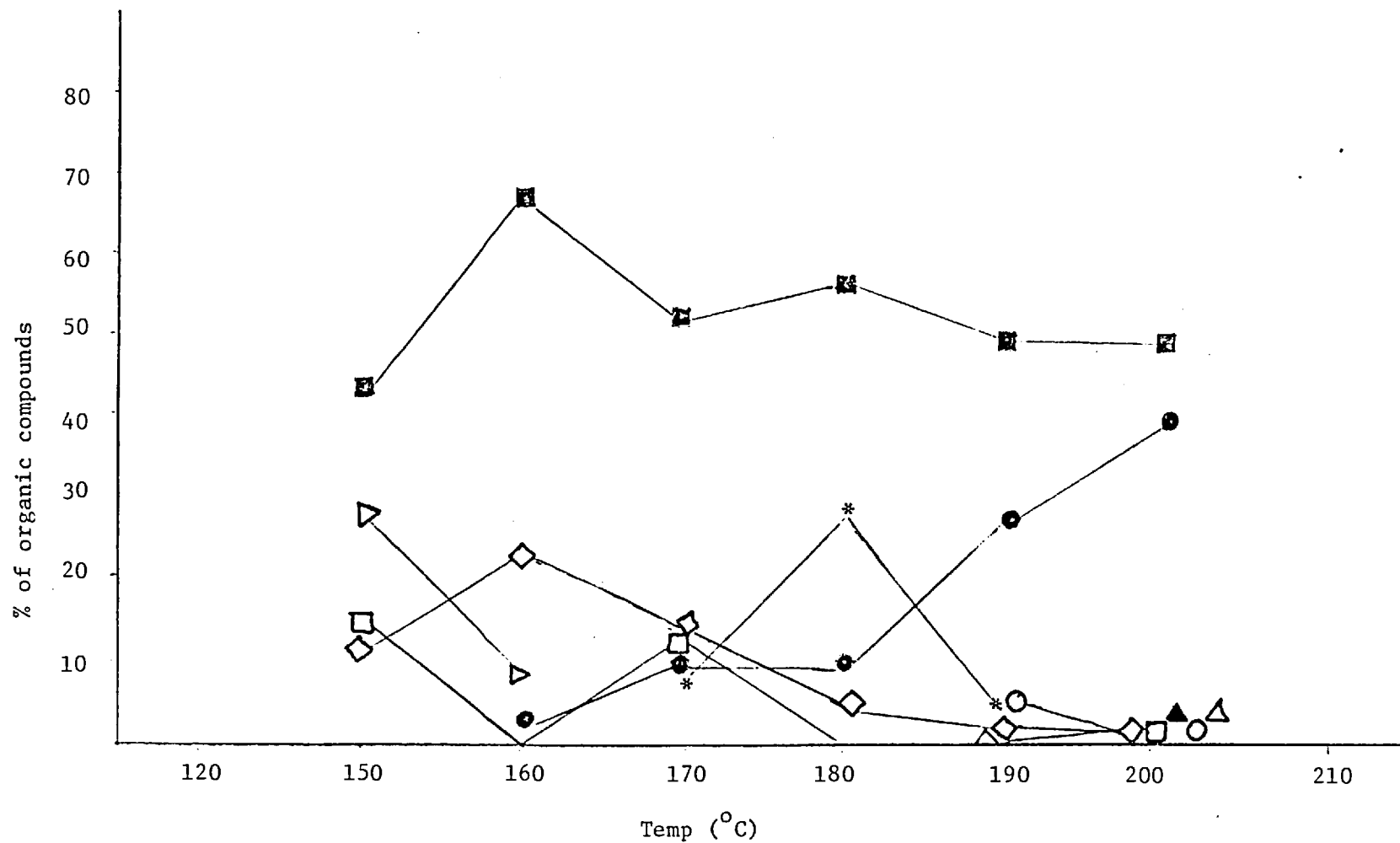
The best temperature range to make ethanol from syn-gas was found to be between 190°C and 200°C; above this temperature, the catalyst decomposes; below this temperature selectivity decreases markedly (Graphs II-2, and II-3).

(iii-b) Selectivity as a Function of Solvent.

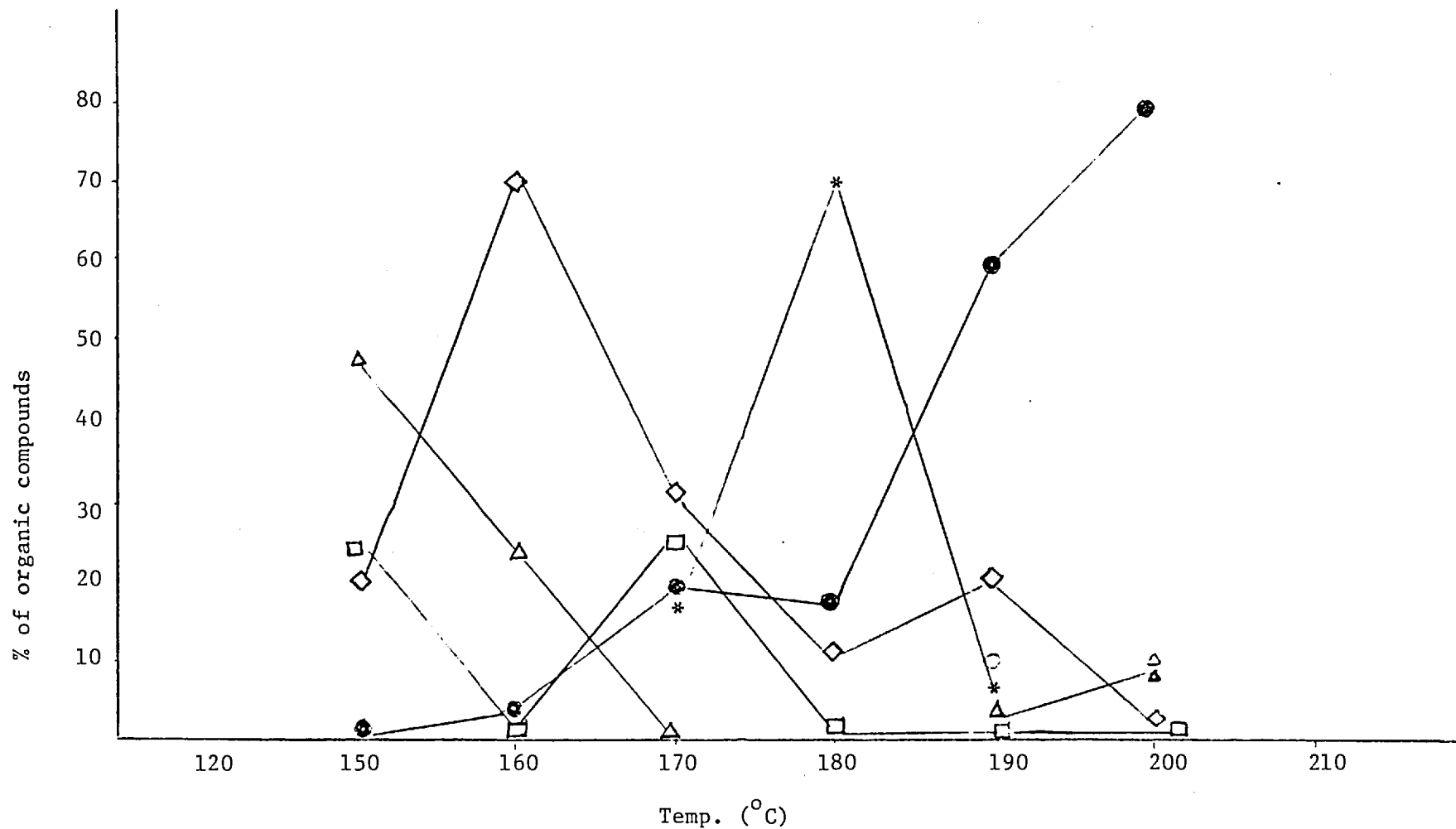
Graph (II-4) shows the relationship between the selectivity of the reaction and solvent at 200°C. Glymes are the best solvents and of these diglyme is the best.

(iii-c) Selectivity as a Function of the Carbon Monoxide: Hydrogen Ratio.

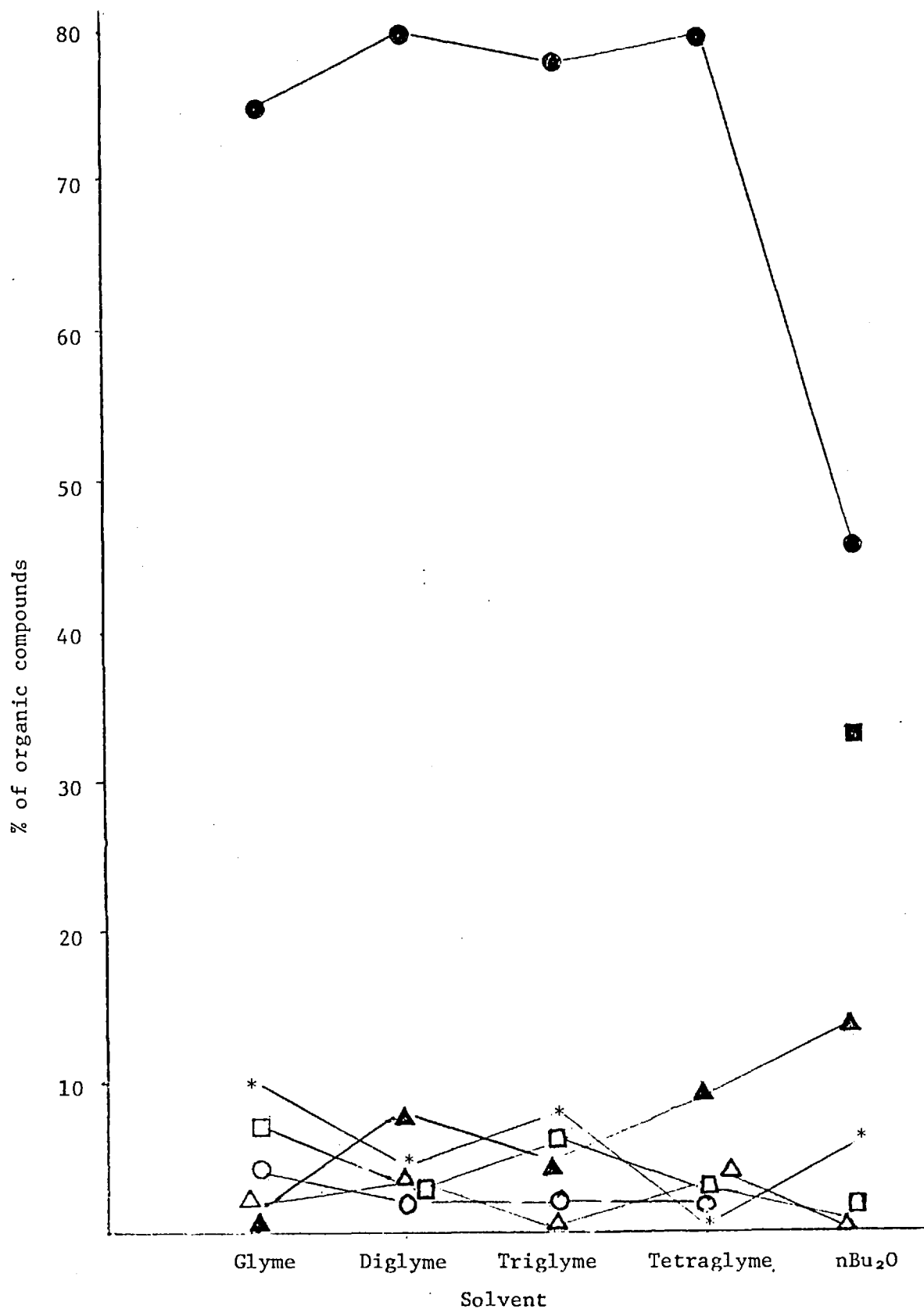
At 200°C, the best selectivity in ethanol was obtained with the H<sub>2</sub>:CO ratio of 1:1; increasing the H<sub>2</sub>:CO ratio increases the rate of reaction but selectivity drops markedly; at H<sub>2</sub>:CO ratios of 3:1, a fast reaction to produce paraffins (with deposition of metal) is observed. Decrease in the CO:H<sub>2</sub> ratio slows the reaction down but ethanol is still the major product; at CO:H<sub>2</sub> ratios of 2:1 no reaction is observed. (Graph II-5).



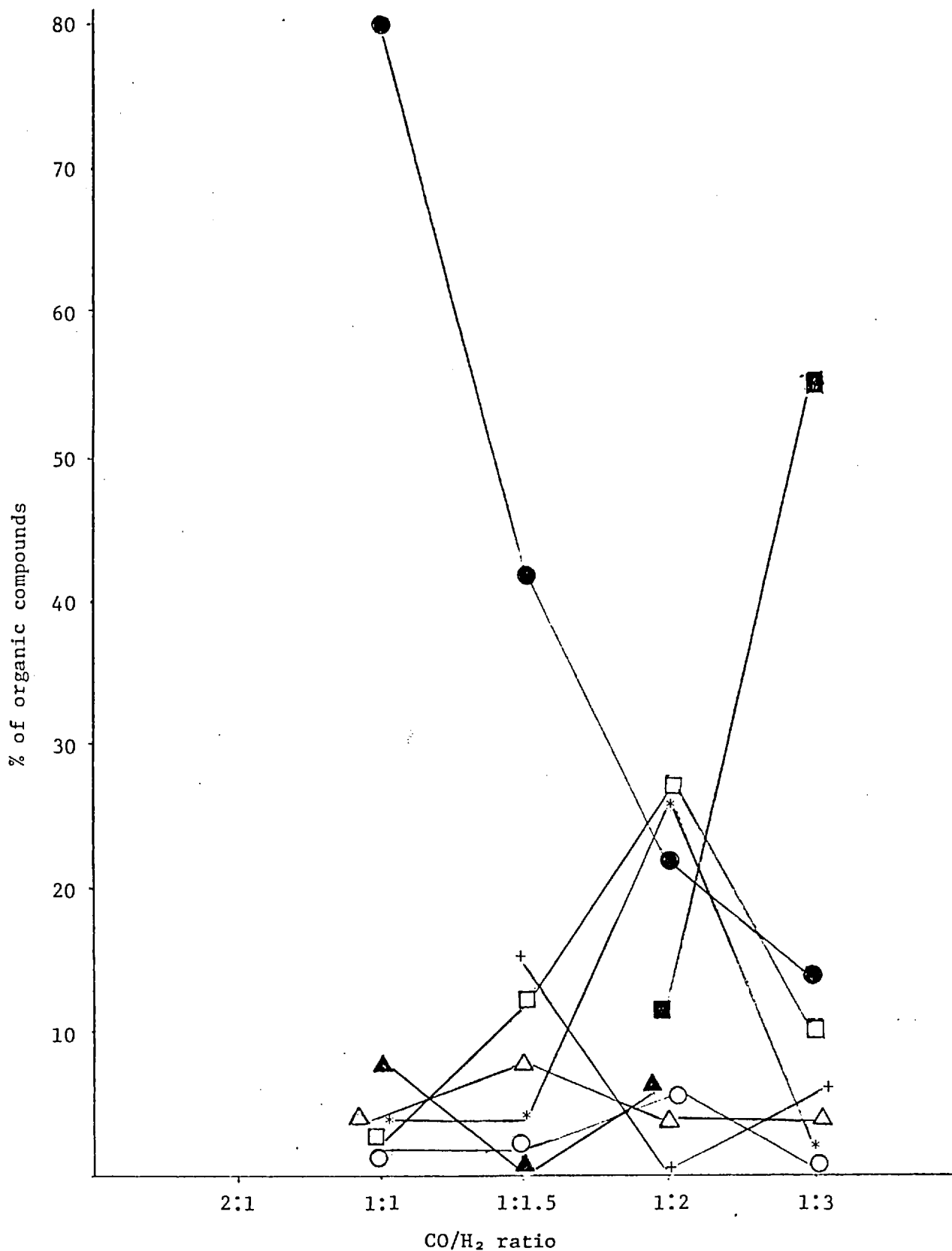
Graph II-2: Total yield of reduction products as a function of temperature (from 150°C to 200°C). Reaction conditions: 25 ml stainless steel bomb; 10 ml of diglyme; 0.3 g of  $\text{Co}_2(\text{CO})_8$ ; 100 atm.  $\text{CO}/\text{H}_2$  (1:1); reaction cycle (cold  $\rightarrow$  hot  $\rightarrow$  cold) 24 hrs.



Graph II-3. Yield of volatile reduction products as a function of temperature. Reaction conditions:  
 25 ml stainless steel bomb; 10 ml diglyme; 0.3 g of  $\text{Co}_2(\text{CO})_8$ ; 100 atm.  $\text{CO}/\text{H}_2$  (1:1);  
 reaction cycle (cold  $\rightarrow$  hot  $\rightarrow$  cold) 24 hrs.



Graph II-4: Selectivity and yield of reduction products as a function of solvent. Reactions conditions:  $\text{Co}_2(\text{CO})_8 = 0.3 \text{ g}$ ; solvent 70 ml;  $200^\circ\text{C}$ ; 80 atm.  $\text{CO}/\text{H}_2$  (1:1): 100 and 200 ml stainless steel bomb. Reaction cycle (cold  $\rightarrow$  hot  $\rightarrow$  cold) 24 hours.



Graph II-5. Selectivity and yield of reduction products as a function of CO:H<sub>2</sub> ratio. Reaction conditions: Co<sub>2</sub>(CO)<sub>8</sub> = 0.5 g; diglyme 70 ml; 200°C; 70 atm. CO/H<sub>2</sub>. 200 ml stainless steel bomb; reaction cycle (cold → hot → cold) 24 hours.

(iii-d) Selectivity and Rate of Reaction as a Function of Catalyst Concentration and Syn-gas Pressure.

The best catalyst concentration in diglyme was found to be 0.1 molar. This corresponds to a concentration of maximum ionic strength based on the Debye Onsager model, but this may be a factuous comparison. Decreasing catalyst concentration below 0.1 M, increases the selectivity in acetaldehyde and decreases that in ethanol

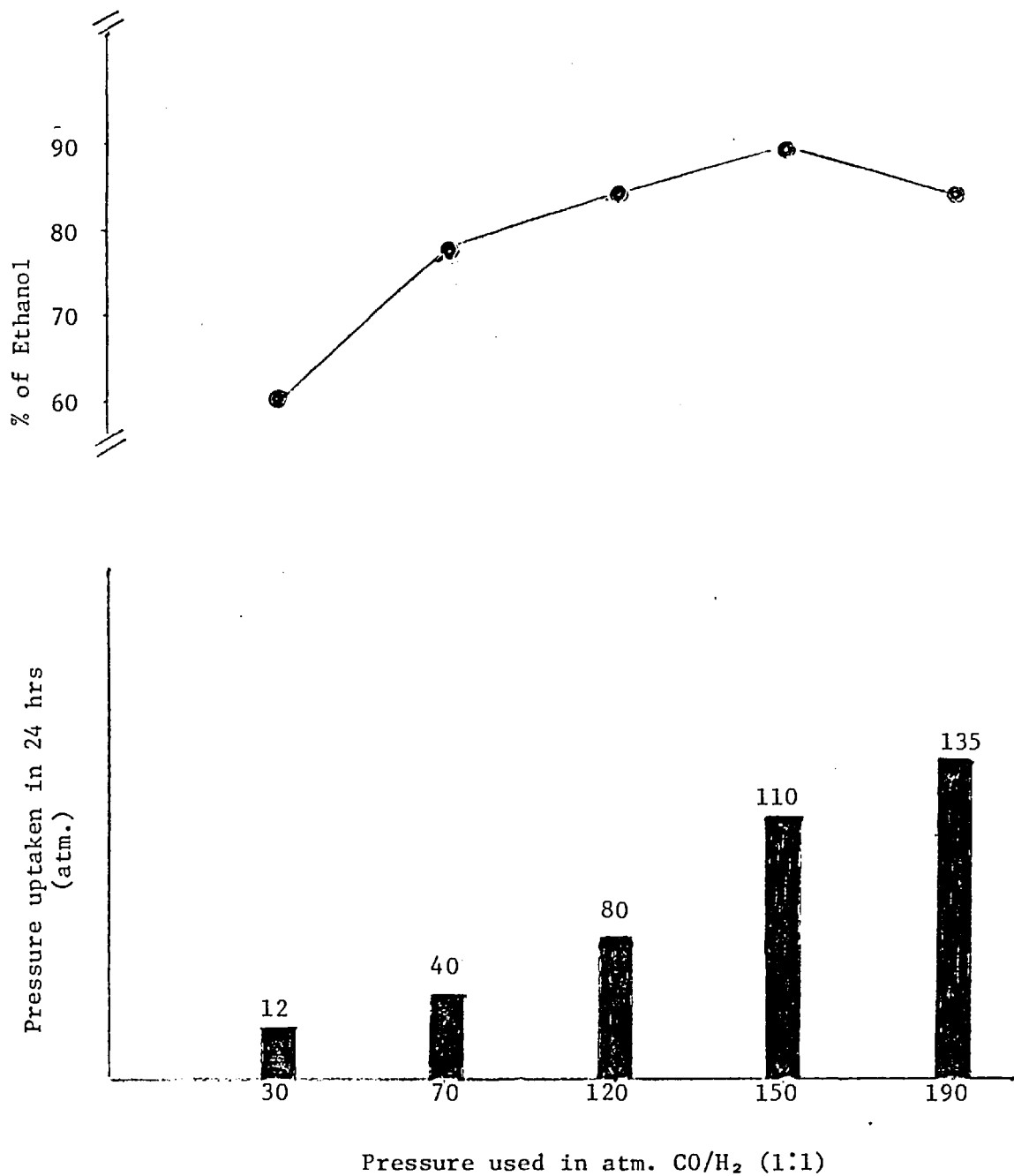
Increasing the catalyst concentration leads to metal deposition. Thus, low catalyst concentration (and lower ionic strength) decrease secondary hydrogenation. It is thus possible that ionic cobalt carbonyl hydride is the hydrogenation agent.

The rate of reaction is roughly in proportion to the syn-gas pressure, (Graph II-6 and Table II-3)

The Hydrogenation of Carbon Monoxide in Diglyme Between 100 and 200°C, using Dicobalt Octacarbonyl as Catalyst.

We delay discussion of the mechanism of ethanol production from syn-gas because it represents an extreme case in the general reactions of syn-gas in oxygenated solvents catalysed by  $\text{Co}_2(\text{CO})_8$ .

We discuss now the general temperature dependance of organic products made from syn-gas in glymes over the temperature range 100°C-200°C. The graph (II-2) illustrates the variation of the organic products as a function of temperature for a  $\text{CO}:\text{H}_2$  ratio 1:1 and a constant catalyst concentration (0.1 M) in diglyme; on regarding this



Graph II-6. Selectivity versus CO:H<sub>2</sub> pressure and gas uptaken in 24hrs. of reaction. Reaction conditions: 0.5 g, Co<sub>2</sub>(CO)<sub>8</sub>; 70 ml diglyme; 200°C; CO/H<sub>2</sub> 1:1; 200 ml stainless steel bomb.

Table II-3: Yield of Reduction Products and Selectivity as a Function of  $\text{Co}_2(\text{CO})_8$  Concentration.<sup>a</sup>

| Products (%) <sup>b</sup> | Cobalt Carbonyl Concentration |        |        |        |
|---------------------------|-------------------------------|--------|--------|--------|
|                           | 0.01 M                        | 0.05 M | 0.10 M | 0.25 M |
| Ethanol                   | 24                            | 38     | 70     | 50     |
| Ethylformate              | 23                            | 14     | 5      | *      |
| Methanol                  | 5                             | 4      |        |        |
| Acetaldehyde              | 39                            | 20     | 1      | 12     |
| Propanol                  | 1                             | 4      | 3.5    | 6      |
| 2-Methoxyethanol          | 6                             | 3      | 3      | 3      |
| Diethylether              |                               | 3      | 2      | 4      |
| 2-Ethoxyethanol           |                               | 3      | *      | 6      |
| Acetone                   |                               |        | 7      | 7      |

\* Traces observed.

<sup>a</sup> Reaction conditions: 25 ml stainless steel bomb; 10 ml of diglyme (solvent); 100 atm.  $\text{CO}/\text{H}_2$  (1:1); 200°C; 24 hrs. reaction cycle (cold → hot → cold).

<sup>b</sup> % calculated by G.L.C.



graph it can be observed that at temperatures below 200°C (the optimum temperature for ethanol formation) faster hydrogenation processes occurred which yielded: hydroxyethyl formate, methoxy-ethanol, acetaldehyde, ethyl formate and methyldigol. All of these compounds are formed preferentially at certain temperatures and reflect the nature of the reduction process and the state and change of state of the active catalyst and unfortunately solvent breakdown. To explain these results clearly, we must first outline the method used in our experiments. A steel autoclave was charged with catalyst solution and syn-gas; the autoclave was then heated from room temperature to the temperature of the reaction. In a reaction cycle [room temperature → reaction temperature → room temperature] of twenty-four hours, at least four hours may be needed to heat the autoclave to the control temperature and six hours to cool to room temperature; during these ten hours of temperature change, gas absorption occurs, and maybe faster than at the control temperature. The size of the gas volume in the autoclave and the rate of heating are therefore, very important.

Thus, in a small autoclave with a low heating and cooling rate up to 30% of the available syn-gas can be absorbed before the control temperature is attained.

We now refer the reader to graphs to illustrate these points. Graph II-4 illustrates that in a quickly heated autoclave with a large gas volume at 200°C, ethanol can be produced in over 80% yield; on the other hand with an identical catalyst solution, reaction in a small slowly heated bomb produces less than a 40%

yield of ethanol at 200°C (Graph II-2). The selective hydrogenation of carbon monoxide in diglyme using  $\text{Co}_2\text{CO}_8$  as catalyst between 120°C and 150°C produces methyldigol (90%) by solvent breakdown. Our temperature control experiments above 150°C were run in a small, slowly heated autoclave. The formation of methyl digol at control temperatures above 150°C can be ascribed to the slow heating process. Thus, the temperature control experiments show a constant value at all temperatures above 150°C for the amount of methyl-digol formed in the approach to the control temperature. We only discuss, therefore, the selectivity of the other organic products formed at the control temperatures. Graph II-3 shows the composition of the organic products formed between 150°C and 200°C. Trends are immediately observable with increasing temperature. Hydroxyethyl formate tails off from a maximum of 50% at 150°C to 0% at 170°C, methoxyethanol fluctuates from 25% at 150°C to 0% at 200°C. Ethyl formate peaks at 180°C and tails to 0% at 200°C.

We propose an explanation of these observations which we will verify later. Our basic assumption is that the first product formed is a glycol derivative formed by coupling two carbon monoxide molecules, one of which is oxygen-bound to cobalt:

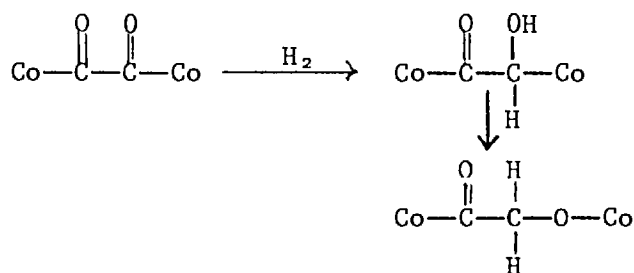
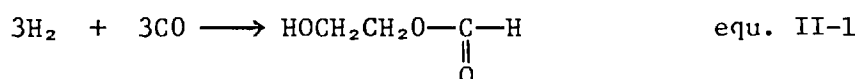


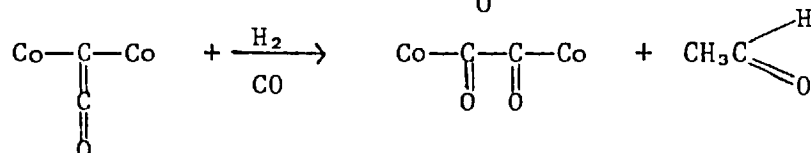
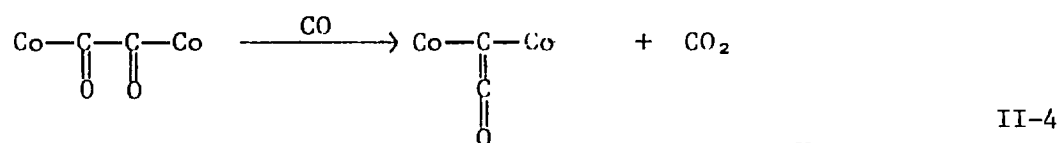
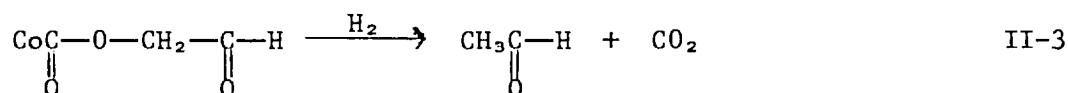
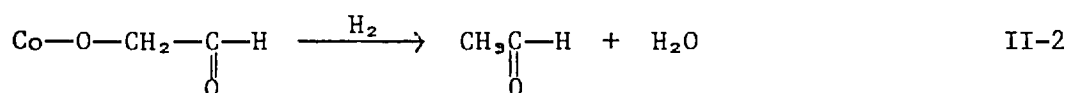
Figure II-1

This readily carbonylates and reductively hydrogenates to yield hydroxyethyl formate and methoxyethanol. Methoxyethanol and ethyl formate may be formed by solvent breakdown, but this is not clear. Studies with D<sub>2</sub>/CO mixtures show that methyl digol is certainly formed by solvent breakdown together with methyl formate. Deuterate products include ethanol and acetaldehyde. The origin of the hydroxyethyl formate is uncertain, but is likely to come from carbonylation of a genuine reduction product (Figure II-1).

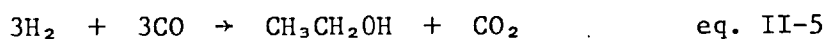
No decarboxylation occurs below 160°C (no CO<sub>2</sub> in autoclave gases). Thus, at 150°C, hydroxyethyl formate is formed preferentially with CO:H<sub>2</sub> ratios of 1:1 (equ. II-1).



At 160°C acetaldehyde is formed preferentially (70%). This can be produced in three simple ways: firstly the hydrogenation of glyoxal derivatives with water elimination or, secondly, the decarboxylation of formyl methyl formate derivatives, [R-C(=O)-O-CH<sub>2</sub>-C(=O)H R = cobalt or H]. Thirdly, the carbonylation of a cobalt carbide formed by decarboxylation of doubly inserted CO (equ. II-2,-3,-4).



The third method is considered the most likely in view of the large quantities of  $\text{CO}_2$  isolated and the nature of the catalyst (Chapter III). At  $170^\circ\text{C}$ , decarboxylation processes are beginning to predominate over reductive dehydration and a mixture of products is obtained notably the amount of ethanol is augmenting. At  $180^\circ\text{C}$ , the major product is ethyl formate which can be formed from the carbonylation of ethanol derivatives  $[\text{CO}-\text{CH}_2\text{CH}_2\text{OC}-\overset{\text{H}}{\underset{\text{O}}{\parallel}}]$  or by the decarboxylation of ethylene diformate derivatives. At  $190^\circ\text{C}$  carbonylation has become insignificant and ethanol is produced in over 85% yield; all other products have tailed off to about 5%. The quantity of  $\text{CO}_2$  produced along with the ethanol was measured as 50% of the value expected for the equation given in (eq. II-5)



Thus, the sequence of processes which lead to organic products as a function of temperature can be expressed as in Scheme II-1.

|                                                   |                                                                                                       |
|---------------------------------------------------|-------------------------------------------------------------------------------------------------------|
| $100^\circ\text{C} \rightarrow 150^\circ\text{C}$ | Reductive carbonylation + reductive oxygen extraction ( $\text{H}_2\text{O}$ )<br>+ solvent breakdown |
| $150^\circ\text{C} \rightarrow 160^\circ\text{C}$ | Reductive carbonylation                                                                               |
| $160^\circ\text{C} \rightarrow 200^\circ\text{C}$ | Reductive carbonylation + decarboxylation ( $\text{CO}_2$ )                                           |

Scheme II-2

The decarboxylation process is independent of the hydrogen concentration, thus at 200°C, a  $\text{Co}_2(\text{CO})_8$  solution in diglyme under 150 atmospheres CO pressure yields  $\text{CO}_2$  (1.8 moles/ $\text{Co}_2(\text{CO})_8$ /24 hours), a soluble cobalt carbide-carbonyl and graphite (see Chapter IV for mechanism). There is no reaction at 150°C under identical conditions and  $\text{Co}_2(\text{CO})_8$  is recovered quantitatively.

(iv) The Hydrogenation of Carbon Monoxide in Monoglyme Between 100 and 200°C using Dicobalt Octacarbonyl as Catalyst.

We have not performed a full temperature control study of the hydrogenation of carbon monoxide in monoglyme but we have, however, observed two highly selective hydrogenation processes. Between 130 and 150°C methoxy ethanol is formed with a selectivity of greater than 70%. Studies of the residual autoclave gases show insignificant quantities of  $\text{CO}_2$  and a good materials balance was obtained overall. Between 190 and 200°C ethanol is formed selectively by the decarboxylation route (large quantities of  $\text{CO}_2$ ). The formation of methoxyethanol comes from solvent breakdown. Two tests prove this.

Firstly the reaction of  $\text{D}_2/\text{CO}$  1:1 syn-gas with  $\text{Co}_2\text{CO}_8$  in glyme produces methoxyethanol with no deuterium in (except the OH group). Secondly, the reaction of syn-gas with glyme-water mixtures (90/10), produces only methoxyethanol and methyl formate. This observation can be explained by extraction of a  $-\text{CH}_2$  group from the solvent followed by a selective hydration and carbonylation; as no methanol is produced, these processes must both occur on the cobalt centre (Chapter IV). The  $\text{CO}:\text{H}_2$  ratio in this experiment was 1:1.

The importance of hydroxyethyl formate or more probably its cobalt-bound precursor can not be underestimated. There is no detectable ethylene diformate in the reactions in diglyme or glyme and thus, if we assume that the first step in all reactions is the hydrogenation of two coupled CO molecules; the result of this hydrogenation is that one carbon-oxygen unit is different from the other, thus allowing for mono-carbonylation to take place. The mechanistic implications of this are discussed in Chapter IV. Further information about volatile compounds formed in mono-glyme is appended in Table III-5.

(v) The Hydrogenation of Carbon Monoxide in Triglyme and Tetraglyme Between 100 and 200°C.

The reaction of CO:H<sub>2</sub> in the ratio 1:1 or 1:1.5 in polyglyme solutions of Co<sub>2</sub>(CO)<sub>8</sub> at 100 atm. and 150°C leads to a very fast carbonylation of the solvent, probably via internal ether bond rupture. Partial reduction to esters is observed. These reactions were not investigated further. At 200°C, on the other hand, in polyglyme solvents, ethanol is produced without solvent breakdown.

(vi) The Hydrogenation of Carbon Monoxide Between 100 and 200°C using 2-Methoxyethanol as a Solvent and Co<sub>2</sub>(CO)<sub>8</sub> as a Catalyst.

Between 130°C and 170°C, syn-gas in ratios of CO:H<sub>2</sub> between 1:1 and 1:1.5 and below 140 atm., in 2-methoxyethanol solutions of Co<sub>2</sub>(CO)<sub>8</sub> produces ethylene glycol, ethanol and hydroxyethyl formate

as major products (Experimental Section, J). Carbonylation and reductive hydrogenation also lead to the formation of 1,3-dioxolane, 2-methyl-1,3-dioxolane and by solvent breakdown to bis(methoxyethoxy)methane. These results are explainable in terms of reductive elimination or reductive cyclisation reactions involving a high valent cobalt catalysts (Chapter IV). At reaction temperatures above  $170^{\circ}\text{C}$ , metal deposits, and only small amounts of paraffins are formed. The formation of ethylene glycol in ethylene glycol as solvent is too slow to be of importance. Small quantities of hydroxyethyl formate and methoxyethanol and large amounts (10%) of 1,3-dioxolane are formed.

The reaction of  $\text{D}_2/\text{CO}$  1.5:1 syn-gas with methoxyethanol (OD) solutions of  $\text{Co}_2(\text{CO})_8$  indicates the production of ethylene glycol from syn-gas only indirectly; because the overall pressure of reaction was high (starting pressure 250 atmospheres) and the  $\text{D}_2$  concentration was high, methoxyethylacetate d-3 and methoxyethoxyethyl acetate d-3 were produced. Glycol was isolated after the reaction as polyglycol by distillation from the cobalt catalyst solutions, the higher the boiling point of the fraction obtained, the higher the quantity of deuterium (asC-D) in the product).

(vii) The Hydrogenation of Carbon Monoxide in 2-Methoxyethanol using the Carbonyls of Manganese, Iron, Ruthenium, Osmium, and Chromium as Catalysts.

The formation of ethylene glycol, a very useful chemical feedstock, from syn-gas at below 140 atmospheres pressure, using a cobalt catalyst, prompted us to look at action of other metal carbonyls in the presence of syn-gas using 2-methoxyethanol as solvent. All the carbonyls investigated, yield selective hydrogenation processes, but which are, in general, slower than those obtained with cobalt. The results are summerised in Table II-5. The significance of this work is apparent when viewed in comparison with other similar studies on carbon monoxide hydrogenation. Table II-6 shows work done in other laboratories using metal carbonyls as catalyst precursors. It is evident that the very high pressures needed to effect reactivity in solvents other than polyethers and polyether-alcohols must be due to the negative role of the solvents used. The nature of the role of the solvent and its ability to yield active catalysts at low pressure is discussed in the next Chapter.

(viii) The Hydrogenation of Carbon Monoxide in other Solvents using  $\text{Co}_2(\text{CO})_8$  as a Catalyst.

Table II-7 illustrates the activity of  $\text{Co}_2(\text{CO})_8$  and the organic products formed from syn-gas reactions in other solvents.



Table II-5. Catalytic Activity of Some Metal Carbonyls in Methoxyethanol as a Solvent. Conditions and Major Products.

| Metal Carbonyl                     | Time (hrs) | CO/H <sub>2</sub> Ratio | Starting Pressure (cold) | Temp. °C | Solvent          | Conversion (%) <sup>b</sup> | Organic Products (%) <sup>c</sup>                                                                                     |
|------------------------------------|------------|-------------------------|--------------------------|----------|------------------|-----------------------------|-----------------------------------------------------------------------------------------------------------------------|
| Fe(CO) <sub>5</sub>                | 24         | 1:1                     | 100                      | 160      | 2-methoxyethanol | 20                          | Diethylether (48), dimethylether (36) acetone (6)                                                                     |
| Mn <sub>2</sub> (CO) <sub>10</sub> | 24         | 1:1                     | 100                      | 160      | 2-methoxyethanol | 10                          | Ethylformate (85), hydroxyethylformate (11), diglyme (condensation of the solvent)                                    |
| Ru <sub>3</sub> (CO) <sub>12</sub> | 48         | 1:1.5                   | 160                      | 150      | 2-methoxyethanol | 50                          | Methanol (40), acetone (30), methylformate (5), hydroxyethylformate (6), 2-methyl-1,3-dioxolene (7)                   |
|                                    | 48         | 1:2                     | 130                      | 180      | 2-methoxyethanol | 60                          | Methanol (45), acetone (4), methylformate (2), hydroxyethylformate (11), 2-methyl-1,3-dioxolane (7), polyglycols (18) |
| Cr(CO) <sub>6</sub>                | 24         | 1:1                     | 110                      | 150      | 2-methoxyethanol | 12                          | Diethylether (45), acetone (34),                                                                                      |
|                                    | 24         | 1:1.5                   | 145                      | 180      | 2-methoxyethanol | 17                          | Diethylether (60), acetone (30),                                                                                      |
| Os <sub>3</sub> (CO) <sub>12</sub> | 48         | 1:1                     | 130                      | 190      | 2-methoxyethanol | 40                          | Methanol (30), methylformate (10), acetone (20), hydroxyethylformate (18), ethylformate (6)                           |
|                                    | 48         | 1:2                     | 130                      | 190      | 2-methoxyethanol | 55                          | Methanol (40), acetone (5), methylformate (15) hydroxyethylformate (8)                                                |

<sup>a</sup> The reactions were carried out in a 200 ml stainless steel autoclave in a batch run. The catalyst concentration was 0.025 M; 20 ml of solvent.

<sup>b</sup> Calculated from the drop in pressure. <sup>c</sup> Compounds identified by GLC/ and GLC/MS yield calculated from GLC.

Table II-6. Published Results for The Homogeneous Hydrogenation of Carbon Monoxide using Metal Carbonyl Catalysts.

| Metal Carbonyl                                                          | Pressure (atm) | Temp. °C | Solvent                     | Conversion %/h | Selectivity (%) (for the major components)                                 |
|-------------------------------------------------------------------------|----------------|----------|-----------------------------|----------------|----------------------------------------------------------------------------|
| W. Keim Results <sup>1</sup>                                            |                |          |                             |                |                                                                            |
| Fe <sub>3</sub> (CO) <sub>12</sub>                                      | 2000           | 230      | Toluene<br>NMP <sup>a</sup> | -<br>0.83      | -<br>Methanol (59.2)                                                       |
| Co <sub>2</sub> (CO) <sub>8</sub>                                       | 2000           | 230      | Toluene<br>NMP              | 19<br>4        | Methanol (31), ethylene glycol (25)<br>Methylacetate (28.9), methanol (14) |
| Ru <sub>3</sub> (CO) <sub>12</sub>                                      | 2000           | 230      | Toluene<br>NMP              | 5.5<br>12.5    | Methyl formate (40, methanol (18)<br>Methanol (62), methyl formate (22.2)  |
| Ir <sub>4</sub> (CO) <sub>12</sub>                                      | 2000           | 230      | Toluene<br>NMP              | 1<br>7         | Methanol (45), methyl formate (18.4)<br>Methanol (81.2)                    |
| Os <sub>3</sub> (CO) <sub>12</sub>                                      | 2000           | 230      | Toluene<br>NMP              | -<br>0.2       | -<br>Methanol (22.2)                                                       |
| Gulf Research and Development Co., Results <sup>2</sup>                 |                |          |                             |                |                                                                            |
| Ru <sub>3</sub> (CO) <sub>12</sub>                                      | 1600           | 230      | n-propanol                  | 1.5            | Ethylene glycol (57), methanol (25)                                        |
| K <sub>4</sub> (CO) <sub>12</sub>                                       | 1600           | 230      | n-propanol                  | 1.4            | Ethylene glycol (43.5), methanol (30)                                      |
| J. Bradley Results <sup>3</sup><br>(Exxon Research and Engineering Co.) |                |          |                             |                |                                                                            |
| Ru <sub>3</sub> (CO) <sub>12</sub>                                      | 1300           | 268      | THF                         | 7.5            | Methanol (80, methyl formate (20)                                          |

Table II-6 (cont.)

| Metal Carbonyl                     | Pressure (atm) | Temp. °C | Solvent        | Conversion %/h | Selectivity (%) (for the major components)                 |
|------------------------------------|----------------|----------|----------------|----------------|------------------------------------------------------------|
| Results of this Thesis             |                |          |                |                |                                                            |
| Fe(CO) <sub>5</sub>                | 120            | 170      | Diglyme        | -              | -                                                          |
|                                    | 140            | 160      | Methoxyethanol | 0.8            | Diethyl ether (48), dimethylether (36)                     |
| Cr <sub>3</sub> (CO) <sub>6</sub>  | 180            | 180      | Methoxyethanol | 1.04           | Diethyl ether (60), ethylformate (20)                      |
|                                    | 120            | 170      | Diglyme        | -              | -                                                          |
| Mn <sub>2</sub> (CO) <sub>10</sub> | 140            | 160      | Methoxyethanol | 0.75           | Ethyl formate (85), hydroxyethyl formate (11)              |
|                                    | 180            | 150      | Methoxyethanol | 7.9            | Ethylene glycol (40)                                       |
| Co <sub>2</sub> (CO) <sub>8</sub>  | 190            | 200      | Diglyme        | 4.6            | Ethanol (85)                                               |
|                                    | 170            | 180      | Methoxyethanol | 1.3            | Methanol (46), acetone (8), hydroxyethylformate (11)       |
| Ru <sub>3</sub> (CO) <sub>12</sub> | 170            | 180      | Methoxyethanol | 0.90           | Methylformate (15), hydroxyethylformate (40); acetone (5). |
| Os <sub>3</sub> (CO) <sub>12</sub> | 170            | 190      | Methoxyethanol |                |                                                            |

<sup>1</sup> W. Kein, M. Burger and J. Schlupp, J. of Catalysis, 61 (1980), 359; <sup>2</sup> U.S. Patents Nos. 4,170,606 and 4,170,605;

<sup>3</sup> J. Bradley in 'Homogeneous Catalysis', Vol. 3, p. 165, Plenum Press, New York, (1978).

<sup>a</sup> NMP = N-methylpyrrolidone.

Table II-7 . Activity of  $\text{Co}_2(\text{CO})_8$  in CO Hydrogenation Reactions with Different Solvents.

| Solvent                      | Temp.<br>°C | CO/H <sub>2</sub><br>Ratio | Cold<br>Pressure | Organic Products (%)                                                                                 | Relative <sup>2</sup><br>Activity |
|------------------------------|-------------|----------------------------|------------------|------------------------------------------------------------------------------------------------------|-----------------------------------|
| Tri-n-butyl phosphate        | 200         | 1:1                        | 80               | -                                                                                                    | -                                 |
| Tetraethyl silicate          | 200         | 1:1                        | 80               | -                                                                                                    | -                                 |
| Di-n-butyl ether             | 200         | 1:1                        | 80               | ethanol (46), acetone (14) ethyl formate (6), paraffin (34)                                          | 10 <sup>-2</sup>                  |
| Butane-1,4-diol              | 200         | 1:1                        | 80               | Co metal                                                                                             | -                                 |
| Trimethyl borate             | 180         | 1:1                        | 90               | -                                                                                                    | -                                 |
| Polyethylene glycol 200      | 150         | 1:1                        | 100              | Co metal                                                                                             | -                                 |
| Sulpholane                   | 200         | 1:1.5                      | 90               | Co metal                                                                                             | -                                 |
| 1,1,3,3-tetramethoxypropane  | 200         | 1:1                        | 100              | Solvent breakdown                                                                                    | -                                 |
| Propylene oxide tetramer     | 200         | 1:1                        | 80               | n-Propanol (from solvent breakdown), ethanol, acetone, diethyl ether, ethylformate                   | 10 <sup>-4</sup>                  |
| Methanol <sup>3</sup>        | 200         | 1:1                        | 100              | Dimethylether, methylformate, acetone, ethanol, propanol(-n, -iso), buthanol.                        | 10 <sup>-3</sup>                  |
| Ethanol <sup>3</sup>         | 200         | 1:1                        | 100              | Dimethyl ether, ethylformate, ethyl acetate, acetaldehyde, propanol (-n,-iso), buthanol, polyethers. | 10 <sup>-3</sup>                  |
| Tetrahydrofuran <sup>4</sup> | 200         | 1:1                        | 100              | Methyl and ethyl formates, acetone, methanol, ethanol (traces), paraffin.                            | 10 <sup>-3</sup>                  |

Table II-7 (cont.)

| Solvent              | Temp.<br>°C | CO/H <sub>2</sub><br>Ratio | Cold<br>Pressure | Organic Products (%) <sup>1</sup>                                                                                                                                                    | Relative<br>Activity <sup>2</sup> |
|----------------------|-------------|----------------------------|------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------|
| Dioxan <sup>4</sup>  | 200         | 1:1                        | 100              | Methyl and ethyl formates,<br>diethyl ether, acetone, methanol<br>ethanol, paraffin                                                                                                  | 10 <sup>-2</sup>                  |
| Pyridine             | 200         | 1:1                        | 100              | Carbonylation of solvent                                                                                                                                                             | -                                 |
| Piperidine           | 200         | 1:1.5                      | 100              | Carbonylation of solvent                                                                                                                                                             | -                                 |
| Pyrrolidine          | 200         | 1:1.5                      | 100              | Acetaldehyde, methanol, solvent<br>carbonylation derivatives                                                                                                                         | 10 <sup>-4</sup>                  |
| Ethanolamine         | 150         | 1:1                        | 100              | Solvent carbonylation                                                                                                                                                                | -                                 |
| Dimethylacetamide    | 200         | 1:1                        | 100              | -                                                                                                                                                                                    | -                                 |
| Toluene + 18-crown-6 | 200         | 1:1                        | 100              | Diethyl ether (38), methyl-<br>formate (46), ethanol (16)                                                                                                                            | 10 <sup>-3</sup>                  |
| Benzene + 18-crown-6 | 190         | 1:1                        | 120              | Acetaldehyde (10), methyl-<br>formate (6), ethylformate (1)<br>acetone (20), methanol (25) +<br>benzene derivatives                                                                  | 1                                 |
| Glyme + 19-crown-6   | 150         | 1:1                        | 90               | Acetaldehyde (7), acetone (20)<br>ethanol (56), methoxyethanol (13)                                                                                                                  | 10 <sup>-3</sup>                  |
| Diglyme + 18-crown-6 | 200         | 1:1                        | 80               | Diethyl ether (1), acetaldehyde<br>(10), ethylformate (30) ethanol<br>(24), hydroxyethyl formate (19),<br>propanol (2), methoxyethanol (3),<br>ethoxyethanol (2), methyldigol<br>(7) | 10 <sup>-3</sup>                  |

Table II-7 (cont.)

| Solvent                    | Temp.<br>°C | CO/H <sub>2</sub> | Cold<br>Pressure | Organic Products (%)                                                                                     | Relative<br>Activity |
|----------------------------|-------------|-------------------|------------------|----------------------------------------------------------------------------------------------------------|----------------------|
| Phenoxyethanol             | 150         | 1:1               | 120              | -                                                                                                        | -                    |
| Tetrahydrofurfuryl alcohol | 140         | 1:1.5             | 170              | Acetone (15), ethanol (3)<br>ethylene glycol (5), propanol (3)<br>ethoxyethanol (7), polyglycols<br>(22) | 1                    |

1. Identified by G.L.C.; the solvent derivatives were not completely identified.
2. Compared with the activity of  $\text{Co}_2(\text{CO})_8$  in diglyme.
3. Probably only homologation of the alcohol.
4. Results similar to those obtained by Feder.<sup>20</sup>

Nitrogen bases readily carbonylated and in some cases, hydrogenate. Mono ethers are much less activating as solvents than poly ethers. Mono-alcohols do not significantly homologate. Non-polar solvents like benzene and hexane lead to formates as observed by Feder<sup>20</sup> and Keim.<sup>21</sup>

Due to their relatively poor reactivity only exploratory experiments have been performed in these solvents: further work seems at this time inappropriate.

(ix) The Hydrogenation of Carbon Monoxide as a Function of the CO:H<sub>2</sub> ratio in Oxygen-Containing Solvents.

There is a general high plateau of reactivity for carbon monoxide: hydrogen ratios between 1:1 and 1:1.5 for all reactions investigated. Selectivity is maximum when the gas ratios are those represented in the stoichiometry of the reaction. In diglyme for instance, high CO/H<sub>2</sub> ratios produces acetates and high H<sub>2</sub>/CO ratios produce paraffin and parafino-ethers.

(x) The Hydroformylation of Paraformaldehyde.

The reaction of diglyme solutions of paraformaldehyde with syn-gas and a cobalt carbonyl catalyst yield methyldigol; when glyme is used as a solvent, insoluble formates are produced. Methyldigol is also made when 2-methoxyethanol is used as a solvent. Paraformaldehyde is known to give glycol aldehyde in 1,3,5-trioxane solvent using Co<sub>2</sub>(CO)<sub>8</sub> catalyst and syn-gas.<sup>22</sup> We feel that paraformaldehyde yields C-2 units which either couple or link to alkoxide groups. The simplest way to make methyldigol in diglyme from paraformaldehyde is to break diglyme internally as shown in Figure II-3.

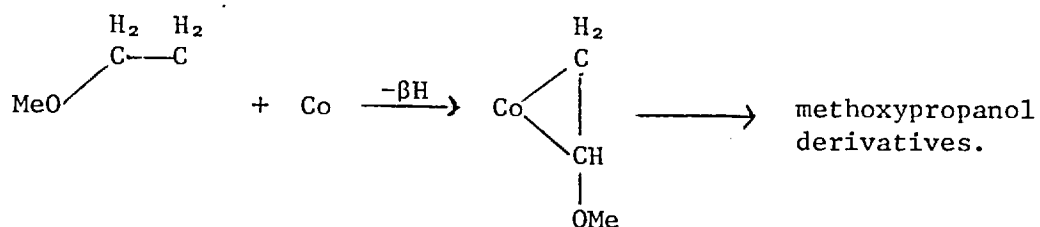
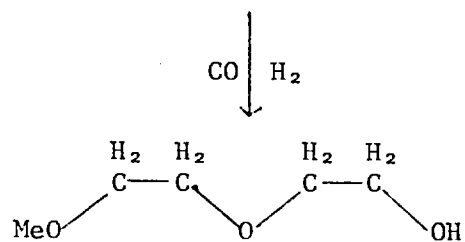
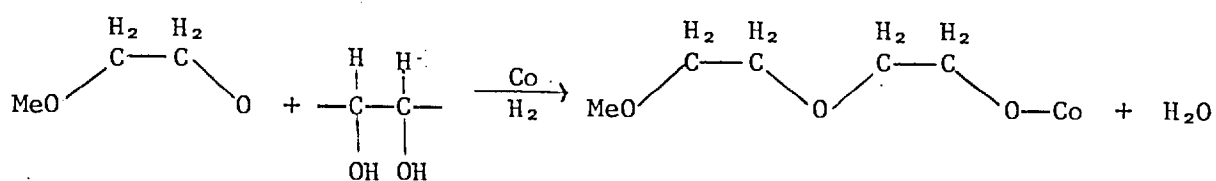
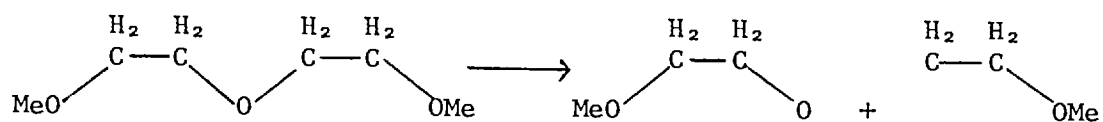


Figure II-3



## CHAPTER III

### THE NATURE OF THE CATALYTIC SPECIES AND THE ROLE OF THE SOLVENT.

We believe one of the fundamental reasons for the selective hydrogenation of carbon monoxide in polyethers and ether-alcohols is the special ligating properties of the solvents due to the justa position of two oxygen atoms separated by two carbon atoms and the coordinating characteristics of oxygen at high temperature ( $> 100^{\circ}\text{C}$ ).

The role of oxygen in catalysis is extremely important; several examples can be cited. The fastest ethylene polymerisation catalyst known is based on a bis-cyclopentadienyl zirconium dimethyl complex, activated by alkyl aluminium compounds after the introduction of water. The active co-catalyst is believed to be a cyclo-aloxane.<sup>23</sup> The transfer of alkyl groups from one transition metal to the other occurs fastest in the presence of oxygen or metal bonded oxygen.<sup>24</sup> Fast methathesis catalysts contain metal bonded oxygen.<sup>25</sup> The activation of molecular oxygen on copper(I) is thought to occur best in  $\mu$ -oxo bridged systems of copper blue enzymes.<sup>26</sup> Practically every heterogeneous catalyst support contains oxygen. Zeolites can convert methanol to benzene<sup>27</sup> or petrol.<sup>28</sup> The Fischer-Tropsch<sup>29</sup> and original Haber-Bosch<sup>30</sup> processes were performed using oxygen-based supports. Even the activation of molecular dinitrogen can be accomplished in magnesium oxide, vanadium oxide gels.<sup>31</sup>

The presence of oxygen in all these catalytic systems is interesting. We therefore, have investigated the properties of oxygen solvents on cobalt carbonyl.

#### Properties of Glymes as Solvents for Cobalt Carbonyl

Dicobalt octacarbonyl dissolves in 2-methoxyethanol to give firstly, a red-brown solution and after about 15 minutes a pink solution. Carbon monoxide is evolved slowly throughout. Dicobalt octacarbonyl dissolves quickly in glyme with carbon monoxide evolution. The solution remains red-brown ( $\nu_{\text{CO}} = 1890 \text{ cm}^{-1}$ ).<sup>\*</sup> Cobalt carbonyl dissolves slowly in diglyme with carbon monoxide, evolution ( $\nu_{\text{CO}} = 1890 \text{ cm}^{-1}$ ).<sup>\*</sup> In both glyme and diglyme between 1.5 and 2 moles of carbon monoxide are evolved per cobalt dimer. In 2-methoxyethanol over 2 moles of CO are evolved per cobalt dimer ( $\nu_{\text{CO}} = 1890 \text{ cm}^{-1}$ ).<sup>\*</sup>

$\text{Co}_4(\text{CO})_{12}$  dissolves in glymes with no carbon monoxide evolution to yield identical solution to those prepared from  $\text{Co}_2(\text{CO})_8$ .  $\text{Co}^{++}\text{Co}_6(\text{CO})_{15}^{2-}$ <sup>49</sup> in glymes, under CO reverts to the same solution ( $\nu_{\text{CO}} = 1890 \text{ cm}^{-1}$ ).<sup>\*</sup> The red-brown glyme solutions and the pink 2-methoxyethanol solutions yield  $\text{Co}^{++}\text{Co}_6(\text{CO})_{15}^{2-}$  under vacuum at 60°C. These solutions do not add CO at room temperature.

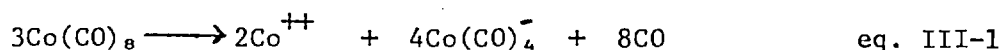
Measurements of magnetism by the Evans' method<sup>32</sup> showed 1.4 B.M. per cobalt at 37°C for the diglyme solutions. The variation with temperature of the paramagnetism is hysteretically reversible up to 60°C, where irreversible clusterisation occurs. At 60°C the paramagnetism has fallen to 2.6 B.M. per 4 cobalt atoms. The u.v./vis. spectra of the glyme solutions show no  $\text{Co}^{++}$  absorption at 520 nm below 60°C.

---

\* This is the only carbonyl band observed.

In monoethers, dioxane\*, non-polar solvents, cobalt carbonyl does not eliminate carbon monoxide at ambient temperatures.

We assume that in alcohols including 2-methoxyethanol the normal disproportionation reaction<sup>34</sup> occurs (eq. III-1)



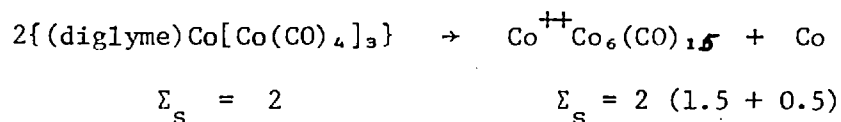
in glymes cobalt carbonyl dissociates forming  $\text{Co}(\text{CO})_4$  radicals. These radicals are stabilised by two processes; oxygen binding and clusterisation under conditions of spin-parity, (Scheme III-1).

We assume that at room-temperature the free electron in the  $\text{Co}(\text{CO})_4$  radical is delocalised in the ether via the two oxygen atoms. This does not occur to any great extent with monoethers. The cluster carbonyl (c) with  $\mu = 2.54$  B.M. may contain high spin cobalt(I) and thus can be obtained via spin conservation from four  $\text{Co}(\text{CO})_4$ -ether radicals

$$\Sigma_S = 2 \rightarrow \text{possible products } \Sigma_S = 2, 1, 0$$

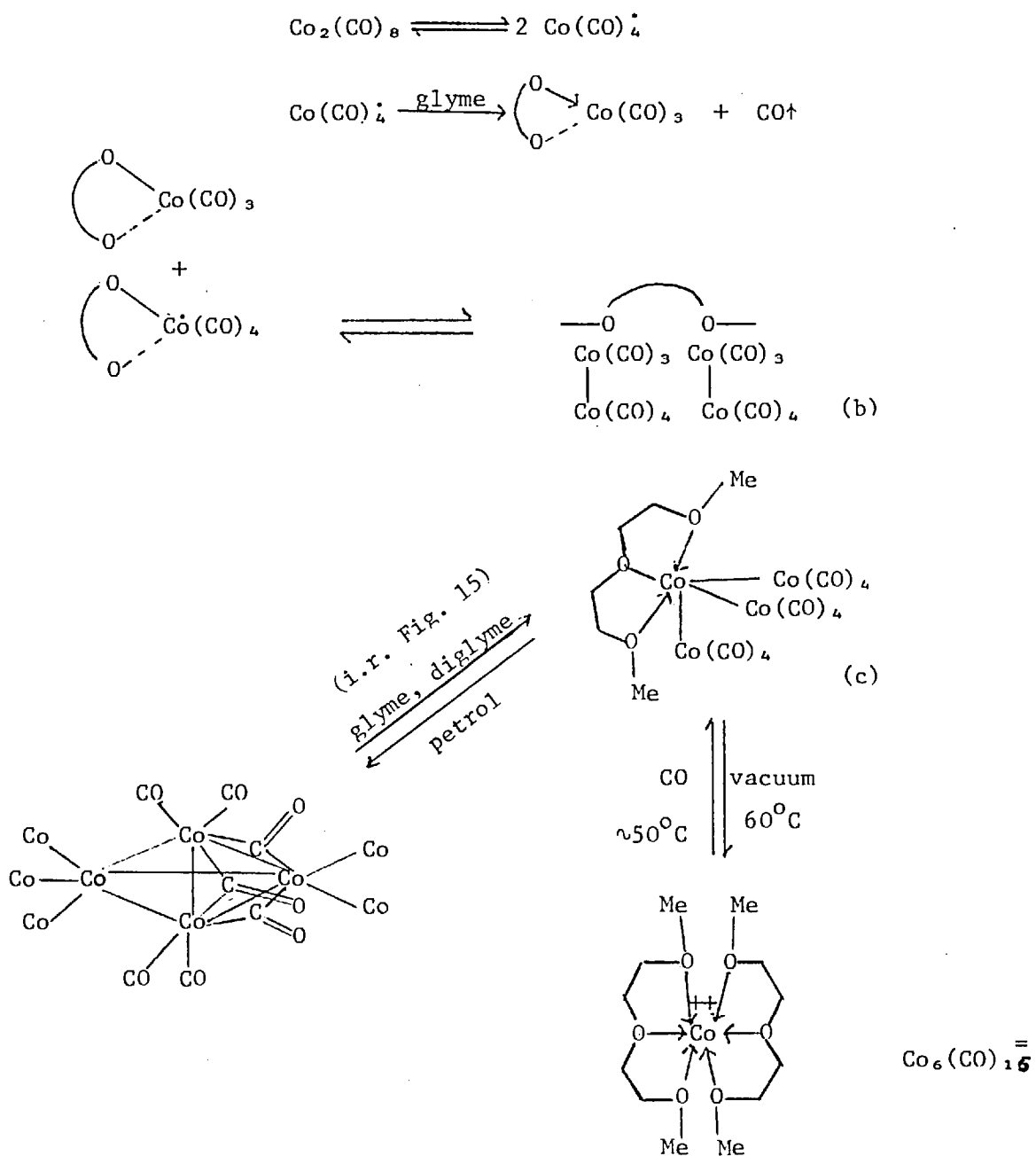
for (b) and (c)  $\Sigma_S = 0, \Sigma_S = 1$

clusterisation to  $\text{Co}^{++}\text{Co}_6(\text{CO})_{15}$  can also occur with spin conservation



if Co atoms ( $S = \frac{1}{2}$ ) are formed. Metal is always deposited during

\* Dioxane is claimed to form  $\frac{1}{2}$  dioxane  $\text{Co}^{\text{II}}\text{Co}(\text{CO})_4$  at elevated temperatures<sup>33</sup> which is probably a dioxane solvate of poly- $\text{Co}(\text{CO})_3$ .

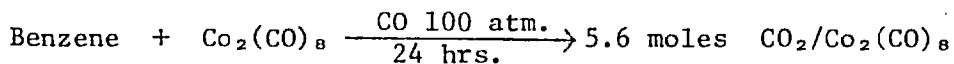
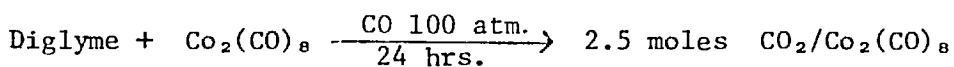
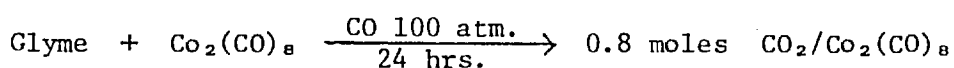


SCHEME III-1

the formation of  $\text{Co}^{++}\text{Co}_6(\text{CO})_{15}$ . Cluster (c) will carbonylate slowly at  $60^\circ\text{C}$  on bubbling CO through its diglyme solution; one new carbonyl band is observed ( $2040\text{ cm}^{-1}$ ) after 24 hours.

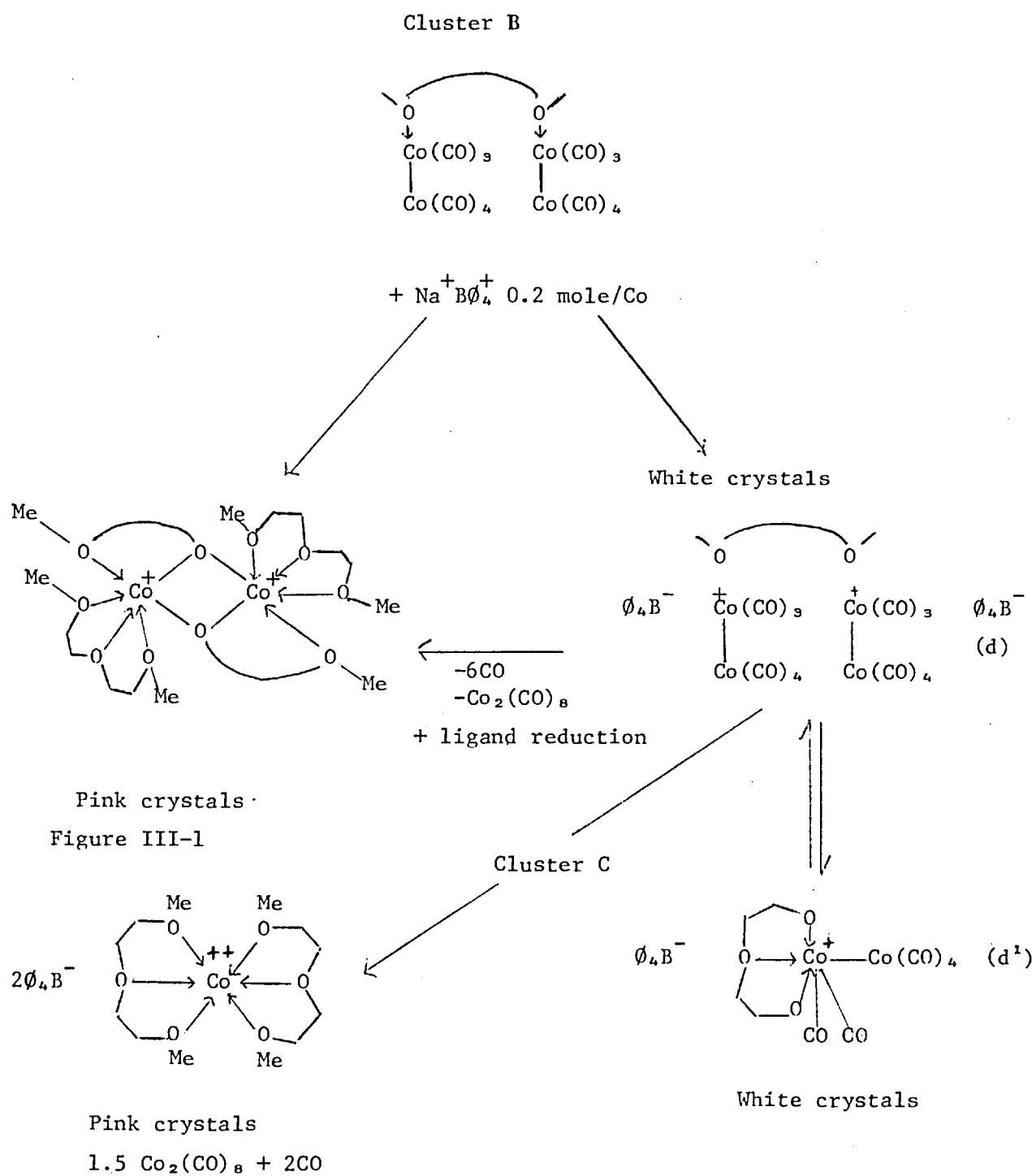
Addition of sodium tetraphenylboron to diglyme solution of cluster (b) at room temperature produces a remarkably unstable cobalt(I) complex (white) which loses  $\text{Co}_2(\text{CO})_8$  on washing with non-polar solvents; after longer times bis-diglyme  $\text{Co}^{++}(\phi_4\text{B})_2^-$  crystallises as a second product and a small amount of a binuclear cobalt(II) complex formed by solvent breakdown is obtained as a third product (see Scheme III-2 and Figure III-1).

All these clusters and radicals revert to  $\text{Co}_2(\text{CO})_8$  under CO pressure. Diglyme, glyme and 2-methoxyethanol solutions of these cobalt clusters produce only  $\text{Co}_2(\text{CO})_8$  under 100 atmospheres CO pressure at  $150^\circ\text{C}$ . At  $200^\circ\text{C}$ , decarboxylation produces carbon dioxide without solvent breakdown and solutions are yellow and contain oxygen-bonded cobalt.



In benzene solvent breakdown probably occurs but no isolable organometallic products have been obtained. It is possible that

## SCHEME III-2



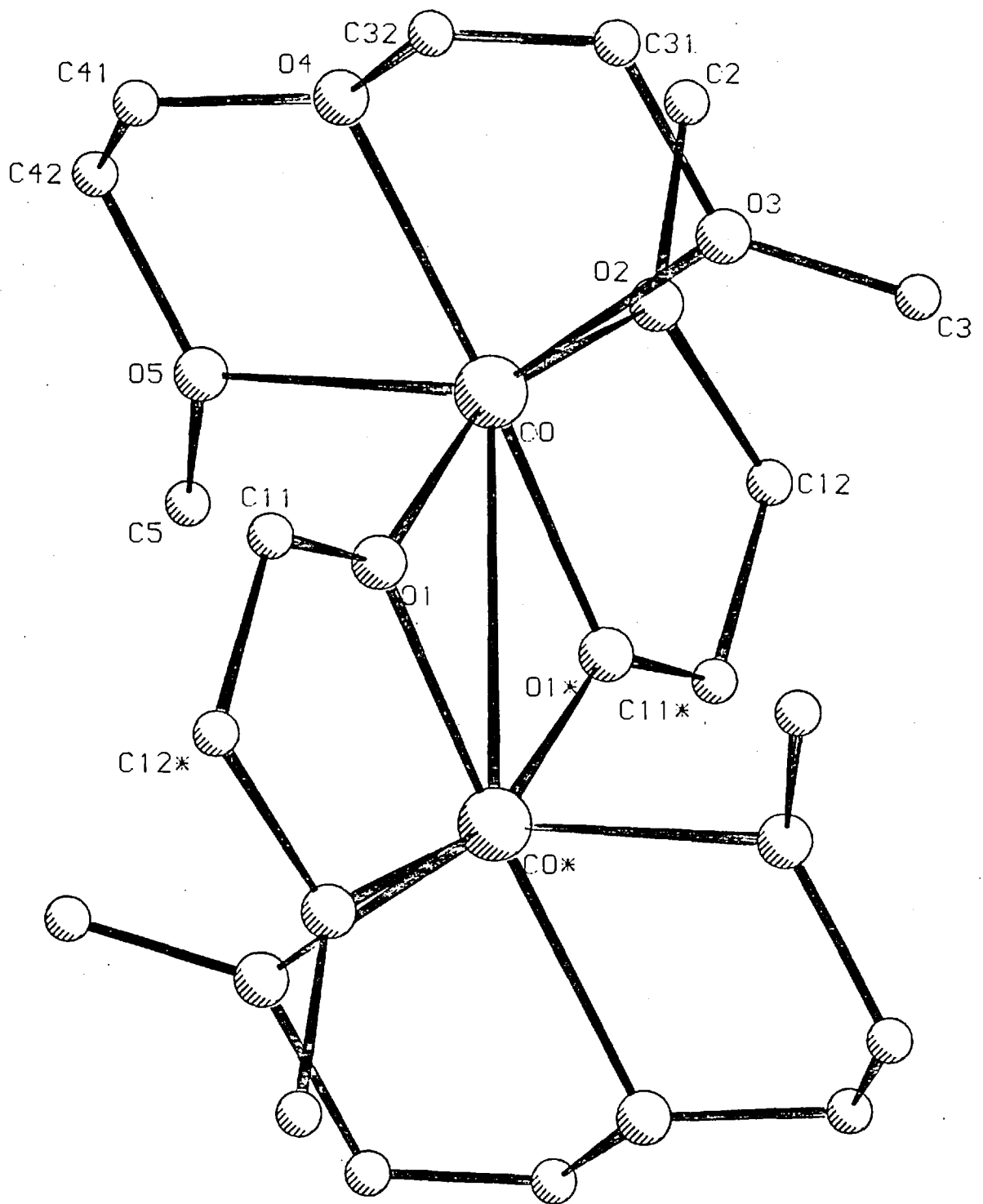
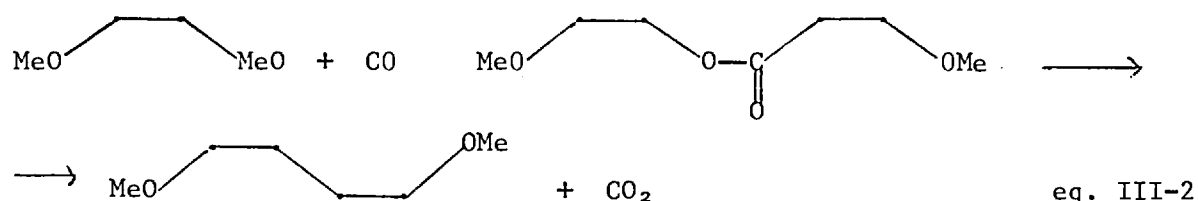


Figure III-1. Crystal structure of  $[\text{Co}_2(\mu\text{-OCH}_2\text{CH}_2\text{OCH}_3)_2(\text{diglyme})_2][\text{BPh}_4]_2$ ; The two  $\text{BPh}_4$  are omitted for clarity.

there could be a slight solvent building\* in diglyme in the presence of CO and decarboxylation of the internal ester (eq. III-2);



However, no dimethoxybutane or methoxyethylether was detected by gas chromatography. At 200°C, under 100 atmospheres H<sub>2</sub> pressure metal is quickly precipitated and with no solvent breakdown

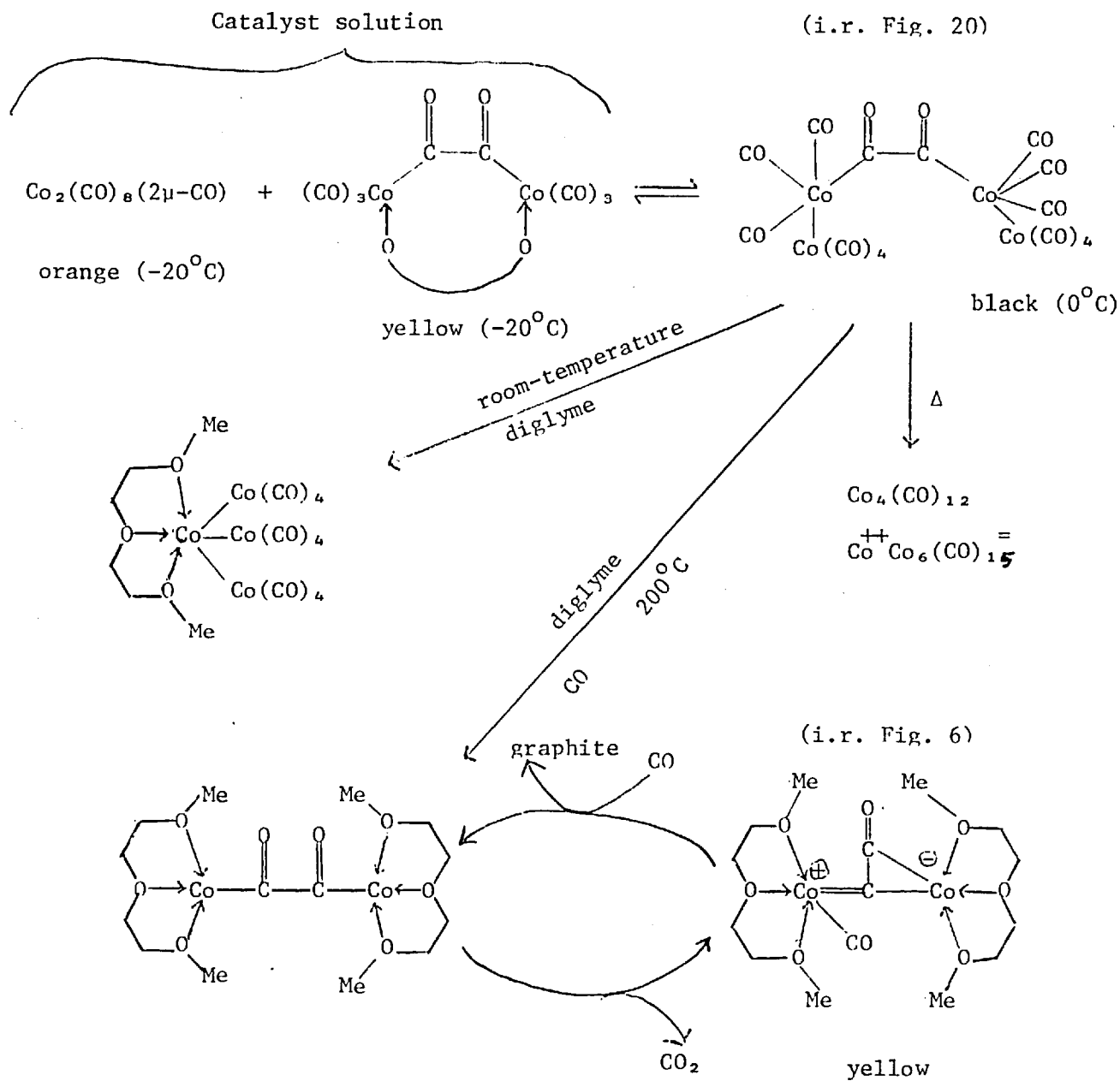
#### Isolation of Catalysts from Co<sub>2</sub>(CO)<sub>8</sub> Solutions at Temperature Control Experiments.

The autoclaves were off-gassed and the cold solution was immediately examined in an inert atmosphere. At -20°C a yellow orange solution was obtained and large orange crystals were isolated and identified as Co<sub>2</sub>(CO)<sub>8</sub> (i.r.), which converted to cluster (c) at room temperature: if the catalyst solution was allowed to warm to between 0°C and room temperature, the orange crystals dissolved and black crystals precipitated. This process was reversible (twice). The black crystals were unstable and reverted to Co<sub>4</sub>(CO)<sub>12</sub> which is also black. We assume the following equilibrium to take place (Scheme III- 3).

---

\* Solvent build up occurs in tetraglyme via internal carbonylation.





SCHEME III-3

No concrete evidence as to the nuclearity of the catalyst at 200°C was obtained, except that the colour yellow is not normally associated with cobalt clusters.

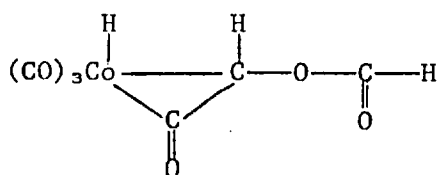
#### The Catalyst Gases.

In glyme and diglyme as solvent with CO/H<sub>2</sub> ratios of 1.5:1, the reaction is very slow over 16 - 24 hours, producing brown solutions from which cobalt carbonyl [Co<sub>2</sub>(CO)<sub>8</sub>] may be crystallised at -80°C. These solutions were trap-to-trap distilled very quickly after removing from the autoclave to yield a distillate containing a yellow crystalline material at -80°C, and a residue containing the solvent involatile products and cluster (c).

The yellow distillate, which contained acetaldehyde, ethanol and methyl formate was hydrated with H<sub>2</sub>O. The g.l.c. and <sup>1</sup>H nmr now showed the presence of methanol and above the yellow solution yellow gases were obtained. These were trapped in an i.r. gas cell and their spectra recorded. The gases cannot be HCo(CO)<sub>4</sub> because they are stable over several days at room temperature. Comparative tests suggest that sometimes the ν<sub>CH<sub>3</sub></sub> and ν<sub>CO</sub> at 2900 cm<sup>-1</sup> and 1750 cm<sup>-1</sup> respectively, may be due to a mixture of methyl formate and acetaldehyde.

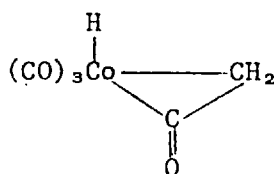
The purification of these gases proved very difficult; in the end we obtained what we believe to be three principle gases

Firstly,



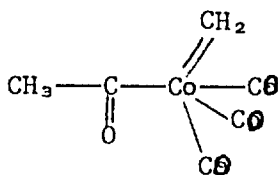
gas-1

and probably mixed with



gas-2

a third gas we believe to be



gas-3

The evidence for the structure of these gases is limited. The direct evidence is indeed their gas-phase infrared spectra and esr spectra, and a comparable gas from the reaction of ethylene with CO and  $\text{Co}_2\text{CO}_8$  in dyglyme. A spectroscopic analysis of the gases is impractical because they are always contaminated with methyl formate and sometimes acetaldehyde.

Gas-1: Is relatively stable in the gas phase, it has a carbonyl stretching frequency at  $1820 \text{ cm}^{-1}$  characteristic of a three-membered cyclic ketone, one hydride band established by deuteration studies and produces  $\text{CO}_2$  on decomposition. Its existence can be easily fitted into a mechanistic scheme, (Figures 2 and 4).

Gas-2: Is just the decarboxylated version of gas-1, which has an almost identical infrared spectrum as gas-1, but is more stable in the gas phase and does not eliminate  $\text{CO}_2$  over three days, and can be obtained from the catalyst solutions making ethanol without introduction of water, (Figure 3).

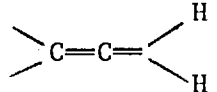
Gas-3: is very reactive, contains no carbonyl at  $1820\text{ cm}^{-1}$ .

The gas self-destructs to produce acetone, (Figure 1).

Gas-4: is made from ethylene, CO and  $\text{Co}_2\text{CO}_8$ . It is also very reactive and produces acetone. This gas is discussed later, (Figure 5).

Gas-5: is obtained from hydrolysing reaction solutions of  $\text{Co}_2\text{CO}_8$  in ethylene glycol after catalysis (Figure 7b).

Gases 1-4 are diamagnetic over the temperature range  $77^\circ$  to  $293^\circ\text{K}$ . The catalyst solutions from which gases 1-3 are obtained react with water and acetaldehyde to give methanol and acetone respectively. The gases therefore, come from a solution rich in reactive methylene ( $\text{CH}_2$ ). The precursor of these gases maybe obtained by solvent breakdown extraction of methylene or by reduction of CO.

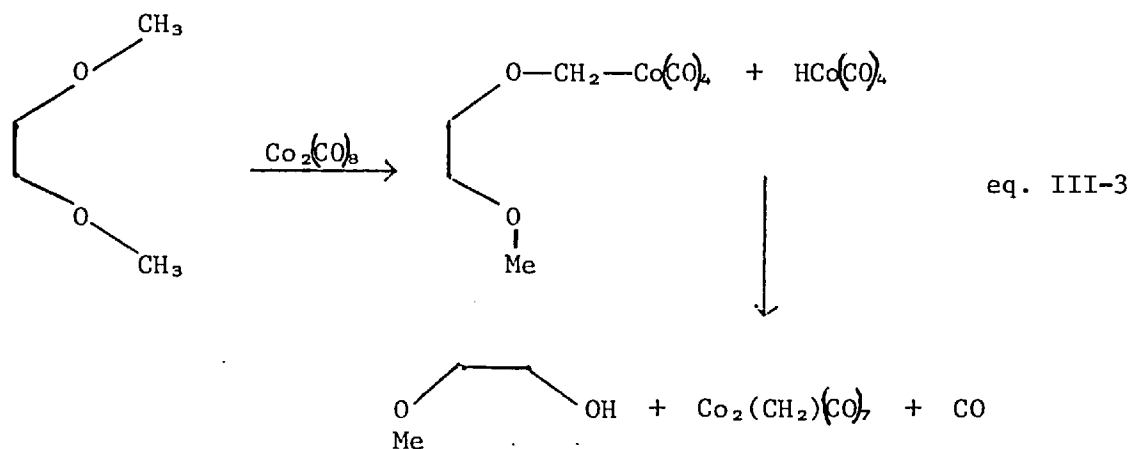
In some instances, the hydrolysis of a catalyst solution produced a volatile organic material with an absorption at  $1970\text{ cm}^{-1}$  which we believe to be an allene ( $\text{>C=C=}$  ). This, coupled with the numerous products which yield  $^{13}\text{C}$  spectra consistent with their formulation as  $(\text{RO})_4\text{C}$ ,  $(\text{RO})_3\text{CH}$ ,  $(\text{RO})_2\text{CH}_2$  and  $(\text{RO})\text{CH}_3$  have lead us to believe that the gases and products of catalysis can be obtained from the step-wise hydrogenation and carbonylation of a carbide carbon bound to two cobalts.

We believe the carbide to be hydrogenated by cobalt carbonyl hydride. These in CO rich syn-gas catalysis is slower and leads to partially hydrogenated products, amongst which are the yellow gases.

Solvent Breakdown and its Relevance to the Nature of the Catalyst.

The solvents diglyme and glyme react with  $\text{Co}_2(\text{CO})_8$  and syn-gas between 120 and 150°C to yield large amounts of methyldigol and methoxy-ethanol respectively. Experiments with deuterium showed that these products are obtained principally by solvent breakdown.

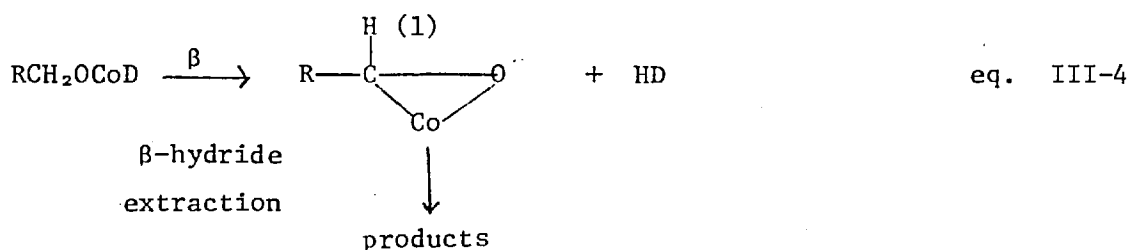
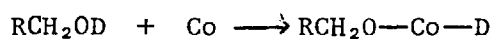
The extraction of a methylene group from the solvent by a cobalt species may lead to cobalt compounds which are active as catalysts in the conversion of syn-gas to organic products.



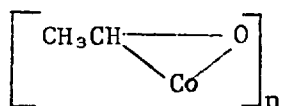
The Reaction of  $\text{Co}_2\text{CO}_8$  with syn-gas in the Solvents MeOD and EtOD as an Aid to Establish the Nature of the Cobalt Catalysts in Glyme Solvents.

The homologation of  $\text{CH}_3\text{CH}_2\text{OD}$  with  $\text{D}_2/\text{CO}$  using  $\text{Co}_2\text{CO}_8$  as a catalyst yields ethyl formate, n-propanol, i-propanol, ethylacetate and traces of propanediol, together with  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . The breaking of CH bonds must have occurred; no significant CH exchange was observed.

The homologation of  $\text{CH}_3\text{OD}$  with  $\text{D}_2/\text{CO}$  and a  $\text{Co}_2(\text{CO})_8$  catalyst yields methylformate, dimethylether, methyl acetate and a small amount of ethanol. Large quantities of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are produced. The reaction is much faster for methanol than for ethanol. Again, no significant CH exchange was observed. It appears, therefore, that a CH bond is broken, with the irreversible formation of a cobalt alkyl intermediate. This intermediate reacts to give other products (eq. III-4).



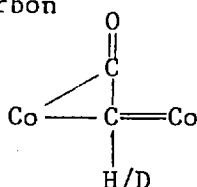
The intermediate (1) was precipitated from diglyme solutions after the catalytic reactions, to make ethanol. Its actual structure is uncertain, but its chemical analysis corresponds to



Other organic products observed in the homologation of  $\text{MeOD}$  were  $(\text{MeO})_2\text{CDH}$ ,  $\text{CH}_3\text{O}-\text{CDH}-\text{C}(=\text{O})-\text{OMe}$  and can be considered to be formed from a carbene intermediary made from syn gas and cobalt carbonyl by the catalytic route available in glymes.

Thus, for alcohols, both CH bond rupture and methylene formation can lead to organic products, but most importantly, the deuterio ethanol, formed in catalysis reactions from  $D_2/CO$  cannot exchange CD for CH after its initial formation, and therefore, the amount of deuterium in the ethanol reflects the amount in gas from which it was made.

The glyme solutions after catalytic reactions to produce ethanol are yellow coloured. Their  $^1H$  nmr spectrum shows the presence of acetaldehyde, formates, ethanol and a singlet at 2.7  $\tau$  ascribed to a carbene. Their  $^{13}C$  nmr shows signals corresponding to ethanol, acetaldehyde, ethyl formate and  $(EtO)_2CDH$  and  $(EtO)_3CD/H$  and also a signal at 160.5ppm, corresponding, we believe to the carbene carbon



We could not detect metal carbonyl signals.

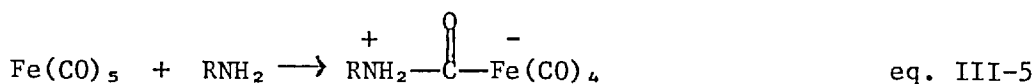
The carbene is the precursor of the yellow gases and the polyalkoxy products.

#### Isolation of Catalyst From Other Metal Carbonyl Systems.

When  $Fe(CO)_5$  and  $Ru_3(CO)_{12}$  are dissolved in 2-methoxyethanol under syn-gas mixtures and the solutions are recovered after reaction and gas blow off, the solutions show no carbonyl bands in the infrared and no free carbon monoxide. After about 1 day the carbonyl bands reappear,  $Fe(CO)_5$  can be distilled out and  $Ru_3(CO)_{12}$  crystallised. Manganese  $[Mn_2(CO)_{10}]$  and chromium  $[Cr(CO)_6]$  solutions in

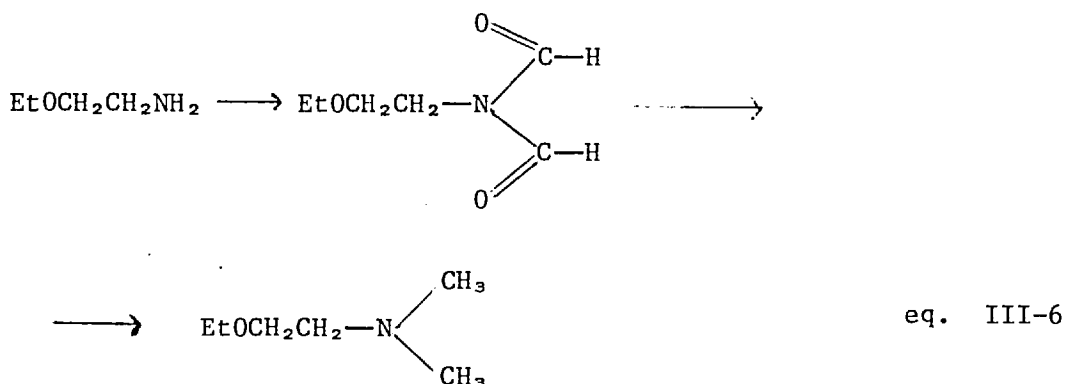
2-methoxyethanol under the same conditions show only the presence of the pure carbonyl in the infrared spectra.

It has been known for many years that amines activate iron pentacarbonyl<sup>35</sup> in the following manner (eq. III-5):



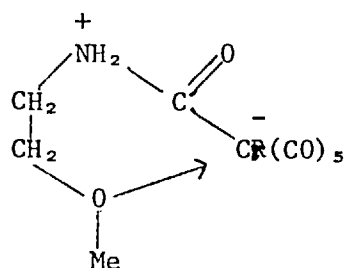
we therefore investigated 2-ethoxyethylamine as a solvent.

The rates of reaction were initially high for cobalt. This was due to the carbonylation and hydrogenation reaction (eq. III-6).



Dimethyl(2-ethoxyethyl) amine was recovered in 100% yield.

However, with the less reactive chromium carbonyl where, for instance, little or no absorption was observed, we isolated a white unstable complex:



v i.r.  $\text{Cr}(\text{CO})_5$  1970  $\text{cm}^{-1}$ , 1870  $\text{cm}^{-1}$

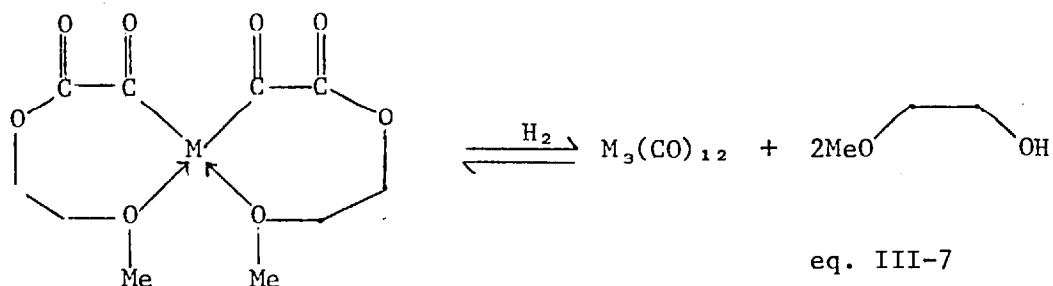
v  $\overset{\text{O}}{\parallel}{\text{C}}$  1725  $\text{cm}^{-1}$

v  $\text{—NH}_2$  3100  $\text{cm}^{-1}$   
+



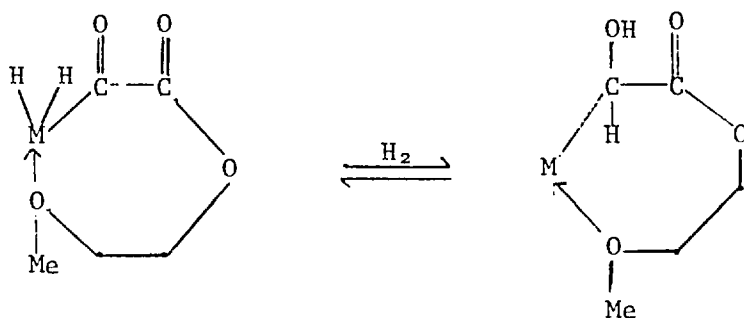
This reverted to  $\text{Cr}(\text{CO})_6$  and 2-ethoxyethylamine on drying or washing with other solvents, (Figure 9).

We believe that in the case of Fe, Ru and Os carbonyls, the solutions of 2-methoxyethanol contain either mono- or doubly-inserted carbon monoxide bound in a ketonic fashion, such that after reaction deinsertion and hydrogenation leads to polynuclear carbonyls (eq. III-7).

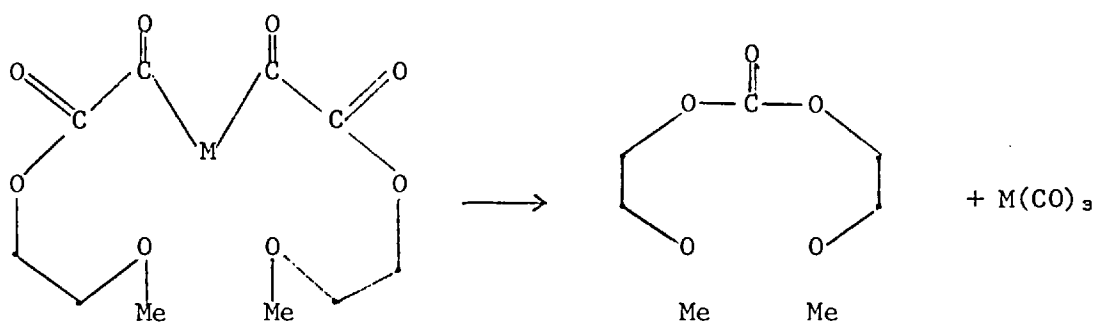


M = Ru, Os, Fe [When M = Fe:  $\text{Fe}(\text{CO})_5$ ]

The role of hydrogen in this respect is mysterious and it may be that partial reduction is reversible (eq. III-8),



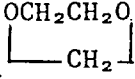
providing a pathway for 2-methoxyethanol formation, or that reductive coupling of the solvent is the only way of regenerating the metal carbonyls (eq. III-9). Metal hydride signals were detected in the  $^1\text{H}$  nmr of osmium catalysts, and by partial  $^1\text{H}$  decoupling in the  $^{13}\text{C}$  of ruthenium catalysts (Chapters IV, V).



eq. III-9

Certainly, product analysis shows that besides the volatile methanol, acetone, dimethyl and diethylether (the catalysis products) the major heavy products come from solvent build-up and reductive elimination. These products are listed in the cobalt section (see page

#### The Cobalt Catalyst in 2-Methoxyethanol Solutions.

The preparation of ethylene glycol in 2-methoxyethanol is best achieved using dilute solutions of cobalt carbonyl. The major products are then ethylene glycol and 1,3-dioxolane  $\text{OCH}_2\text{CH}_2\text{O}$  . High concentration of cobalt produce bis(2-methoxyethoxy)-methane which is observed in all metal carbonylsyn gas reactions in 2-methoxy ethanol together with 2-methyl-1,3-dioxalane. A detailed list of the G.C.-mass spectra is given in Table III-1.

The cobalt distills with alcohol derivatives as was observed in the formation of methyl digol. Thus, distillation of the products methyl digol, methoxyethanol, or ethylene glycol yields inseparable solutions of alcohol bound cobalt. Many solutions have  $\nu_{\text{CO}}$  1890 and  $1725 \text{ cm}^{-1}$  and are colourless and yield formates on exposure to moisture. Sometimes a solution containing  $\nu_{\text{CO}}$  2050, 2020, 1990 and  $1728 \text{ cm}^{-1}$  was obtained. This ~~loses~~  $\nu_{\text{CO}}$  2050, 2020 and  $1990 \text{ cm}^{-1}$  after several hours.

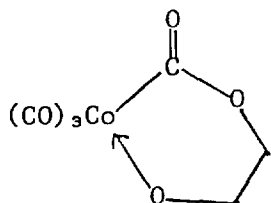
Table III-1. Organic products from CO and H<sub>2</sub> and from solvent breakdown or build up in the reactions with Co, Ru, Os, Cr, Mn and Fe carbonyls, identified by g.l.c., i.r., <sup>1</sup>H nmr, <sup>13</sup>C nmr and GC/MS spectra.

| Catalyst                           | GLYME                                                                                                          |                                                                                                                              | DIGLYME                                                                                                                        |                                                                                                | 2-METHYOXYETHANOL                                                                                                                                                        |                                                                                                                                        |
|------------------------------------|----------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|
|                                    | From CO/H <sub>2</sub>                                                                                         | From Solvent                                                                                                                 | From CO/H <sub>2</sub>                                                                                                         | From Solvent                                                                                   | From CO/H <sub>2</sub>                                                                                                                                                   | From Solvent                                                                                                                           |
| Co <sub>2</sub> (CO) <sub>8</sub>  | Ethanol<br>n-propanol<br>i-propanol<br>ethylformate<br>hydroxyethyl-<br>formate<br>acetone<br><br>acetaldehyde | 2-methoxyethanol<br>2-ethoxyethanol<br>methanol<br>methylformate<br>2-methoxyethyl-<br>formate<br>2-methoxyethyl-<br>acetate | Ethanol<br>n-propanol<br>i-propanol<br>ethylformate<br>hydroxyethyl-<br>formate<br>diethylether<br>acetone<br><br>acetaldehyde | Methylformate<br>methyldigol<br>methyldigol-<br>formate<br>methyldigol-<br>acetate<br>methanol | Acetone<br>ethanol<br>hydroxyethyl-<br>formate<br>ethylformate<br>1,3-dioxolane<br>diethoxymethane<br>triethoxymethane<br><br>ethylene glycol<br>ethylene glycol acetate | Bis(2-methoxyethyl)-<br>carbonate<br>bis(2-methoxyethoxy)-<br>methane<br>2-methoxyethylformate<br>2-methoxyethylacetate<br>methyldigol |
| Ru <sub>3</sub> (CO) <sub>12</sub> |                                                                                                                |                                                                                                                              |                                                                                                                                |                                                                                                | Methanol<br>methylformate<br>ethylformate<br>ethanol<br>hydroxyethyl-<br>formate<br>propanol<br>acetone<br><br>2-methyl-1,3-dioxolane                                    | 2-methoxyethylformate<br>2-methoxyethylacetate<br>bis(2-methoxyethyl)-<br>carbonate<br>bis(2-methoxyethoxy)-<br>methane<br>methyldigol |

Table III-1, (continued).

| Catalyst                           | GLYME                  |              | DIGLYME                |              | 2-METHOXYETHANOL                                                                      |                                                                                                               |
|------------------------------------|------------------------|--------------|------------------------|--------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
|                                    | From CO/H <sub>2</sub> | From Solvent | From CO/H <sub>2</sub> | From Solvent | From CO/H <sub>2</sub>                                                                | From Solvent                                                                                                  |
| Os <sub>3</sub> (CO) <sub>12</sub> |                        |              |                        |              | Methanol<br>hydroxyethyl-<br>ethylformate<br>ethylformate<br>methylformate<br>ethanol | 2-methoxyethylformate<br>2-methoxyethylacetate<br>bis(2-methoxyethoxy)-<br>methane<br>methyldigol             |
| Cr(CO) <sub>6</sub>                |                        |              |                        |              | diethylether<br>acetone                                                               | 2-methoxyethylacetate<br>2-methoxyethylformate<br>diglyme<br>methyldigol                                      |
| Mn <sub>2</sub> (CO) <sub>10</sub> |                        |              |                        |              | ethylformate<br>hydroxyethyl-<br>formate                                              | 2-methoxyethylacetate<br>diglyme<br>methyldigol<br>bis(2-methoxyethoxy)-<br>methane                           |
| Fe(CO) <sub>5</sub>                |                        |              |                        |              | diethylether<br>dimethylether<br>acetone                                              | 2-methoxyethylacetate<br>bis(2-methoxyethyl)-<br>carbonate<br>bis(2-methoxyethoxy)-<br>methane<br>methyldigol |

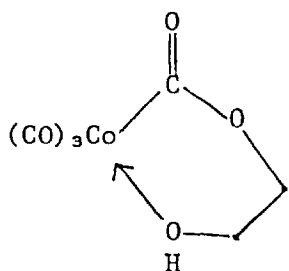
We formulate these complexes in the following way (Scheme III-4):



Me

Stable, colourless,

$\nu_{\text{CO}}$  1890 and 1725  $\text{cm}^{-1}$

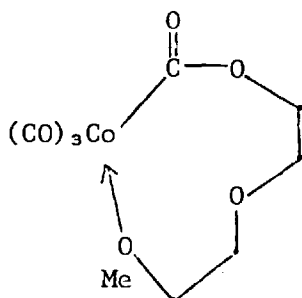


H

Unstable, colourless,

$\nu_{\text{CO}}$  2050 and 1990  $\text{cm}^{-1}$   
2020 1728

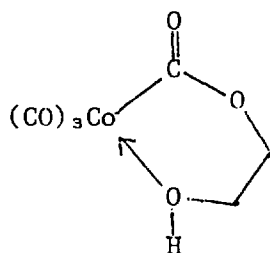
(turns yellow after several hours).



Me

Colourless,  $\nu_{\text{CO}}$  1890 and 1725  $\text{cm}^{-1}$

$\text{H}_2\text{O}/\text{air} \rightarrow$  methyldigol formate

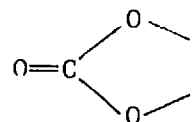


H



$\text{HCo}(\text{CO})_3$

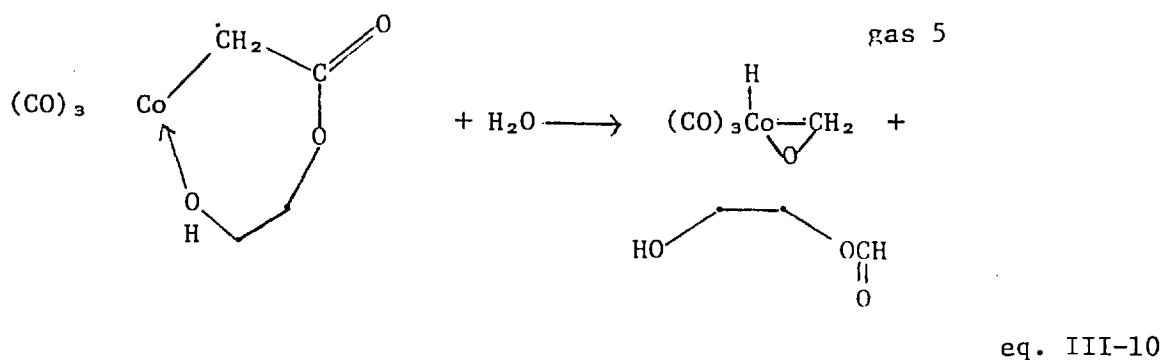
+



Possible decomposition  
route

Scheme III-4

A yellow unstable gas can be obtained from the catalyst solutions in 2-methoxyethanol. Its i.r. spectrum is similar to that for gas 3. (eq. III-10).



#### The Gas Chromatography-Mass Spectrum as an Aid to Catalyst Definition.

The G.C. - M.S. of reaction in diglyme and 2-methoxyethanol show clearly that cobalt can be distilled from the reaction solution coordinated to glycol and digol derivatives. Distillation in air causes the complexes to carbonylate and hydrolyse to formates and acids.

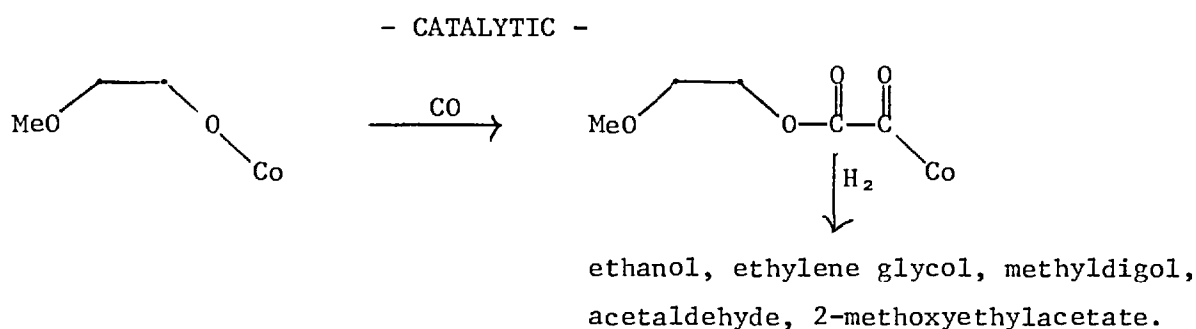
A detailed analysis of the products of reaction from the preparation of ethylene glycol in 2-methoxyethanol as obtained from the G.C.-M.S. is given in Table III-1. The G.C.-M.S. shows clearly that reaction continues over several days in these solutions under ambient conditions. None of these cobalt-bonded polyol derivatives can be complex to phosphines or methyl iodide.

The G.C.-M.S. of the breakdown on Fe, Ru and Os catalyst solutions after removal of volatiles and solvent and vacuum distillation show exactly the same products as in the cobalt case. These products correspond to condensation products of glycol, 2-methoxyethanol and methylene (see Scheme III-4 and Table III-1). It is quite clear that any transition metal can act as a template for polyol condensation.

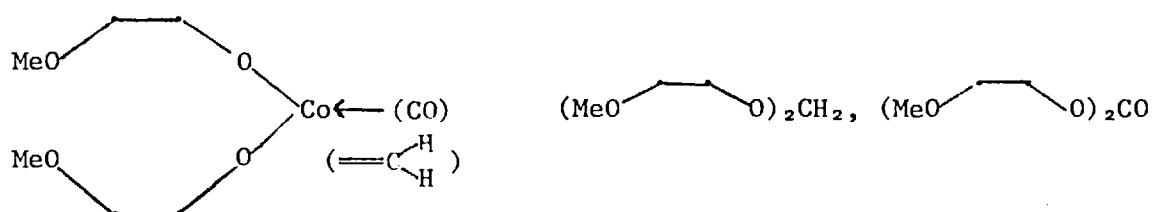
#### Solvent Reaction in 2-Methoxyethanol.

The major products in 2-methoxyethanol due to solvent reaction are methyldigol, propanediol, 2-methoxyethylacetate and bis(2-methoxyethoxy)methane. In the presence of cobalt catalyst over a period of days at ambient temperature, further high boiling-point glymes and polyols are formed.

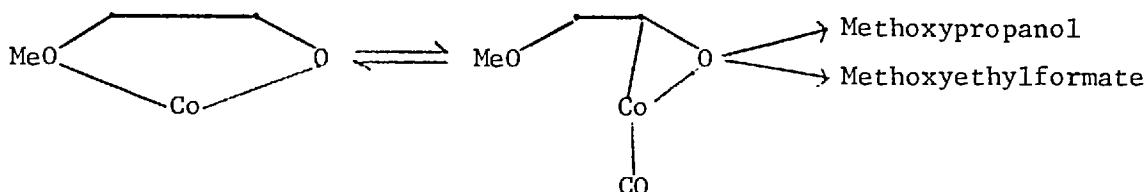
The major processes can thus be tabulated (Scheme III-5).



#### - COUPLING -



## - HOMOLOGATION -



Scheme III-5

As an illustration that the catalytic route in our Scheme is correct, the compound  $(\text{CO})_4\text{Co}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_2\text{CH}_2\text{OCH}_3$  made in the laboratory from  $\text{NaCo}(\text{CO})_4$  and  $\text{Cl}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_2\text{CH}_2\text{OCH}_3$  is reduced with hydrogen gas at 5 atmospheres to a one-to-one mixture of acetaldehyde and 2-methoxyethanol (+ polymers).

The reaction of all metal carbonyls in 2-methoxyethanol produce, by solvent reaction bis(2-methoxyethoxymethane), propanediol and methyldigol, together with small amounts of 1,3-dioxolane 2-methyl-1,3-dioxolane and bis(methoxyethyl)-carbonate . Thus, the primary reaction of metal carbonyls is the loss of terminal CO by an insertion reaction with the formation of formates which are relatively stable, this is followed by further CO insertion and hydrogen reduction to yield products. The mechanism is illustrated in the next Chapter.



## CHAPTER IV

### THE MECHANISM OF THE HOMOGENEOUS HYDROGENATION OF CARBON MONOXIDE

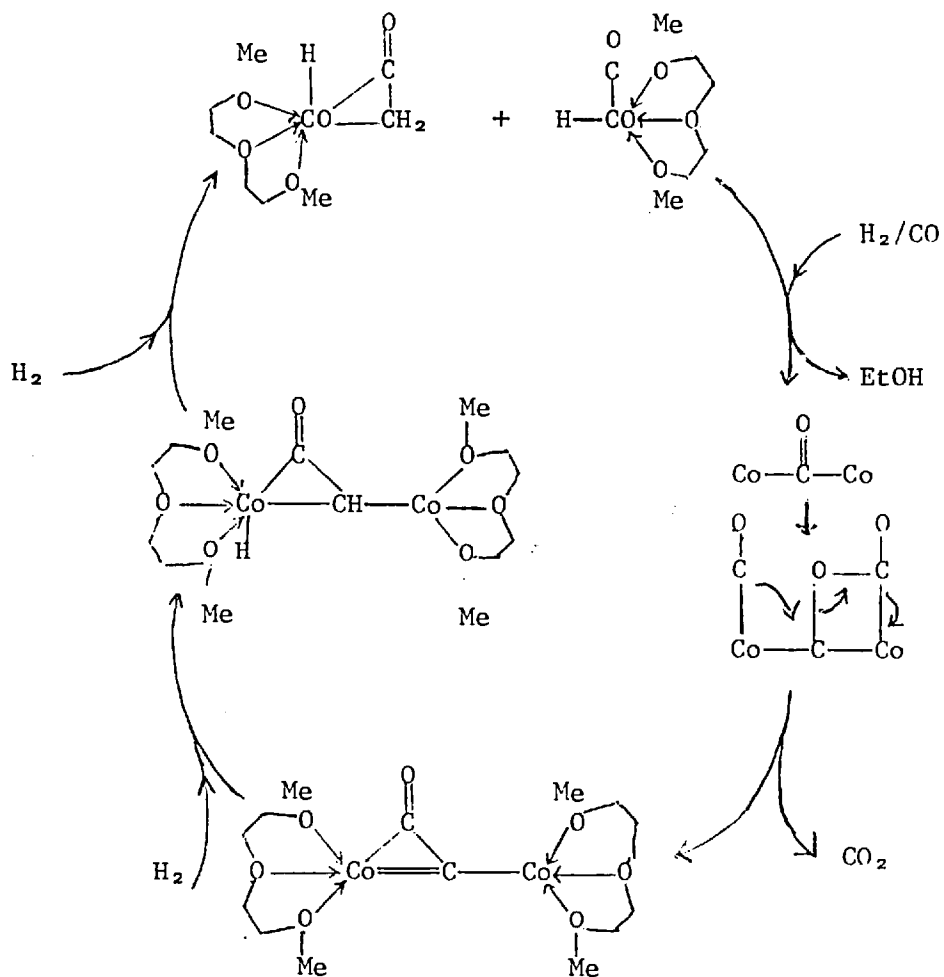
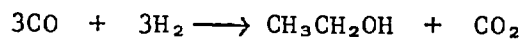
#### INTRODUCTION

In the previous chapters we have presented some rather superficial and intuitive mechanism for carbon monoxide reduction. We present now a more formal analysis of the mechanism of the reactions involved in the production of all organic products.

#### THE FORMATION OF ETHANOL USING COBALT CATALYSTS

Two pieces of information have led us to believe that ethanol is primarily formed by a decarboxylation mechanism at 200°C.

Firstly, the best syn-gas ratio for ethanol is CO/H<sub>2</sub> 1:1 secondly, the isolation of up to 50% theoretical of CO<sub>2</sub>, based on equation III-1 . However, it is clear that ethanol can also be formed in a solvent breakdown reaction. We propose the following mechanism:

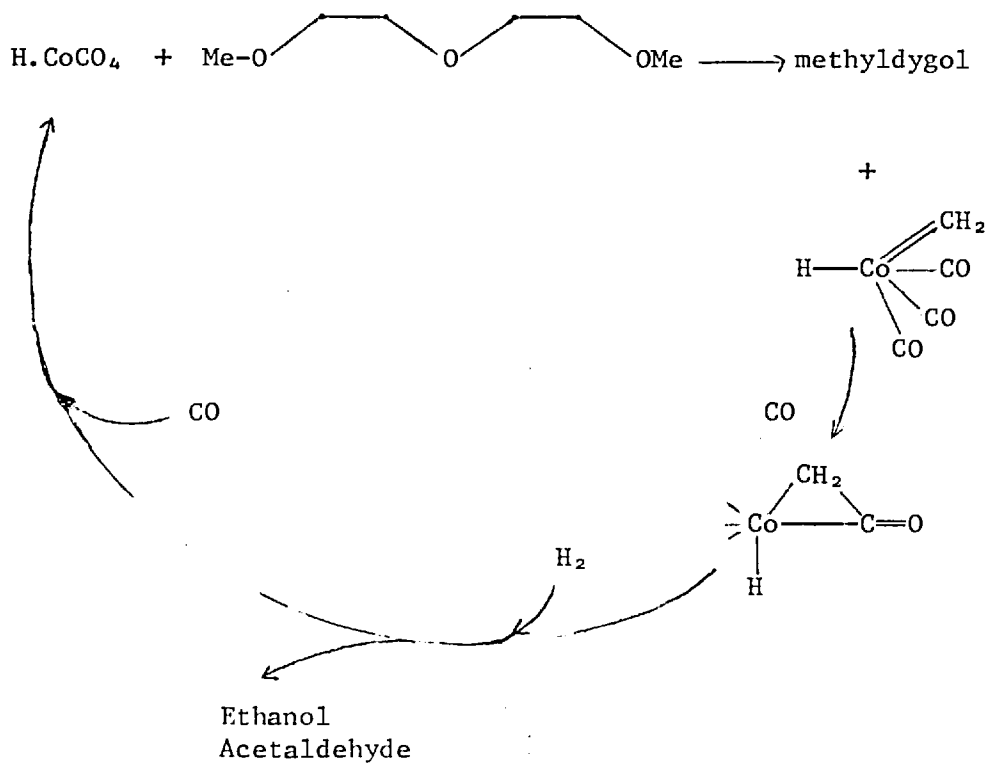


Scheme IV-1

As the reaction progresses another mechanism becomes possible due to the presence of alcohols.



The active part of the catalyst can be formed from solvent breakdown, e.g., for diglyme

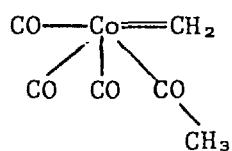


Scheme IV-3

The product of the reaction of glyme with cobalt carbonyl in the presence of water support our theory of carbene formation.

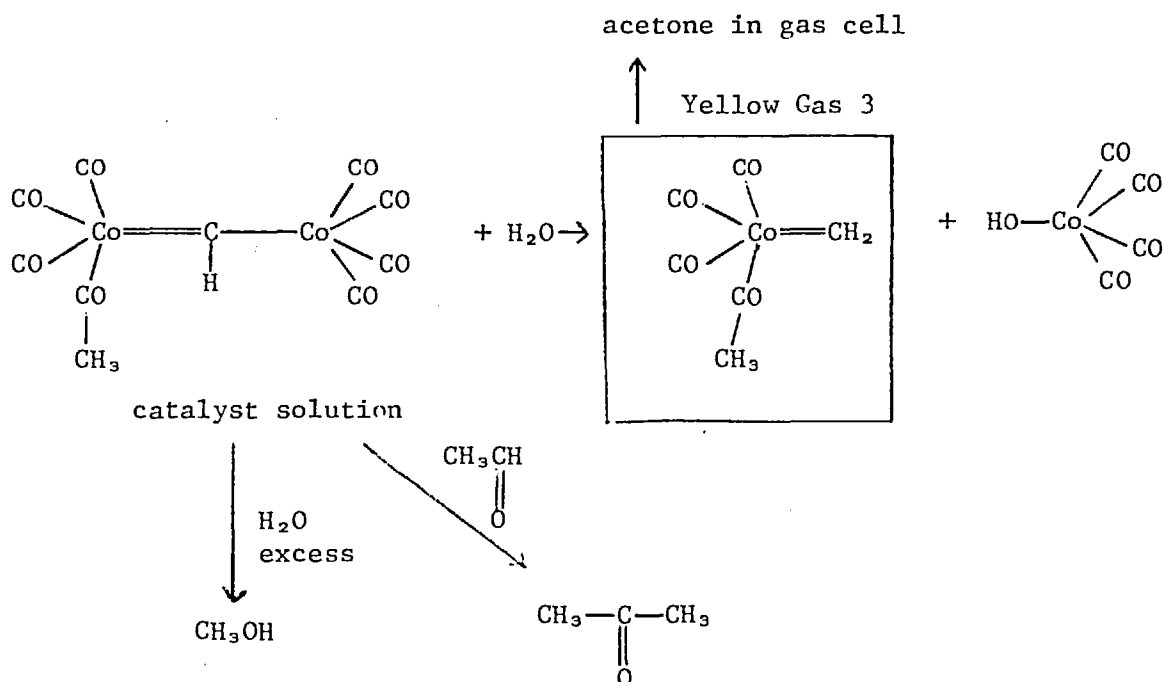
Normally a carbene reacts with water to give methanol. Under high CO pressure and  $150^{\circ}\text{C}$  the carbene attacks water resulting in the formation of methylformate exclusively. No methanol is formed (Scheme IV-4 and IV-5).

The Gas 3,



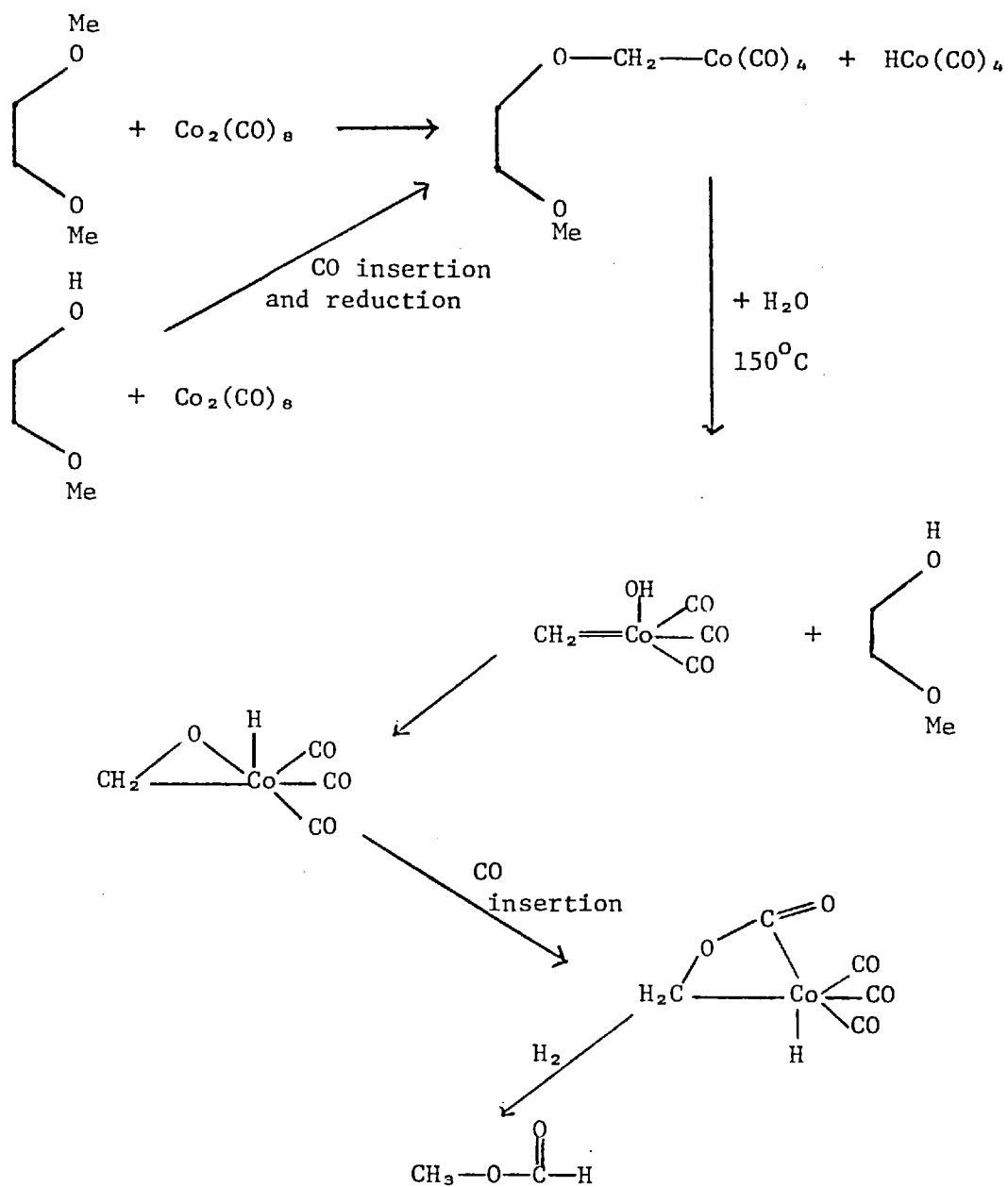
Methanol and Acetone Formation

on Two Cobalts. Bench Experiment..



SCHEME IV-4

Formation of Methyl formate, Catalytic Experiment.



SCHEME IV-5

### DEUTERATION STUDIES.

Studies with mixtures of deuterium and carbon monoxide have proved only of limiting value in determining the reaction mechanisms.  $D_2$ -syn-gas reactions with cobalt catalysts yield clearly ethanol and acetates in which the D/H ratio in the  $CH_2CH_3$  group is as high as four to one. On the other hand, solvent breakdown in glyme or diglyme yields methoxyethanol methylformate, and methyldigol containing no deuterium. We believe that hydroxy ethylformate is made by the catalytic hydrogenation processes but, as yet, we have not isolated this as a pure substance. (Scheme IV-6). Ethyl formate also contains deuterium.

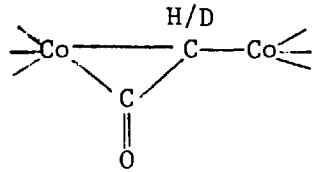
We believe that there are at least three ways to make ethanol:  
 The solvent breakdown route (Scheme IV-3)  
 The decarboxylation route (Scheme IV-1,6)  
 The alkoxide route (Scheme IV-2).  
 and we believe that all are operative in all dioxygen solvents. Furthermore we have to accept that the catalyst changes as the reaction proceeds. Clearly, in diglyme at the start of the reaction (which is slow) the main catalytic pathways are those using solvent breakdown and decarboxylation. As the reaction proceeds a mechanism involving an alkoxide (which is faster) can become more important.

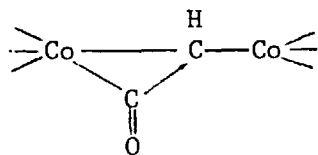
We believe we have established in the catalytic solutions after the reaction, the presence of cobaltacarbene precursors of the hydrido-cobaltacyclopropanones. The evidence for these carbenes is from  $^{13}C$  nmr and the presence of products derived from a carbene carbon atom (Table IV-1). By the end of the reaction the carbene has incorporated deuterium and hydrogen in a ratio which reflects that in the methyldigol OH group, and the hydrogen gas  $H_2/D_2$ .





Table IV-1.  $^{13}\text{C}$  nmr and  $^1\text{H}$  nmr of a diglyme solution after reaction with  $\text{Co}_2(\text{CO})_8$  and  $\text{CO}/\text{H}_2$  (or  $\text{CO}/\text{D}_2$ ) (1:1) at  $200^\circ\text{C}$ . Reaction time 24 hrs.

|                                                                                   |                                 | $^{13}\text{C}$ nmr (TMS = 0) from the reaction with $\text{CO}/\text{D}_2$ (1:1) |                            |                        |                 |
|-----------------------------------------------------------------------------------|---------------------------------|-----------------------------------------------------------------------------------|----------------------------|------------------------|-----------------|
|  | 169.5 ppm                       | triplet (1:1:1)                                                                   | for C-D                    | } H/D ratio            |                 |
|                                                                                   |                                 | singlet                                                                           | for C-H                    |                        | $\frac{1}{1.5}$ |
| $\text{CD}_3\text{-CD}_2\text{OD}/\text{H}$                                       | $\text{-CD}_3$ 16 ppm           | heptet                                                                            | for $\text{-CD}_3$         | } $\sim \frac{1}{4}$   |                 |
|                                                                                   |                                 | quintet                                                                           | for $\text{-CD}_2\text{H}$ |                        |                 |
|                                                                                   | $\text{-CD}_2\text{-}$ 54.5 ppm | quintet                                                                           | for $\text{-CD}_2\text{-}$ | } $\sim \frac{1}{4}$   |                 |
|                                                                                   |                                 | triplet                                                                           | for $\text{-CDH-}$         |                        |                 |
| $(\text{EtO})_4\text{C}^*$                                                        | 145 ppm                         | singlet                                                                           |                            |                        |                 |
| $(\text{EtO})_3\text{CD}/\text{H}$                                                | 129 ppm                         | triplet                                                                           | for $\text{>CD}$           | } $\sim \frac{1}{1.5}$ |                 |
|                                                                                   |                                 | singlet                                                                           | for CH                     |                        |                 |
| $(\text{EtO})_2\text{C}(\text{D}/\text{H})_2$                                     | 94 ppm                          | triplet                                                                           | for CDH                    | } $\sim \frac{1}{1.5}$ |                 |
|                                                                                   |                                 | singlet                                                                           | for $\text{-CH}_2$         |                        |                 |



$^1\text{H}$  nmr (TMS  $\tau=10$ ) reaction  $\text{CO}/\text{H}_2$  (1:1)

$\tau = 2.75$  ppm      singlet

$d_3$ -Acetate formation is easily explained by a double insertion into an alkoxide followed by selective reduction (Scheme IV- 7). It is undoubtedly the predominant reaction in hydroxyglyme solvents using a cobalt catalyst with CO/D<sub>2</sub> ratios higher than 1:1.

In methoxyethanol solvents, the results of using D<sub>2</sub>-syn-gas indicate unambiguously the presence of deuteriated ethanol and acetates. We believe most of the ethylene glycol to come from solvent breakdown.

It was shown unambiguously that methanol produced in reaction of D<sub>2</sub>-syn-gas with ruthenium carbonyl in methoxy ethanol is fully deuteriated at the carbon atom.

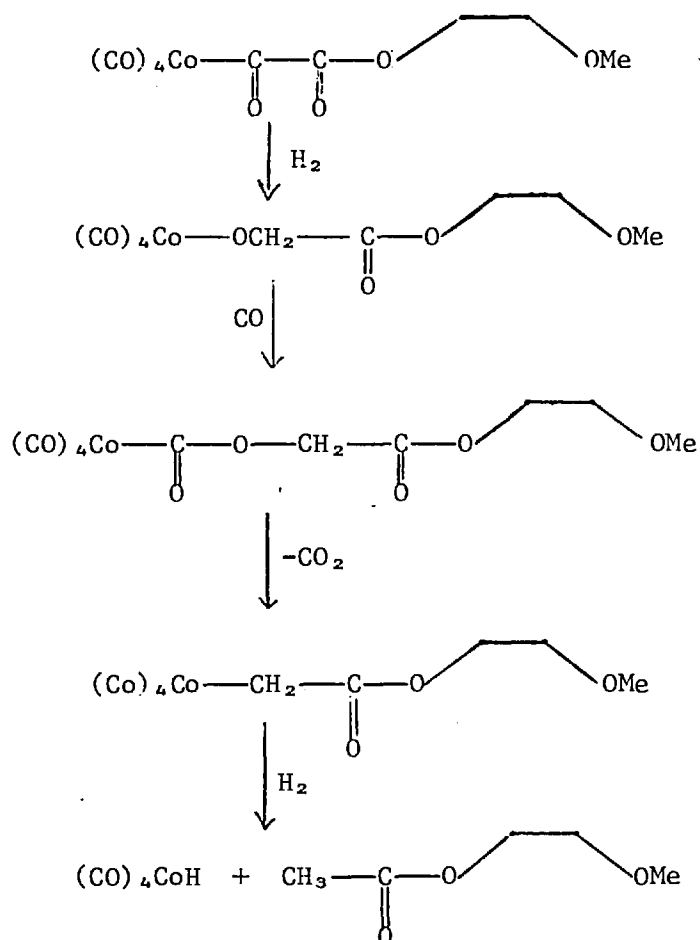
#### Mechanism of Formation of Organic Products from Iron, Ruthenium and Osmium Carbonyl Catalysts.

The predominant unifying feature for the iron and ruthenium catalysts is the total absence of terminal or metal bridging carbonyl bands in the infrared immediately after the reaction.

The osmium case is more complicated, carbonyl bands were observed immediately after the reaction and two known osmium hydride carbonyl clusters were isolated ( $H_2OsCO_4$ , <sup>36</sup> $H_2Os_2CO_8$  <sup>37</sup>).

$FeCO_5$ ,  $RuCO_5$ ,  $Ru_3CO_{12}$ ,  $Os_3(CO)_{12}$  and unidentifiable iron and ruthenium alkoxides were secondary products. The

Acetates (CO-rich Syn-Gas) From Formates at 200°C



1. reduction
2.  $\beta$ -hydride shift
3. oxygen coordination

SCHEME VI-7

evidence for intermediary ruthenium hydrides is not direct; in a 0 to 10 ppm decoupled  $^{13}\text{C}$  spectrum of the ruthenium reaction solution, trace carbon peaks in the region 0 to 3 ppm ( $^{13}\text{C}$ ) showed a weak  $^1\text{H}$  coupling which must come from a terminal or bridging metal hydride outside the range of the decoupler.

Our mechanisms for the catalysis based on iron, ruthenium and osmium are essentially the same, and are very simple. They involve either terminal or bridging alkoxide ligands (Scheme IV-8). No evidence for the nuclearity of the catalysts could be obtained, but binuclearity gives simpler catalytic cycles (Scheme IV-9), (Figures 10, 11, and 12).

C-1 hydrocarbon products are considered formed by a carbene mechanism, which can explain adequately all products.

No  $\text{CO}_2$  is produced in the process to make methanol and therefore as ruthenium is a gas-shift catalyst, water is probably not formed either. We did not test for this.

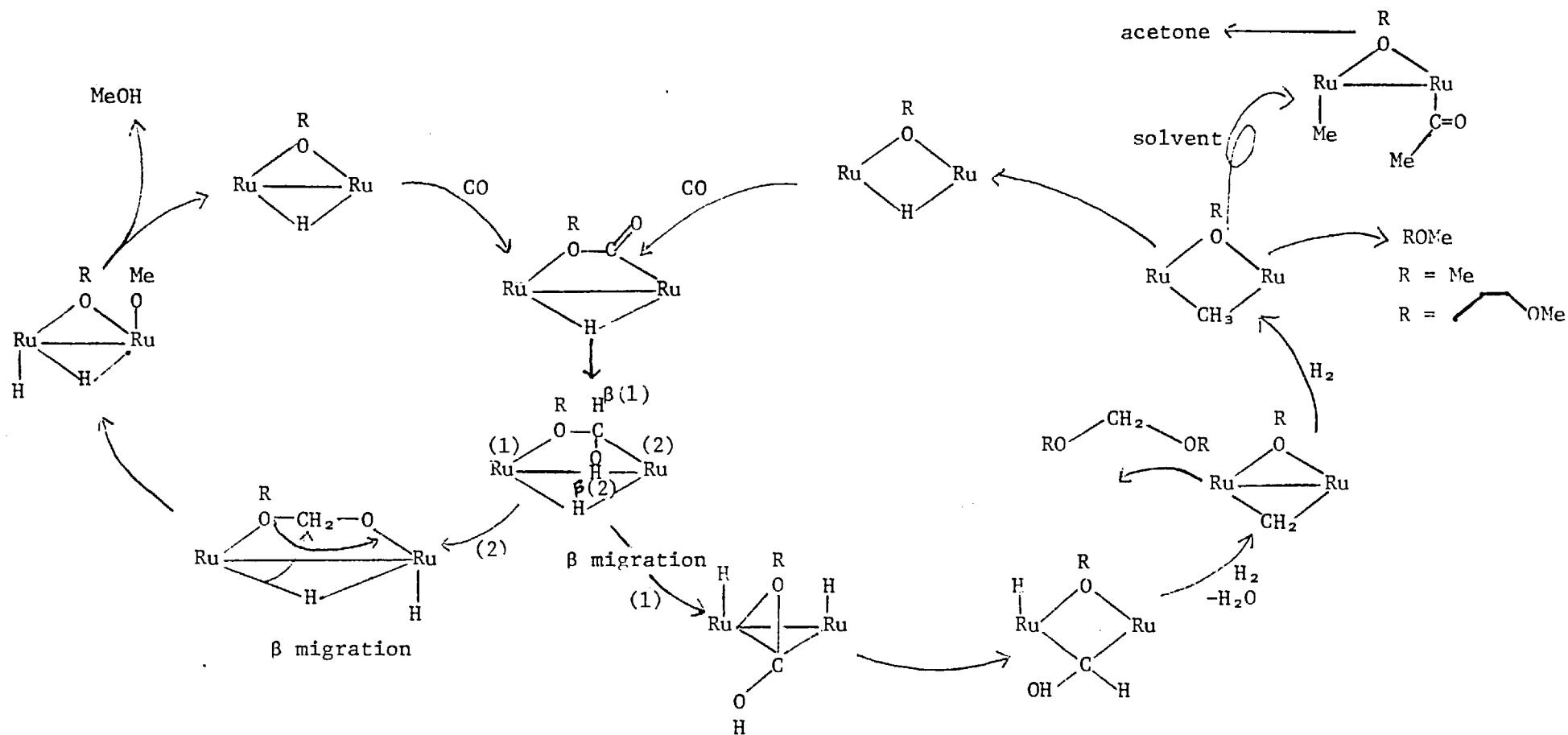
The best condition to make methanol with the ruthenium catalyst is with  $\text{H}_2/\text{CO}$  ratios of 2:1, and therefore, we consider that water, together with  $\text{CO}_2$  comes from the secondary products, acetone and dimethylether, (Scheme IV-9).

#### The Mechanism for Manganese Catalysts.

The products of reaction using manganese catalyst are hydroxyethylformate and ethylformate. Manganese is clearly an element in which double CO insertion is predominant, similar to cobalt, leading to C-2 products. The recovered catalyst was  $\text{Mn}_2(\text{CO})_{10}$  only and no

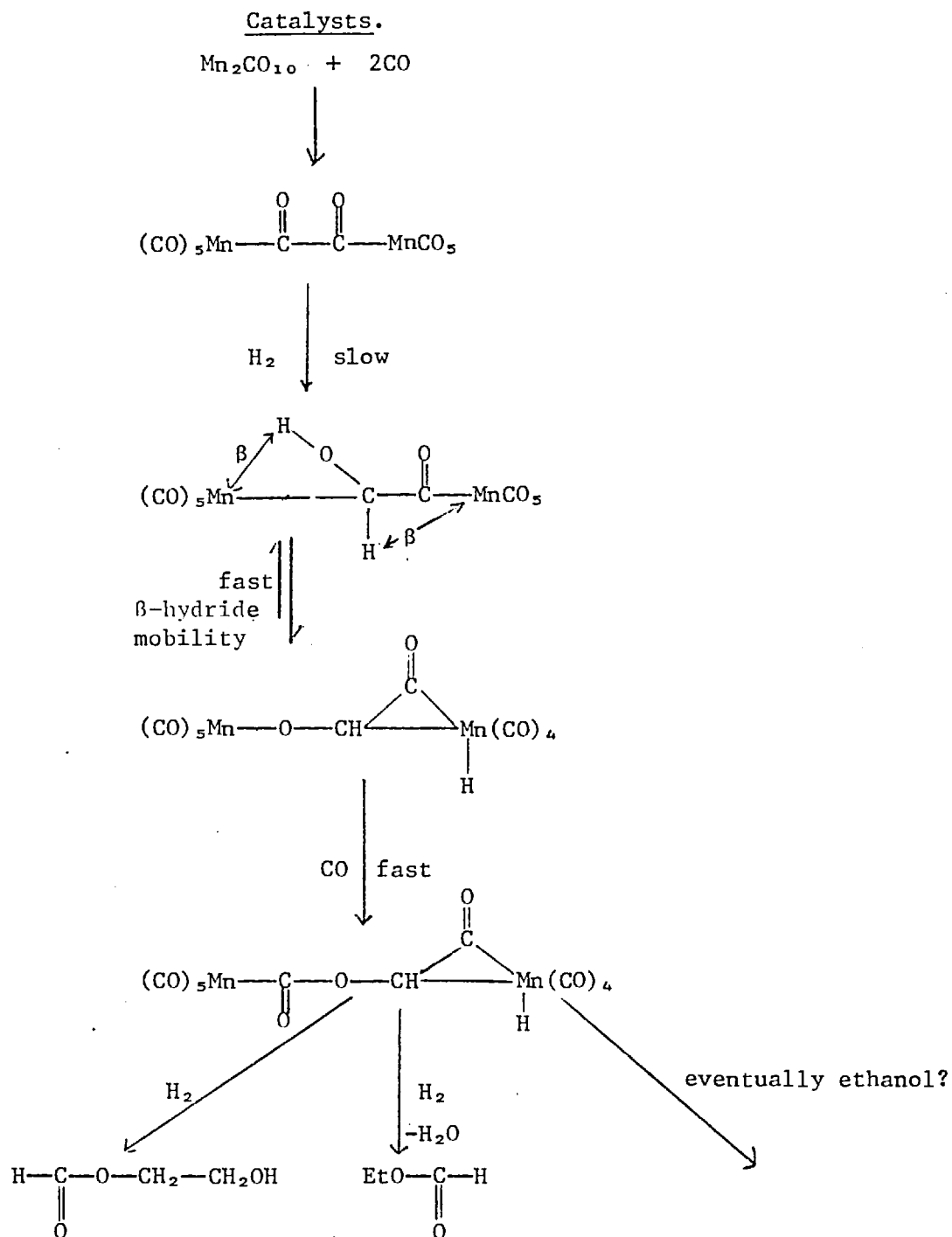


Methanol, Dimethylether and Acetone on a Binuclear Ruthenium Catalyst. SCHEME IV-9





The Formation of Hydroxyethyl formate and Ethylformate with Manganese

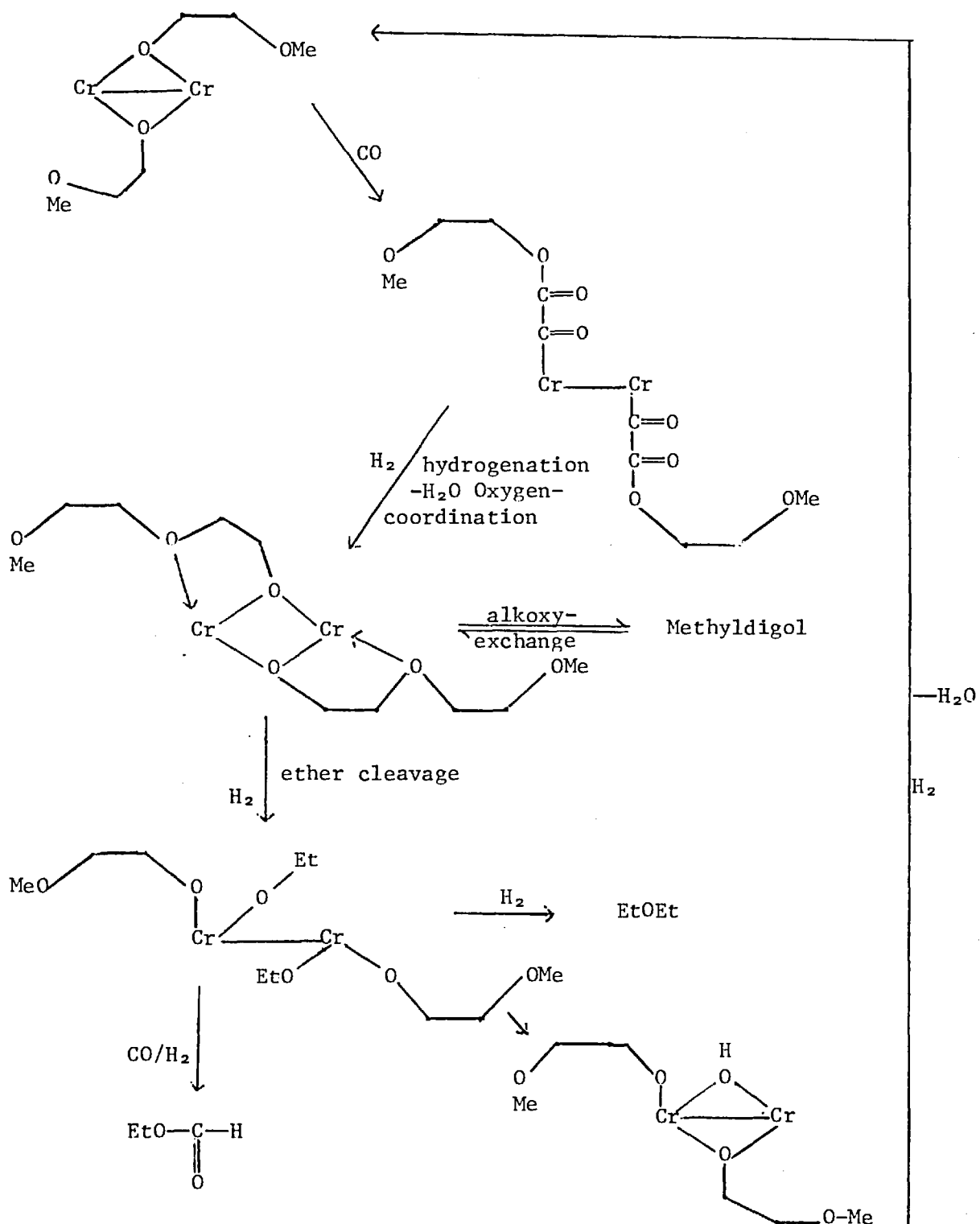


SCHEME IV-10

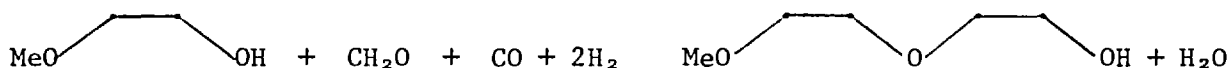


Methyldigol · Ethyl formate and Diethylether Formed on a Chromium

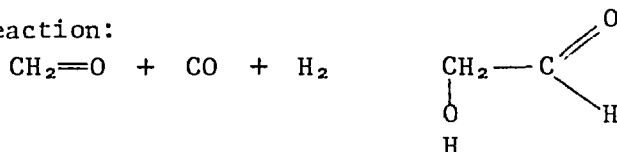
Catalyst (Solvent: Methoxyethanol)



SCHEME IV-11



and equal amounts of hydrogen-rich syn-gas and  $\text{CH}_2\text{O}$  are consumed and where methoxy ethanol may come from diglyme breakdown. In our experiment, 10 mg of syn gas was consumed with 7 g of paraformaldehyde. In trioxane the reaction:



has been established. The  $\text{CH}_2\text{O}$  may be derived from the solvent or the paraformaldehyde.

At  $120^\circ\text{C}$ , diglyme may break more easily at the middle oxygen than the end oxygen. At  $200^\circ\text{C}$ , this effect is evidently reversed.

We have proposed a variety of mechanisms for the formation of C-2 fragments and C-1 fragments. The evidence points towards binuclear species in alcohol solvents but is not conclusive. A distinct difference exists between the iron triad and the other elements.

#### Alkoxide Systems in the Literature.

Bradley's production of methanol using a ruthenium catalyst is very important.<sup>5</sup> Allowing for a stoichiometric breakdown in THF (the solvent) which is not cited in the literature, it appears that methanol and methylformate can be produced only in the presence of methanol (or methoxide) and methylformate. This is corroborated by the Gulf results using a mixed Ru/Co phosphite catalyst to form and homologate methanol. We believe, therefore, that these reactions occur by CO insertion into a metal oxygen bond.

### The Special Case of Rhodium

Since this work began rhodium has been activated by syn-gas. Activity at 200 atmospheres syn-gas pressure (CO/H<sub>2</sub>,1:1) is poor, but almost pure, ethanol and methyldigol were produced. The two catalysts used were the bridging alkoxide complex<sup>40</sup> and the cluster complex Na<sub>2</sub>Rh<sub>12</sub>CO<sub>30</sub><sup>46</sup> both deposit rhodium metal during the reaction, but no clusterisation occurs.

Rh<sub>4</sub>(CO)<sub>12</sub> is inactive forming quickly Rh<sub>6</sub>(CO)<sub>16</sub>, which is insoluble at 200°C in all solvents used. Mechanisms of alcohol formation probably parallel those for cobalt.

### SUMMARY OF RESULTS

The most important results of this thesis are now summarised.

1. Activation of carbon monoxide by insertion or double insertion into a metal oxygen bond.
2. Selective formation of C-2 fragments for catalyst derived from Co, Mn and Cr with either elimination of water at low temperature or CO<sub>2</sub> at high temperature.
3. The selective production of ethanol in glymes and hydroxyglymes from H<sub>2</sub> and CO at 200°C, with a cobalt catalyst.
4. The transformation of glyme solvents into alcohols by methylene extraction and their subsequent build up to other polyalcohols and acetates by double CO insertion and selective hydrogenation.
5. The selective formation of methanol using catalysts derived from ruthenium carbonyl.

6. The isolation of hydridocarbonyl-cobaltacyclopropanones and hydrido cobalta methylene carbonyls active as catalysts.
7. Of the C-2 compounds produced with cobalt carbonyl catalysts, ethanol and ethylformate, some acetaldehyde and probably hydroxyethyl formate are formed from syn-gas. The others, notably methylformate some acetaldehyde, methoxyethanol, methyl digol, and ethyleneglycol are formed from solvent breakdown.
8. The products formed from solvent buildup are methyl digol (hydroformylation of paraformaldehyde) methoxy-ethoxy-ethyl acetate\*, methoxy ethylacetate, ethylene glycol—monoacetate, bis(methoxyethoxy)methane, C-methylmethyl digol (2 isomers) and propylene glycol.
9. The overriding importance of ethylene glycol monoformate as the key intermediate, formed by the hydrogen reduction of two <sup>ketonic</sup> carbon monoxide molecules and the inversion of only one  $\begin{array}{c} \text{OH} \\ | \\ -\text{CH}-\text{Co} \end{array}$  group to  $\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{O}-\text{Co} \\ | \\ \text{H} \end{array}$ , a fact controlled by  $\beta$ -hydride mobility and illustrated in Scheme IV-6.

Reaction of Ethylene with Carbon Monoxide and  $\text{Co}_2(\text{CO})_8$  in Diglyme

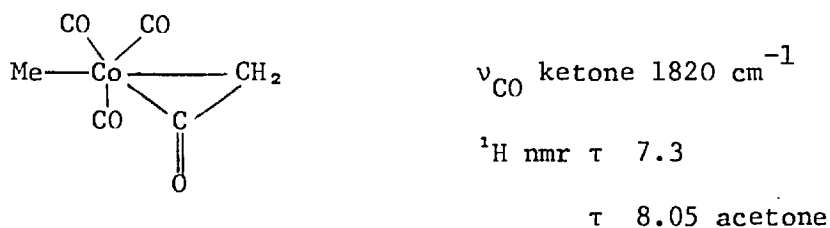
The reaction of ethylene and carbon monoxide and  $\text{Co}_2(\text{CO})_8$  in diglyme yields a variety of products, including cyclopropane, cyclopropanone, vinylaldehyde, propanal, alkenes and some acetates; it also yields a yellow gas with a cobaltacyclopropanone skeleton but no hydride. The gas decomposes to acetone, (Figure 5).

---

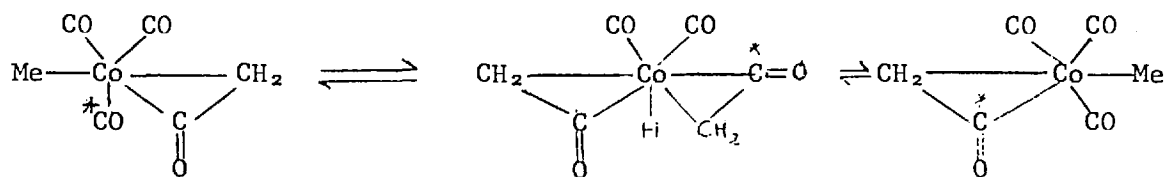
\* Underlined substituents contain deuterium.

The reaction in diglyme is so fast that the methylene units are more likely to come from ethylene breakdown rather than solvent breakdown, although the latter is clearly responsible for the formation of methoxy ethanol and acetates. We propose a bimetallic catalyst and a series of  $\beta$ -hydride transfers to explain all the products formed, (Scheme IV-12).

The yellow gas-4 is probably similar to the yellow gas-3 which also gives acetone on decomposition. We propose the structure

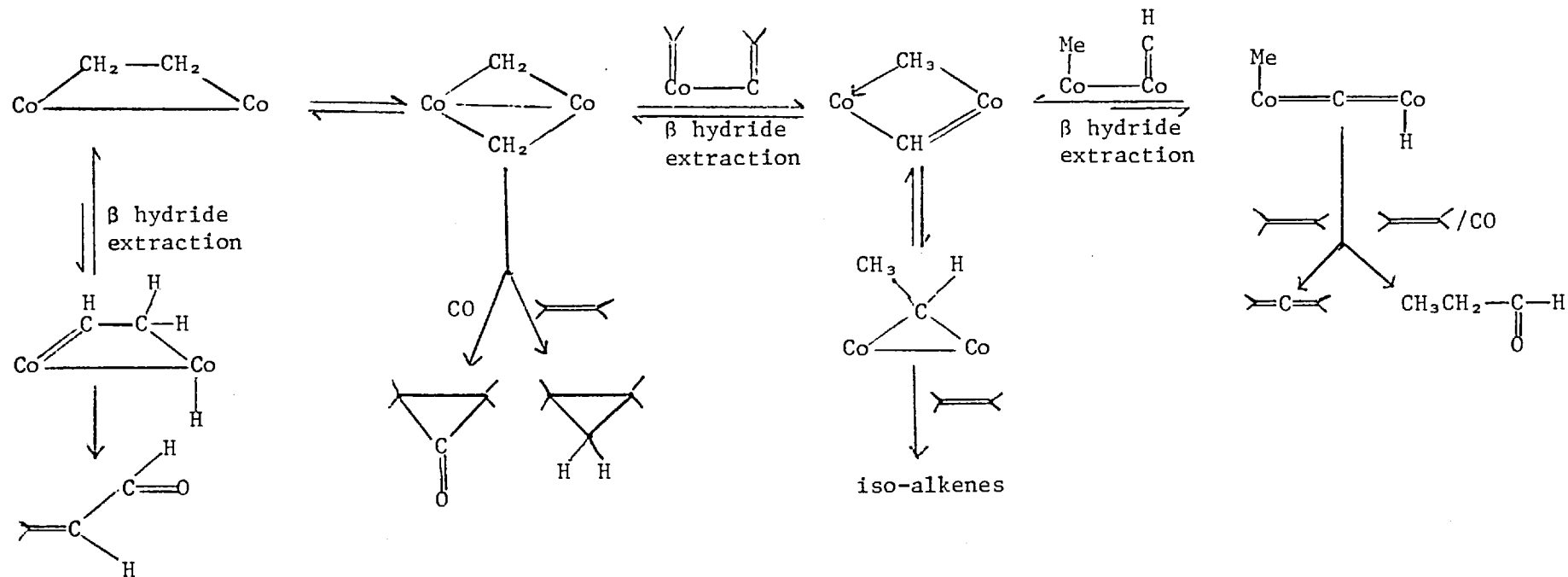


The molecule could be fluxional

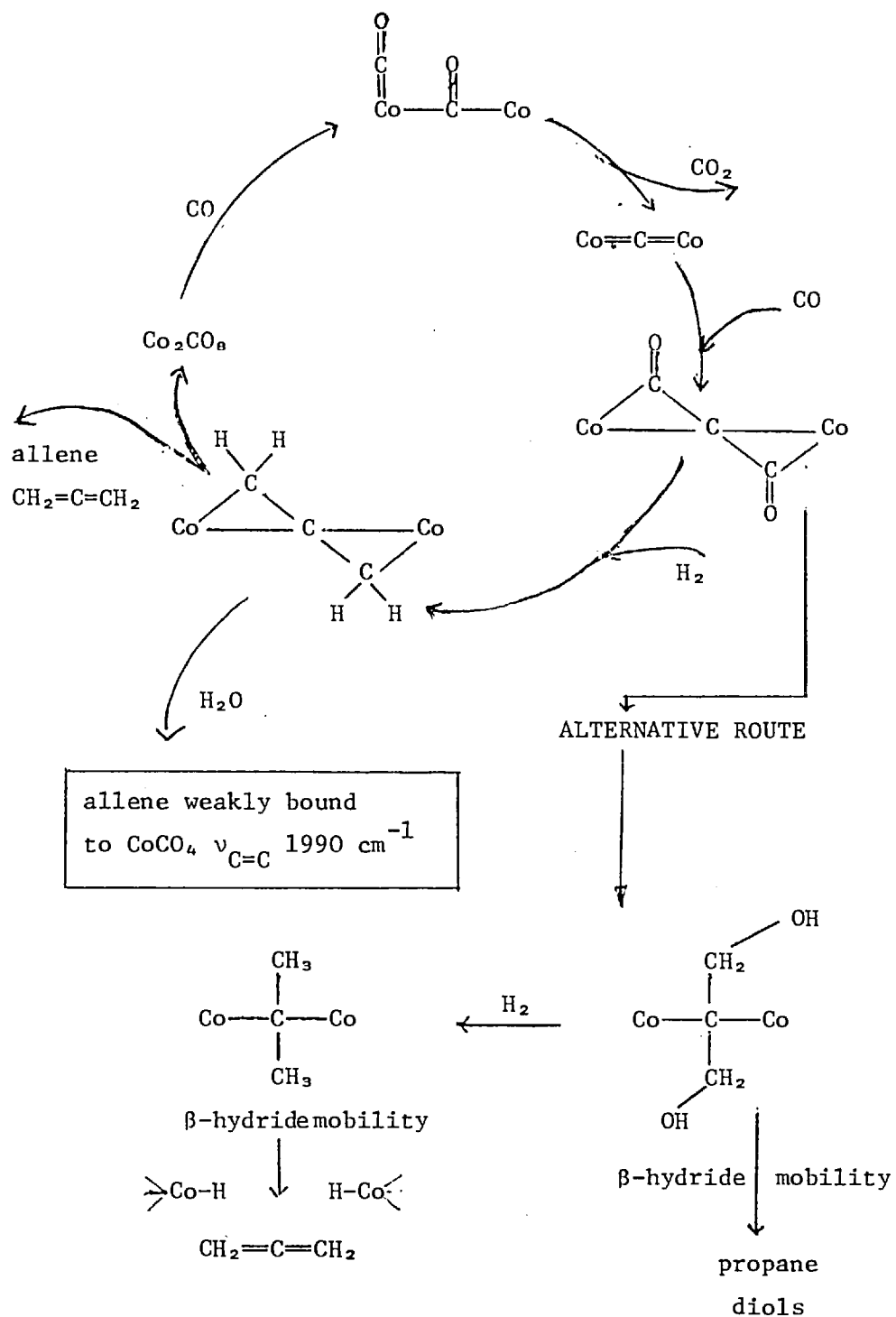


explaining the singlet at  $\tau 7.3$ .

Cobalt-Ethylene-CO- Reactions. SCHEME IV-12

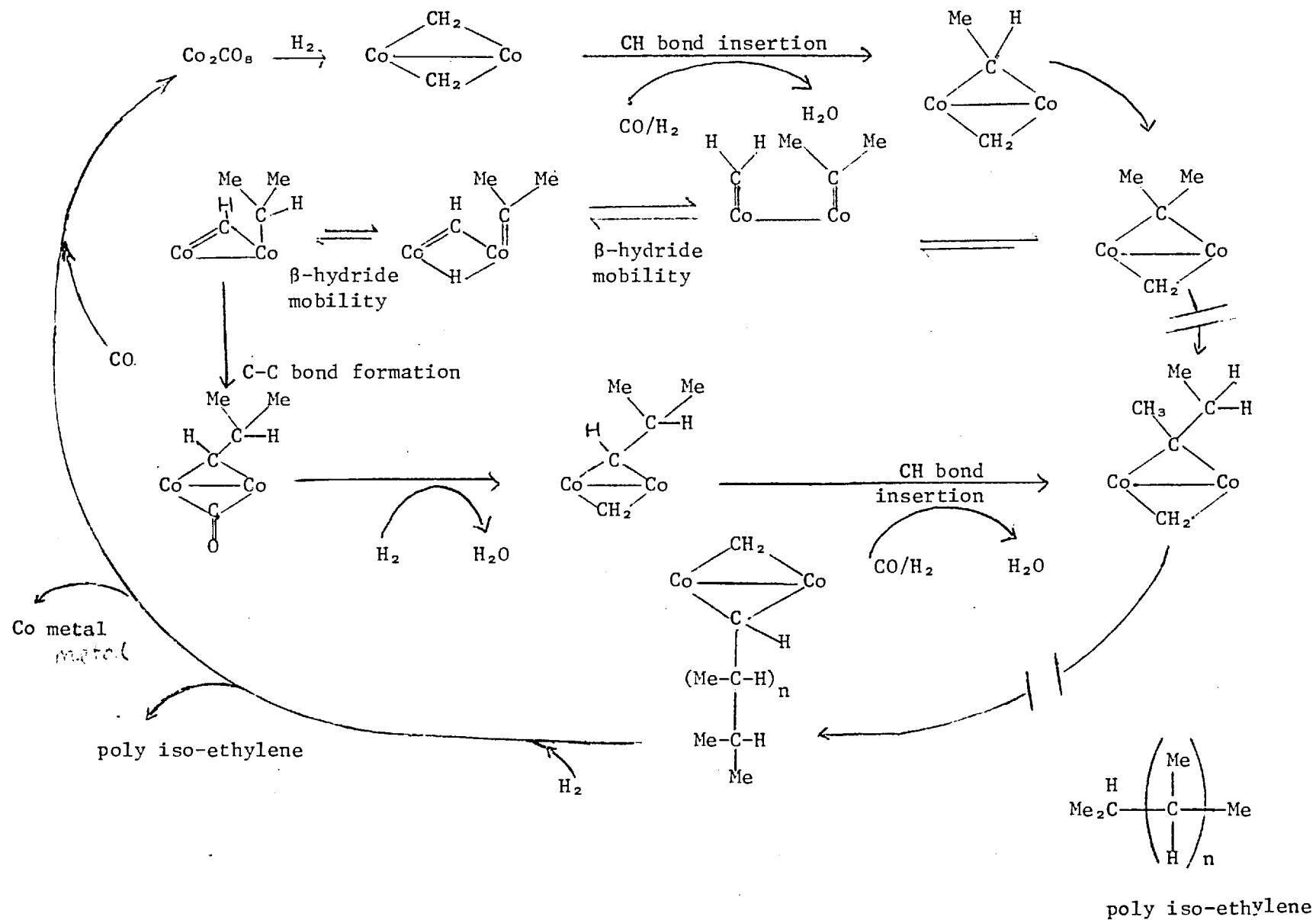


Mechanism of Allene Formation in CO-rich Syn-Gas Mixtures.



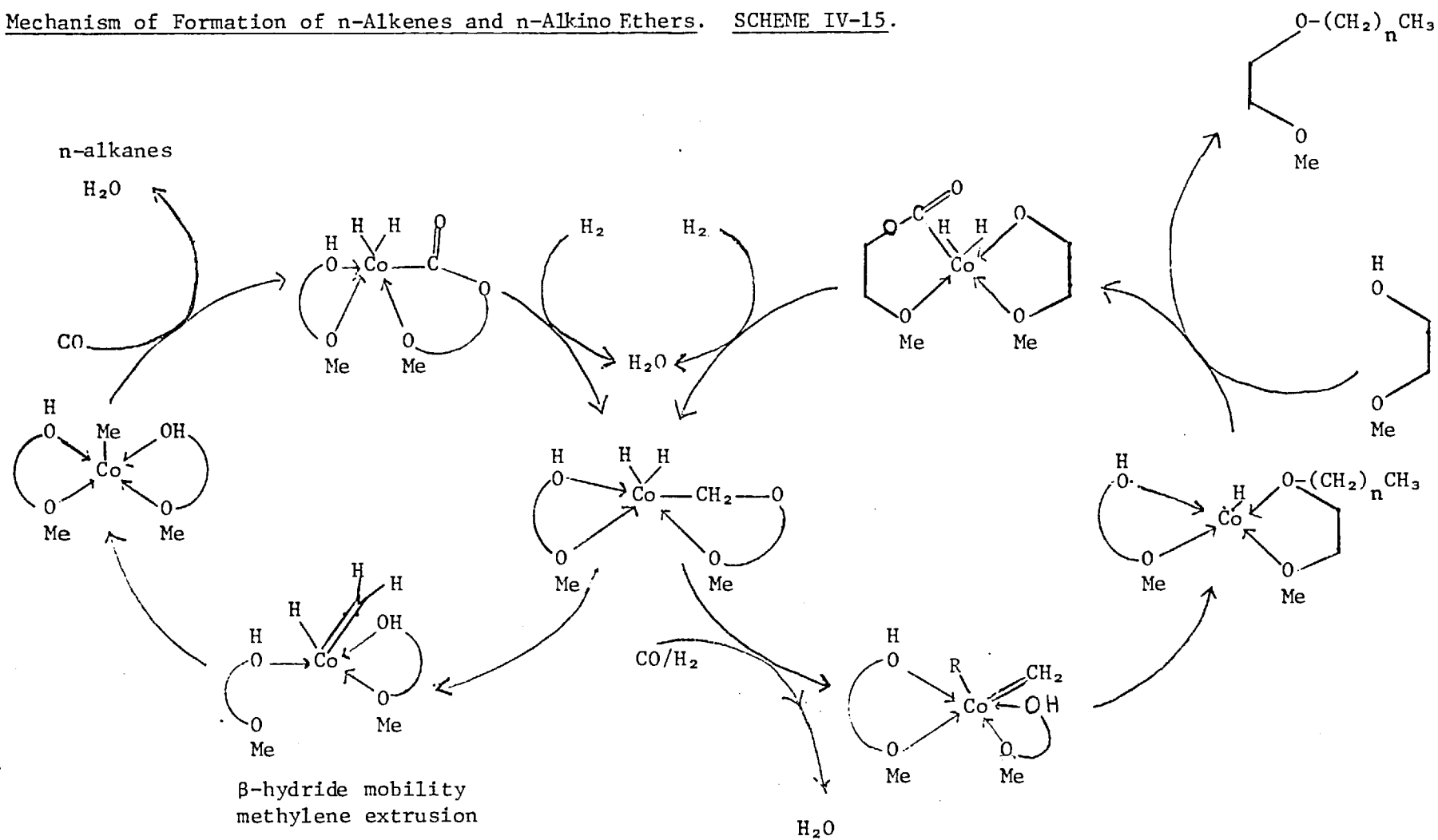
SCHEME IV-13

SCHEME IV-14. i-Alkanes and i-Alkino Ethers.





Mechanism of Formation of n-Alkenes and n-Alkyl Ethers. SCHEME IV-15.



## EXPERIMENTAL SECTION

Microanalysis were performed by the Imperial College, Butterworth Microanalytical Consultancy Limited and Pascher (Bonn), Laboratories.

### 1. INSTRUMENTS

Infrared spectra were recorded on a Perkin-Elmer spectrometer models 325, 457 and 597. U.V.-vis. spectra were run on a Perkin-Elmer spectrophotometer model 551 coupled with PE-56 Recorder.  $^1\text{H}$  nmr on a Perkin-Elmer R12A (60 MHz) and R32 (90 MHz);  $^{13}\text{C}$  nmr on a Varian Associates XL-100 (100 MHz, F.T. mode with noise proton decoupling) and Bruker WM-250 (250 MHz) operating at 62.9 MHz on carbon. G.l.c. measurements were carried out using a Perkin-Elmer F33 and a Perkin-Elmer sigma 1B analyser chromatographs fitted with flame ionisation detectors (F.I.D.). The peak-areas were obtained with a Infotronics automatic digital integrator model CRS-208 (coupled with a Monroe 1310 printer), and a Perkin-Elmer sigma 1B gas chromatographic system. The separations were performed in columns packed with chromosorb 101 (80-100 mesh), and 15% carbowax 20 M on chromosorb (80-100 mesh). Gas-chromatography - mass spectra were obtained

in a P.E. Gas Chromatograph coupled to a VG-Micromass 7070B double focussing mass spectrometer via a jet separator, and P.E. sigma 3 chromatograph coupled to a Kratos MS 25 mass spectrometer\* via a glass jet separator. The spectra were processed by a Kratos DS 50S data system.

## 2. SOLVENTS AND REAGENTS.

Benzene, toluene, petroleum-ether (b.p., 30-40°C), diethyl-ether, tetrahydrofuran were dried over sodium-benzophenone by refluxing under N<sub>2</sub> or argon and distilled immediately before use. Dichloromethane and acetonitrile were dried over CaH<sub>2</sub> by refluxing under N<sub>2</sub> and distilled prior to use.

Monoglyme, diglyme, triglyme, tetraglyme, di-n-butylether were dried by refluxing over sodium and under N<sub>2</sub> and on distillation only the main fraction ( $\pm 1^\circ\text{C}$  of the b.p.) was collected. The purity was determined by gas-chromatography. Crown-ethers were used without further purification.

Methanol, ethanol, 2-methoxyethanol, 2-ethoxyethanol, tetrahydrofurfuryl alcohol were dried by refluxing over the corresponding Mg-alkoxide under N<sub>2</sub> and when distilled before use only the main fraction was collected. Acetone was dried over molecular sieve, 3A and ethylene glycol over MgSO<sub>4</sub>. Other solvents used were purified by single distillation.

---

\* This service was run by the University of London at Queen Elizabeth College.

$\text{Ru}_3(\text{CO})_{12}$ ,<sup>41</sup>  $\text{Mn}_2(\text{CO})_{10}$ ,<sup>42</sup>  $\text{Os}_3(\text{CO})_{12}$ ,<sup>43</sup>  $\text{Co}_2(\text{CO})_8$ <sup>44</sup> and  $\text{Rh}_4(\text{CO})_{12}$ ,<sup>45</sup> were prepared by methods described in the literature. These carbonyls were purified by several recrystallisations, dried in a carbon monoxide stream.  $\text{Na}_2\text{Rh}_{12}(\text{CO})_{30}$ ,<sup>46</sup>  $\text{NaCo}(\text{CO})_4$ ,<sup>47</sup>  $[\text{MoH}_3(\text{PMe}_2\text{Ph}_2)_3]\text{BF}_4$ <sup>14</sup> and  $[\text{WH}_5(\text{PMePh}_2)_4]\text{BF}_4$ <sup>14</sup> were made by known methods.  $\text{Fe}(\text{CO})_5$  (Fluka AG),  $\text{Cr}(\text{CO})_6$  (Pressure Chemical Company),  $\text{Mo}(\text{CO})_6$  (Climax Molybdenum Company) and  $\text{W}(\text{CO})_6$  (Strem Chemicals Inc.) were used without further purification.

Carbon monoxide, hydrogen and deuterium (British Oxygen Company) were used without any purification.

### 3. AUTOCLAVES

High pressure reactions were performed using 25, 50, 100, 200, 300 ml and 1 litre stainless-steel (316) autoclaves and a 100 ml autoclave coated with Hastelloy, utilising rocking agitation or magnetic stirring (Baskerville and Lindsay Limited).

Before each reaction the autoclaves were thoroughly cleaned in the following manner: washing with water, then concentrated  $\text{HNO}_3$ , again with water, then scoured with an abrasive plastic cloth, again washed with water and finally rinsed several times with acetone and dried in an oven at  $120^\circ\text{C}$ . Before adding the catalytic solutions, the autoclaves were flushed with carbon monoxide.

#### 4. IDENTIFICATION OF THE REDUCTION PRODUCTS FROM CATALYSIS.

After completing the reaction cycle (24 hrs) the autoclave was cooled to ca. 0°C and the residual pressure slowly released. For analysis of the gas phase a sample was collected straight from the bomb in a gas-cell and injected into a mass-spectrometer. For quantitative analyses of the CO<sub>2</sub>, the off-gases were bubbled through a concentrated Ba(OH)<sub>2</sub> solution. The Ba(CO)<sub>3</sub> formed was filtered, washed several times with water and dried.

The bombs' pressure was completely released and the solution was quickly transferred to a flask under an inert atmosphere; a sample was immediately analysed by gas-liquid-chromatography (g.l.c), using two different columns: a) Chromosorb 101, 80-100 mesh (packed,  $\frac{1}{8}$ " internal diameter, 4 metres long) and, b) 15% carbowax 20 M on chromosorb, 80-100 mesh (packed,  $\frac{1}{8}$ " internal diameter, 4 metres long). The carrier-gas used was N<sub>2</sub> with a flow-rate of 30 ml/min. Different column temperatures programming were used:

1 - constant programme

oven - 100°C; injector and detector 150°C

2 - constant programme

oven - 150°C; injector and detector 200°C

3 - variable temperature programme

oven - started at 100°C and held at this temperature for 10 min, then with a 10°C/min rise to 170°C ;  
injector and detector = 200°C.

The peaks in the chromatogramme were identified by adding standard samples to the reaction solution. The correct concentration of each component was determined by adding a weighted sample of cyclododecane to a weighted sample of the reaction solution and the peak-areas compared. The variation in G.C. peak areas with concentration was established and the ratios between the areas of the main peaks at different concentrations could be related directly to concentration.

After identification by g.l.c. the reaction solution was fractionally distilled, sometimes at reduced pressure, and the components analysed by  $^1\text{H}$  nmr and infra-red. The spectra were compared with those of authentic samples. Again, the distilled products were re-checked by g.l.c.

A repeat reaction was performed. This time the reaction solution was analysed by gas-chromatography/mass-spectrum using the same column as those used in the g.l.c.. The conditions used were: Helium was the carrier-gas with a flow-rate of 30 mls/min; glass jet separator at  $250^\circ\text{C}$ ; ionisation current of 100 mamps; source temperature at  $150^\circ\text{C}$ ; ionising potential : 70 eV and 20 eV. A better separation of peaks was obtained using a temperature programme: Starting at  $60^\circ\text{C}$  for 10 mins., then with a  $2^\circ\text{C}/\text{min}$  rise to  $150^\circ\text{C}$ ; after 10 min. at  $150^\circ\text{C}$ , a rise of  $10^\circ\text{C}/\text{min}$ . to  $180^\circ\text{C}$ .

The mass-spectrum obtained for each peak in the chromatogramme was compared with authentic samples. The distillation was repeated and the main components analysed directly on a mass-spectrometer.

## 5. CATALYTIC SOLUTIONS AND REACTIONS.

A)  $[\text{MoH}_3(\text{PMePh}_2)_3]\text{BF}_4$  (0.14 g) and  $[\text{Rh}_{12}(\text{CO})_{30}]\text{Na}_2$  (0.2 g) were dissolved in 10 ml of tetrahydrofuran (THF) under  $\text{H}_2/\text{CO}$  (1:1) at 1 atm pressure and stirred for 1 hr. After filtering, the solution was placed in a 25 ml stainless-steel rocking bomb. The bomb was pressured to 20 atm. with  $\text{CO}/\text{H}_2$ , (1:1), and heated to  $150^\circ\text{C}$ . After 12 hrs. reaction time the bomb was cooled to roomtemperature and the residual pressure released. In the reaction solutions ethylene glycol and benzene (from decomposition of  $\text{PMePh}_2$ ) were detected by g.l.c. (chromosorb 101, 80-100 mesh) and further identified by their  $^1\text{H}$  nmr, mass, and infrared spectra. In diglyme the same organic products were detected after 6 hrs. However, no organometallic compounds were identified in both solutions after the reaction.

B)  $[\text{WH}_5(\text{PMePh}_2)_4]\text{BF}_4$  (0.1 g) was reacted with  $[\text{Rh}_{12}(\text{CO})_{30}]\text{Na}_2$  (0.12 g) in 10 ml of THF at room temperature and under  $\text{CO}/\text{H}_2$  atmosphere. After stirring for 1 hr. the dark-red solution was filtered and placed in a pop bottle. The bottle was pressured to 6 atm. of  $\text{CO}/\text{H}_2$  (1:1) and heated in an oil-bath to  $80^\circ\text{C}$ . After 12 hrs. of reaction, the homogeneous solution turned to a suspension with precipitation of brown-black powder. The bottle was cooled and the residual pressure released. After filtration ethylene glycol and benzene was detected by g.l.c. and identified by  $^1\text{H}$  nmr and infrared spectra. From the black residues no organometallic compound could be identified.

In diglyme as a solvent, using the same conditions as above, glycol and benzene was detected in the g.l.c.

C)  $[\text{MoH}_3(\text{PMePh}_2)_3]\text{Co}(\text{CO})_4$  (0.3 g) prepared according to Wilkinson, et al.,<sup>14</sup> was dissolved in THF (10 ml). After 12 hrs. reaction time at 150°C and 50 atm. CO/H<sub>2</sub> (1:1), the g.l.c. showed benzene and ethylene glycol. As in the other reactions with phosphine decomposition, no organometallic complexes were identified in the reaction solution.

D)  $[\text{WH}_5(\text{PMePh}_2)_4]\text{Co}(\text{CO})_4$  (0.4 g) prepared by reacting  $[\text{WH}_5(\text{PMePh}_2)_4]\text{BF}_4$  with  $\text{NaCo}(\text{CO})_4$  (same method used for  $[\text{MoH}_3(\text{PMePh}_2)_3]\text{Co}(\text{CO})_4$ ) was dissolved in THF (15 ml) giving a red-brown solution. This was transferred to a pop bottle and after flushing several times with CO/H<sub>2</sub>, pressured to 6 atm. and heated to 80°C. After 12 hrs. reacting the analysis by g.l.c. showed the presence of ethylene glycol and benzene. The use of higher pressure and temperature gave the same result. A black metallic powder (not identified) decanted slowly from the solution.

Results obtained in different conditions (temperature, solvent, pressure) for example, 1 to 4 are listed in Table II-1.

E) Reactions with a mixture of  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Co}_2(\text{CO})_8$ .

E.1 - metal ratio Rh/Co - 1:1

#### Reaction in THF

In a 25 ml stainless-steel rocking autoclave was placed 10 ml of a THF solution containing  $\text{Rh}_4(\text{CO})_{12}$  (0.11 g) and  $\text{Co}_2(\text{CO})_8$  (0.10 g).



The autoclave containing the catalytic solution was flushed several times with carbon monoxide and then pressurized to 80 atm. with CO/H<sub>2</sub> (1:1) and heated to 200°C. After 24 hrs reaction time 20 atms. of syn-gas was absorbed. Analysis by g.l.c., <sup>1</sup>H nmr, infrared and gas-chromatography/mass-spectrum (GC/MS) showed the presence of ethanol and acetone together with polyols. Rh<sub>2</sub>Co<sub>2</sub>(CO)<sub>12</sub> was the organometallic catalyst isolated from the reaction solution.

#### Reactions in diglyme

Rh<sub>4</sub>(CO)<sub>12</sub> (0.11 g) and Co<sub>2</sub>(CO)<sub>8</sub> (0.10 g) was dissolved in 10 ml of diglyme and the solution stirred under carbon monoxide. After stirring for 1 hr. the solution was transferred to a 25 ml stainless-steel (S/S) bomb, pressured to 80 atm. of syn-gas and heated to 200°C. After 24 hrs (with 22 atm absorbed) the bomb was cooled to -78°C. The residual pressure was released and the bomb pressured again with CO/H<sub>2</sub> (1:1). This procedure was repeated during 8 days, consuming about 5 litres of syn-gas. At the end of the eighth day, the bomb was cooled to ca. 0°C, the residual gases released and the catalytic solution analysed. In the g.l.c. (15% carbowax 20 M on chromosorb, 80-100 mesh) ethanol (40%), acetone (42%), diethylether (4%) and n-propanol was found together with other unidentified compounds. Then, the solution was fractionally distilled and the components characterised by <sup>1</sup>H nmr, infrared and mass-spectra. The mixed metal catalyst precipitated out, on cooling, as brown-black crystals, which were identified as

$\text{Rh}_2\text{Co}_2(\text{CO})_{12}$  by infrared spectra and by comparison with its spectroscopic properties described in the literature.<sup>18</sup>

Repeating the reactions for a shorter time (24 hrs.: cold  $\rightarrow$  hot  $\rightarrow$  cold) without refilling the bomb with syn-gas gave the same result as above.

### E.2 Rhodium-rich systems

Using the same reaction conditions as in the example E.2, but increasing the concentration of  $\text{Rh}_4(\text{CO})_{12}$  ( $\text{Rh}/\text{Co} > 1$ ), the gas absorption during 24 hrs. slowed down; on the other hand, the selectivity for ethanol increased, becoming the major component (see Graph II-1). When the metal ratio  $\text{Rh}/\text{Co}$  was 5 or more, rhodium started precipitating out as the insoluble cluster  $\text{Rh}_6(\text{CO})_{16}$ , isolated from the reaction solution as black crystals and identified by its spectroscopic properties. The solution showed a strong yellow colour due to the presence of soluble cobalt. However, no cobalt complex could be identified.

### E.3. Cobalt-rich systems

Reaction conditions: 25 ml S/S bomb, diglyme 10 ml (solvent),  $\text{CO}/\text{H}_2$  (1:1) 80 atm., 200°C,  $\text{Co}/\text{Rh}$  (total weight = 0.25 g) changing the ratio from 1:1 to 1:50.

The gas absorption after 24 hrs. of reaction time increased as the cobalt content increased. G.l.c. analysis from the reaction solutions showed increased selectivity (up to 80%) for ethanol when the amount of cobalt was enlarged. Other reduction products identified were propanol, acetone and diethylether, (see Graph II-1).

No organometallic compound was isolated after the reaction although the presence of  $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$  and  $\text{RhCo}_3(\text{CO})_{12}$  were suspected in the orange solution by infrared evidence.

F) Reactions using  $\text{Co}_2(\text{CO})_8$  as the only catalyst in the reaction mixture.

Using monoglyme, diglyme, triglyme and tetraglyme as a solvent.

Reaction conditions: 150 ml S/S rocking autoclave;  $\text{CO}/\text{H}_2$  (1:1) 80 atm.;  $200^\circ\text{C}$ ; 70 ml of solvent;  $\text{Co}_2(\text{CO})_8$  0.3 g; reaction time (cold  $\rightarrow$  hot  $\rightarrow$  cold) 24 hrs.

$\text{Co}_2(\text{CO})_8$  was dissolved in the glyme solvents under CO and left stirring for 1 hr. After filtration the solution was transferred to the bomb, flushed with CO and  $\text{H}_2$ , pressured to 80 atm. and heated to  $200^\circ\text{C}$ . After 24 hrs., the bomb was cooled to room temperature, the residual pressure released and the reaction solution analysed. G.l.c.,  $^1\text{H}$  nmr, infrared and GC/MS showed the presence of ethanol, diethylether, acetone, propanol, methyl and ethyl formate. The major component in all glymes was ethanol (between 70 and 80%, calculated by g.l.c.).

In dibuthylether as a solvent, ethanol dropped to 45% and high boiling materials appeared in 34% yield (see Graph II-4).

G) Temperature, control experiments.

Temperature control experiments were carried out in a 25 ml S/S bomb with diglyme as a solvent.  $\text{Co}(\text{CO})_8$  0.3 g (0.088 M) and  $\text{CO}/\text{H}_2$  (1:1) 100 atm.

The catalytic solution was prepared as in Example 6. The temperature was carefully controlled with a slow heating system and six experiments were carried out between 150 and 200°C. Before releasing the residual pressure, the bomb was cooled to -78°C. Analysis by g.l.c., <sup>1</sup>H nmr, infrared and GC/MS showed a change in the selectivity as a function of temperature. The main components are: 150°C - hydroxyethylformate (45%); 160°C - acetaldehyde (70%); 170°C - mixture of methoxyethanol, ethanol, acetaldehyde and ethyl formate, 26, 19, 30, 16% respectively; 180°C - ethylformate (70%); 190°C - ethanol (60%); 200°C - ethanol (78%). Methylidigol was also formed (from solvent breakdown) (see Graph II-2 and II-3).

#### H) Co<sub>2</sub>(CO)<sub>8</sub> Concentration experiments.

These were performed using the same reaction conditions as in Example 7. Four basic experiments were made at 200°C using the following molar concentrations of Co<sub>2</sub>(CO)<sub>8</sub> : 0.01 M, 0.05 M, 0.10 M, and 0.25 M. At 0.25 M, small amounts of cobalt metal plated out in the bomb. At 0.05 M, the reaction was very slow, absorbing only 10 atm., in 24 hrs. The best Co<sub>2</sub>(CO)<sub>8</sub> concentration for ethanol synthesis without cobalt plating was found to be 0.10 M. The result of g.l.c., <sup>1</sup>H nmr, infrared and GC/MS analysis is shown in Table II-3.

#### I) Experiments with different CO/H<sub>2</sub> ratios.

These were performed in a 150 ml S/S bomb, 70 ml of diglyme (solvent), 0.5 g of Co<sub>2</sub>(CO)<sub>8</sub>, 70 atm. total pressure, 200°C. The CO/H<sub>2</sub> ratio was changed from 2:1 to 1:3. At CO/H<sub>2</sub> 2:1 no reaction

occurred and after 24 hrs. the solution was still red and on cooling, at  $-20^{\circ}\text{C}$  gave  $\text{Co}_2(\text{CO})_8$  as orange crystals. At 1.5:1 the reaction is slow and the major component identified was acetaldehyde. On cooling the red solution at  $-20^{\circ}\text{C}$ ,  $\text{Co}_2(\text{CO})_8$  precipitated out, leaving in the flask a yellow solution. At ratio 1:1, ethanol was the major component identified and the solution changed to yellow. At 1:2 and 1:3, the reaction is faster. Co-metal starts to plate out and in the g.l.c. alkanes were identified, together with insoluble paraffins and paraffino-ethers. The solution stays pale yellow. The syn-gas mixture of CO and  $\text{H}_2$  were made up in-situ from CO and  $\text{H}_2$  pressure tanks, (see Graph II-5).

J)  $\text{Co}_2(\text{CO})_8$  in ether-alcohols

$\text{Co}_2(\text{CO})_8$  (2.0 g) was dissolved in 150 ml of 2-methoxyethanol. Carbon monoxide is quickly evolved while the solution changes from red to pink during 15 mins., approximately. The pink solution was transferred to a 300 ml S/S bomb, flushed with CO, pressured to 130 atm. of CO/ $\text{H}_2$  (1:1) and heated to  $140^{\circ}\text{C}$ . After 24 hrs. of reaction time the solution (still pink) was analysed by g.l.c. and ethylene glycol (40%) was identified together with ethanol, ethylene-glycol monoformate, 2-methoxyethylacetate. The components were fractionally distilled and confirmed by  $^1\text{H}$  nmr, infrared and GC/MS spectra.

In the same procedure, these results were obtained but in slower reactions using 2-ethoxyethanol and tetrahydrofurfuryl alcohol. In 2-phenoxyethanol no reaction was observed.

K) Reactions using  $\text{Fe}(\text{CO})_5$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{12}$  in 2-methoxyethanol as a solvent.

The metal carbonyls were dissolved in 2-methoxyethanol and the solution transferred to a S/S bomb. The bomb was charged with CO/H<sub>2</sub> to the desired pressure and ratio and heated. After 24 or 48 hrs. of reaction time the solution was analysed in the same method as described previously in the other examples. For the reaction conditions and products obtained see Table II-5.

$\text{Fe}(\text{CO})_5$ ,  $\text{Cr}(\text{CO})_6$  and  $\text{Mn}_2(\text{CO})_{10}$  were recovered quantitatively from the solution after the reaction. In the reaction with  $\text{Ru}_3(\text{CO})_{12}$ , the metal carbonyls identified in solution, after the reaction, were  $\text{Ru}(\text{CO})_5$  (trap-to-trap distilled with the volatile organic compounds) and  $\text{Ru}_3(\text{CO})_{12}$ . From the solution in the reaction with  $\text{Os}_3(\text{CO})_{12}$ , two osmium carbonyl hydrides (formed in the reaction) were identified:  $\text{H}_2\text{Os}(\text{CO})_4$  (<sup>1</sup>H nmr,  $\tau = 18.84$  ppm) and  $\text{H}_2\text{Os}_2(\text{CO})_8$  (<sup>1</sup>H nmr,  $\tau = 20.14$  ppm).

## 6. ISOLATION OF COBALT CATALYST

### A) Glyme solutions of $\text{Co}_2(\text{CO})_8$

Cobalt carbonyl dissolves in monoglyme, diglyme, triglyme and tetraglyme with carbon monoxide evolution (between 1.5 and 2.0 moles of CO per cobalt dimer). In all glyme solutions, the only carbonyl absorption in the infrared spectra appears at  $1890 \text{ cm}^{-1}$ . Attempts to isolate the cobalt compound from the solutions failed, giving only

a purple oil, which was not identified. When the glyme solutions of  $\text{Co}_2(\text{CO})_8$  were saturated with CO and cooled to  $-20^\circ\text{C}$ , small amounts of crystalline  $\text{Co}_2(\text{CO})_8$  were formed. Addition of petrol or monoethers to the solutions, precipitates  $\text{Co}_2(\text{CO})_{12}$  as black crystals (identified by its infrared spectrum).

On heating a diglyme solution of  $\text{Co}_2(\text{CO})_8$  at  $60^\circ\text{C}$ , under vacuum, a green crystalline compound identified as  $[\text{Co}(\text{diglyme})_2]^{++}[\text{Co}_6(\text{CO})_{16}]^{--}$  is formed. Analysis of this compound showed: C = 29.44%; H = 2.62%; O = 30.1% (calculated: C = 29.7%; H = 2.48%; O = 31.17%).

When a diglyme solution of  $\text{NaBPh}_4$  is added to a  $\text{Co}_2(\text{CO})_8$ -diglyme solution slowly an unstable, white crystalline material is formed. On washing with petrol, or diethylether after filtration, the colour changes quickly from white to pink, and in the petrol or diethylether wash-solution,  $\text{Co}_2(\text{CO})_8$  was identified. From the pink crystalline material two cobalt compounds were identified:  $[\text{Co}(\text{diglyme})]^{++}[\text{B}(\text{C}_6\text{H}_5)_4]^{--}_2$  which analysis gave C = 71.66%; H = 7.71%; O = 13.4%; B = 1.84%; Co = 5.36% (calculated : C = 72.0%; H = 7.46%; O = 13.1%; B = 2.0%; Co = 5.4%), and  $[\text{Co}_2(\mu\text{-OCH}_2\text{CH}_2\text{OCH}_3)_2(\text{diglyme})_2][\text{B}(\text{C}_6\text{H}_5)_4]_2$ , identified by X-ray crystallography.

#### B) Polymeric cobalt compounds from the reaction solutions.

To the yellow diglyme solutions obtained after the catalysis reaction with CO and  $\text{H}_2$ , a large excess of petrol was added. Slowly, a white powdered material precipitated out from the solution. After

filtering under  $N_2$ , the solid was dried under vacuum at room-temperature. The analysis gave: C = 21.63% and H = 3.68%, suggesting a polymeric  $[Co(CH_2O)_2]_n$  compound (calculated: C = 20.17%; H = 3.36%). It is moisture-sensitive, giving a pink solid after a short time in the air and decomposes at  $250^\circ C$ .

C) Volatile cobalt compounds from the reaction solutions.

The identification of the volatile cobalt compounds in the form of yellow gases (described in Chapters III and IV) obtained from the reaction solutions in glymes, was made in the following way: after 24hrs. of reaction, the bomb was cooled to  $-30^\circ C$  and the residual pressure released. The solution was quickly transferred to a flask under  $N_2$  and trap-to-trap distilled. A yellow cobalt complex distills over together with the volatile organic compounds. The distillates were allowed to warm to room-temperature and a few drops of  $H_2O$  or  $D_2O$  was added. Immediately, a yellow gas evolved from the solution. This gas was quickly trapped in a infrared-gas cell and an infrared spectrum recorded. One gas shows very high stability decomposing slowly at room-temperature only after several days. Addition of an excess of water to the distilled solution produces methanol, identified by g.l.c. (methanol was not present in the original catalytic solution). The amount of gases formed by the addition of water increases when the reaction is best performed with a rich CO mixture ( $CO/H_2 = 1.5:1$ ). The infrared spectra are shown in Figures -1,-2,-3,-4 .



D) Identification of organic compounds.

To show that the organic products formed during the reaction in the bomb come from CO and H<sub>2</sub> and not from solvent breakdown, some reactions were performed using deuterium in an appropriate CO/D<sub>2</sub> mixture. After the reaction, the products were fractionally distilled and <sup>13</sup>C nmr spectra recorded. The results are discussed in Chapter IV.

7. MISCELLANEOUSA) Synthesis of (CO)<sub>4</sub>Co-C(=O)-C(=O)-OCH<sub>2</sub>CH<sub>2</sub>OMe

NaCo(CO)<sub>4</sub> (2.0 g) was suspended in Et<sub>2</sub>O (50 ml) and cooled to -78°C. Cl-C(=O)-C(=O)-OEtOMe (1.8 g) (made by reaction of Cl-C(=O)-C(=O)-Cl<sub>48</sub> with MeOEtOH by the method described in the literature) was added. The mixture was stirred for 1 hr. at -78°C then warmed slowly to 0°C. The solvent was eliminated under vacuum and the green solid extracted in THF. On cooling at -20°C pale-green powder precipitates. It is very air-sensitive and thermally unstable changing to a blue and then purple solid. The infrared spectrum of the green compound shows the carbonyl absorptions at 2120, 2060, 2050 and 2030 cm<sup>-1</sup>; for the Co-C(=O)-C(=O)-R, two strong absorptions are observed at 1700 and 1750 cm<sup>-1</sup>, suggesting the compound (CO)<sub>4</sub>Co-C(=O)-C(=O)-OEtOMe.

The decomposition to the purple solid occurs with disappearance of the carbonyls and oxalyl absorptions and appearance of a new broad absorption at 1700-1620 cm<sup>-1</sup>, characteristic of carboxylate group.

(Figure -14 )

B) Reaction of  $(\text{CO})_4\text{Co}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OEtOMe}$  with  $\text{H}_2$ .

A THF solution of  $(\text{CO})_4\text{Co}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OEtOMe}$  was placed in a pop bottle and pressurised to 6 atm. with  $\text{H}_2$  and stirred. After 10 hrs. of reaction, filtration gave a purple powdered solid and a colourless solution. G.l.c. analysis of the solution shows equivalent amounts of acetaldehyde and methoxyethanol. The infrared spectrum of the purple solid showed the broad absorption, characteristic for carboxylate groups at  $1700-1620\text{ cm}^{-1}$  and the characteristic absorptions for 2-methoxyethanol.

8. Reaction of  $\text{C}_2\text{H}_4$  and  $\text{CO}$  in diglyme (solvent) with  $\text{Co}_2(\text{CO})_8$  as a Catalyst.

A diglyme solution (60 ml) containing 0.8 g of  $\text{Co}_2(\text{CO})_8$  was transferred to a 200 ml S/S bomb. The bomb was charged with  $\text{CO}$  and  $\text{C}_2\text{H}_4$  (total 120 atms) in the following sequence: 40 atm  $\text{CO}$ , then 40 atm  $\text{C}_2\text{H}_4$  and again 40 atm  $\text{CO}$ . The bomb was heated to  $100^\circ\text{C}$  and left reacting for 1 hr. The bomb was cooled to ca.  $0^\circ\text{C}$ , the residual pressure slowly released and the solution transferred to a flask under inert atmosphere. The volatiles were trapped<sup>P</sup> to an ir-gas cell and an ir spectra recorded (Figure 5). A cobalt complex,  $(\text{CO})_3\text{CO}-\overset{\text{CH}_3}{\text{C}}-\text{CH}_2$  was observed together with ethylene. The ir

spectra recorded at different times show the decomposition reaction of the cobalt-complex and its reaction with ethylene producing aldehyde and acetone.

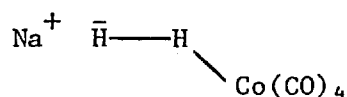
From the solution, propaldehyde and vinyl aldehyde were identified by g.l.c. and  $^1\text{H}$  nmr spectra. The other products allene, cyclopropanone, cyclopropane, acetates, alkenes and propanol were identified by  $^1\text{H}$  nmr only.

#### 9. The Hydrogenation of Dinitrogen.

The reaction of  $\text{H}_2$  and  $\text{N}_2$  in a ratio of 1:1 in diglyme solutions of  $\text{Co}_2\text{CO}_8$  at  $190^\circ\text{C}$  produces nitrogen containing products. The only product we were able to isolate was a gas which appears to be ketenimine (Figure V-17) probably  $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{C}=\text{N-Me} \\ \diagup \\ \text{H} \end{array}$  with a very strong absorption at  $2000\text{ cm}^{-1}$ .

#### 10. The Reaction of $\text{NaCoCO}_4$ , $\text{Co}_2\text{CO}_8$ and Syn Gas in Diglyme.

Apart from the normal catalysis products (ethanol, etc.) reaction of these reagents at  $190^\circ\text{C}$  and total gas pressure of ca. 150 atmospheres produces from the catalysts solution an infrared spectrum with a very strong sharp absorption at  $2340\text{ cm}^{-1}$ . It appears to be too sharp to be  $\text{CO}_2$ . We would like to believe it is dihydrogen activated on the cobalt carbonyl anion (Figure V-16).



The reaction proved difficult to reproduce.

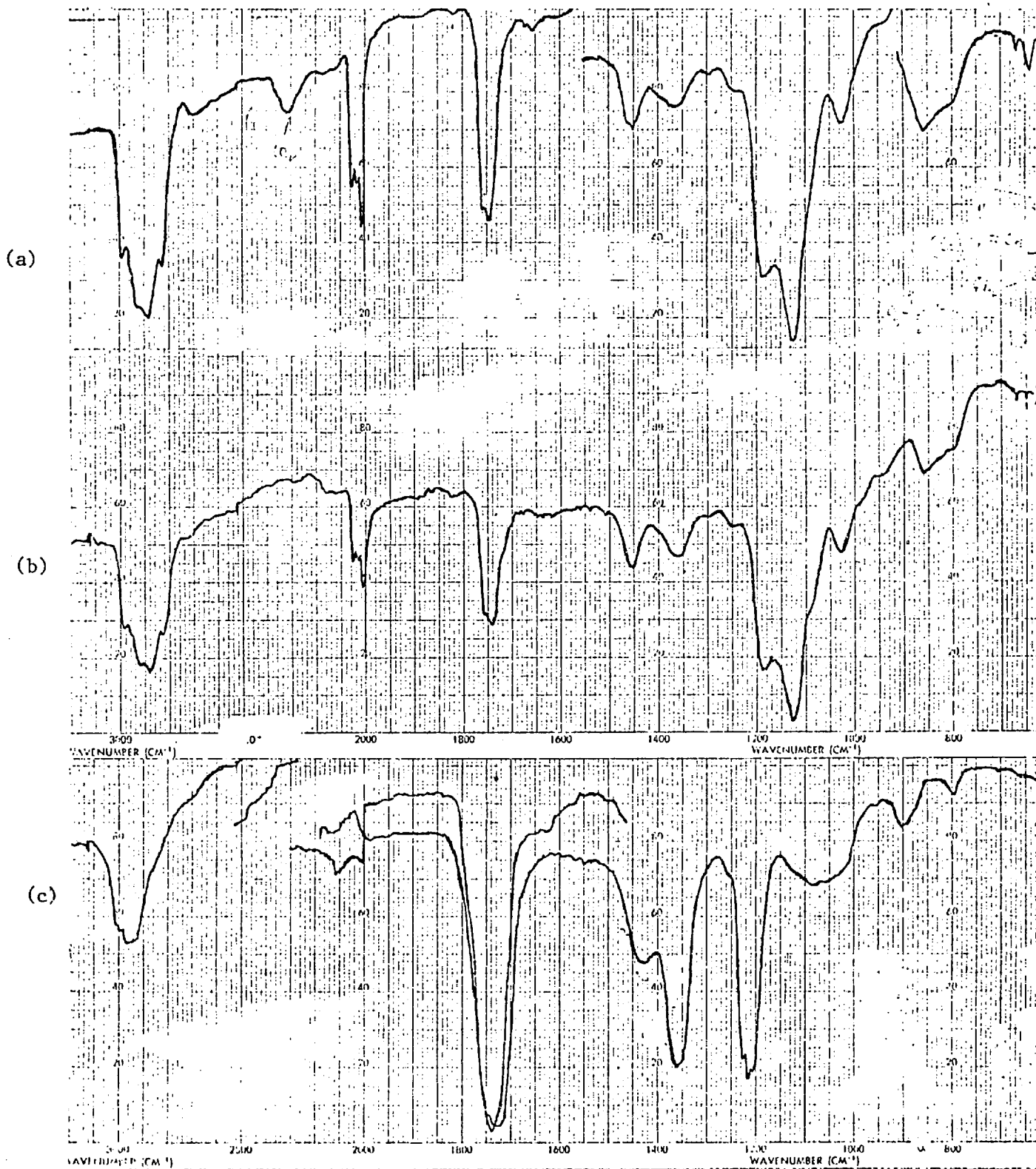


Figure 1. Gas phase i.r. spectra of yellow Gas 3.

- a) Fresh gas immediately after hydrolysis
- b) After removal of  $\text{CO}_2$  by fractional distillation
- c) After 24 hours gas 3  $\rightarrow$  acetone

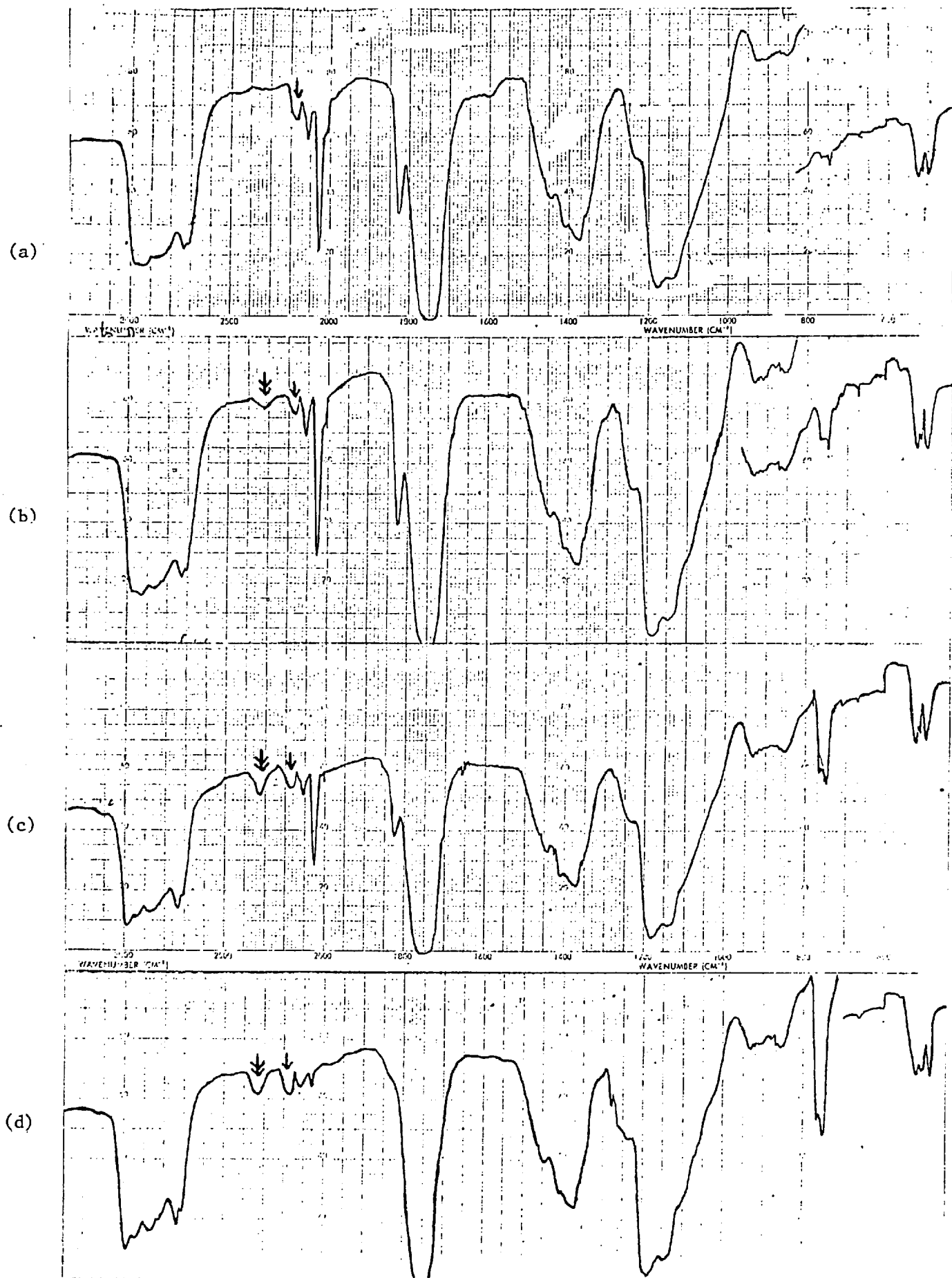


Figure 2. Decarboxylation of yellow Gas 1 (deuteriated) over 40 hrs.  
in the presence of acetaldehyde.

a) 5 mins    b) 2 hrs    c) 15 hrs    d) 40 hrs  
(↓  $\text{CO}_2$     † residual CO in gas cell)

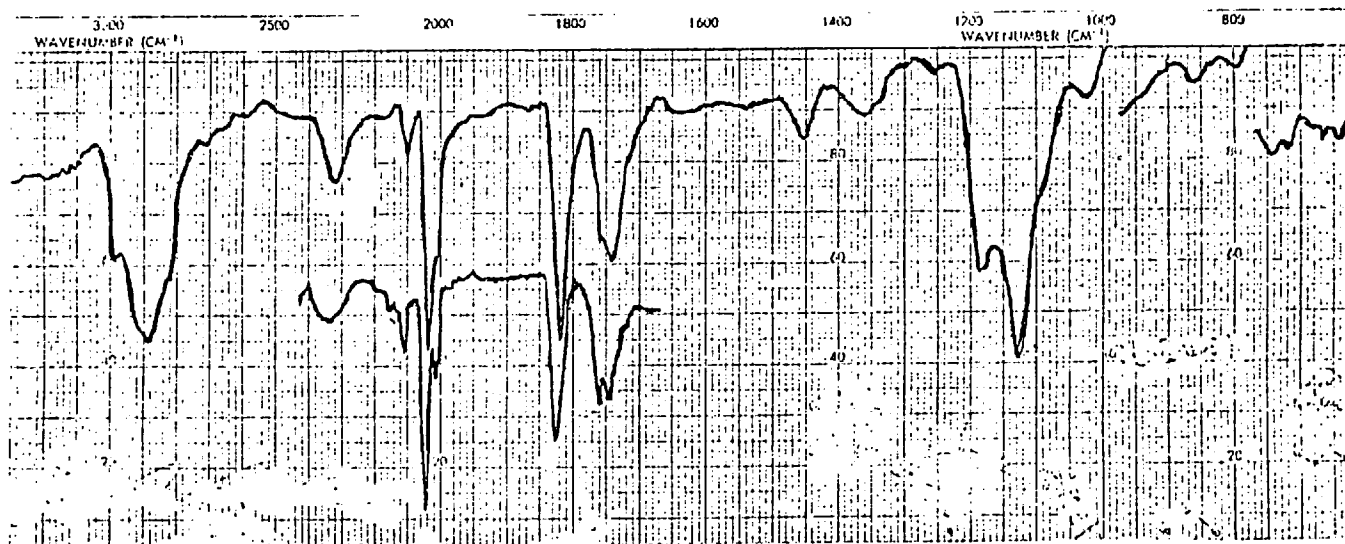


Figure 3. Yellow Gas 1 (and probably 2) at different attenuations.

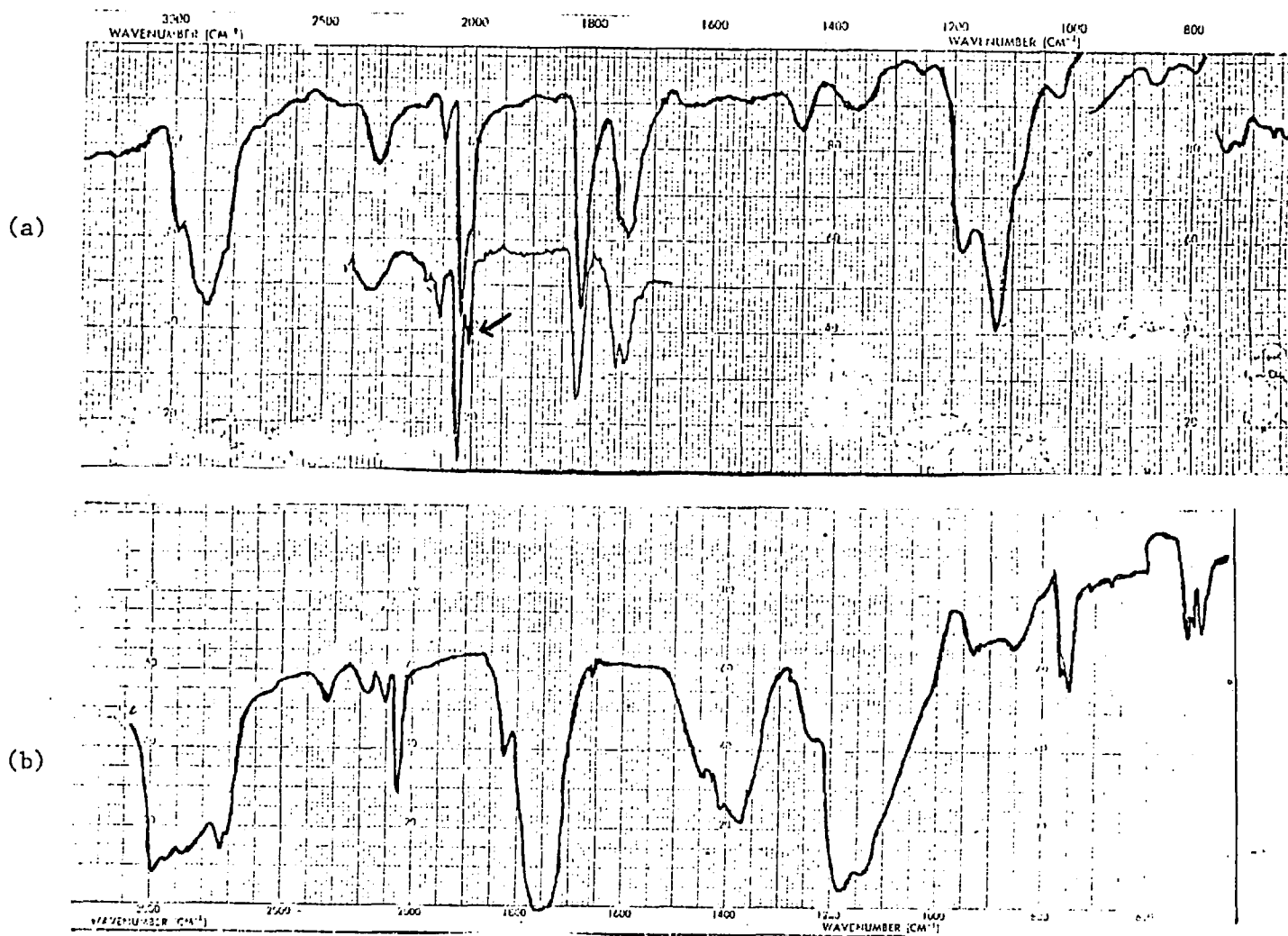


Figure 4. A comparison of yellow Gas 1

a) made from  $\text{H}_2\text{O}$

b) made from  $\text{D}_2\text{O}$  (in the presence of acetaldehyde vapour).

(+ Co-H  $\nu$  2020  $\text{cm}^{-1}$ ).

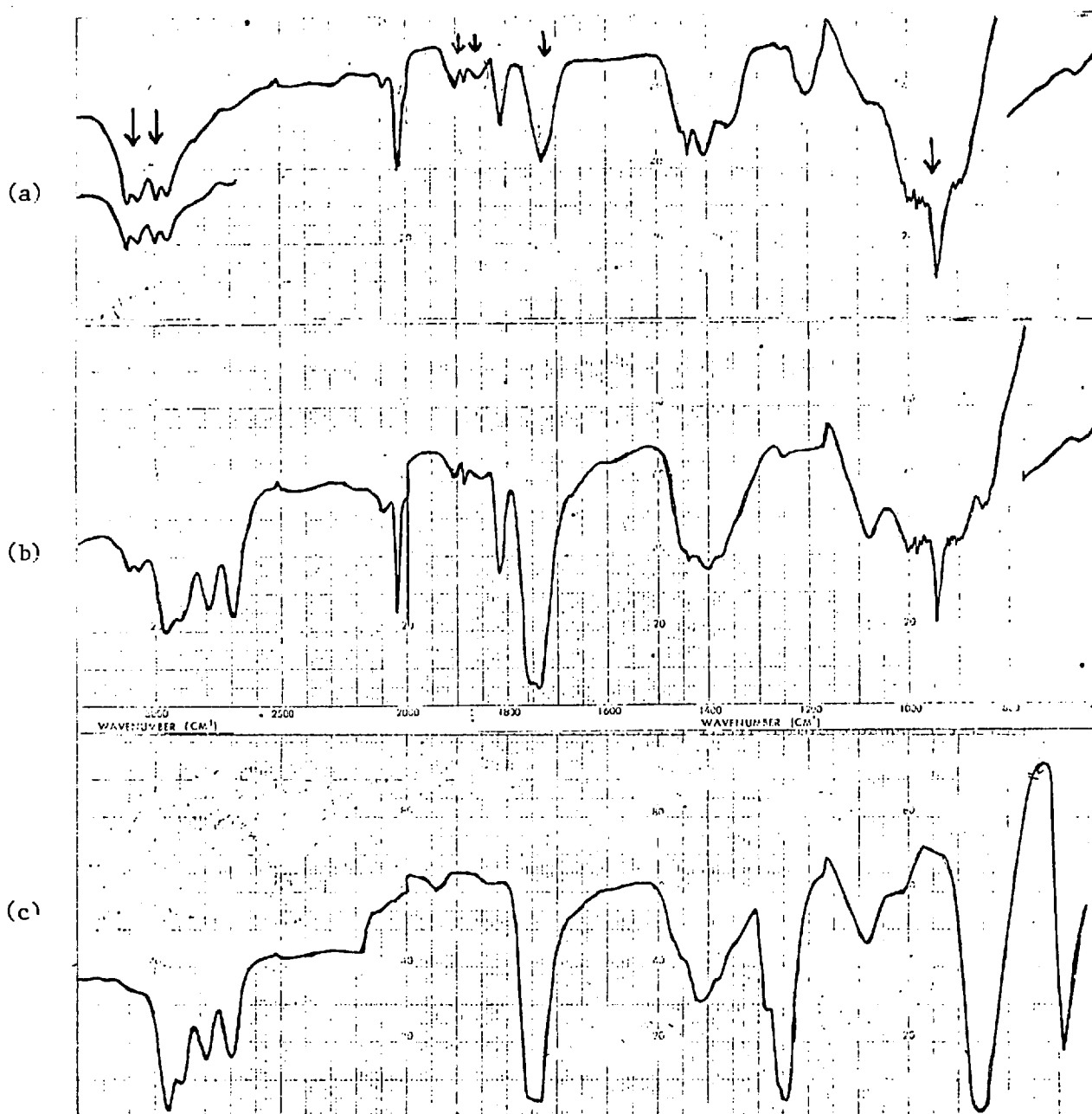


Figure 5. a) Yellow Gas 4 made from  $C_2H_4$ , CO and  $Co_2CO_8$  in the presence of ethylene +

b) Yellow Gas 6 in the presence of aldehydes

c) Decomposition of (b) to acetone.



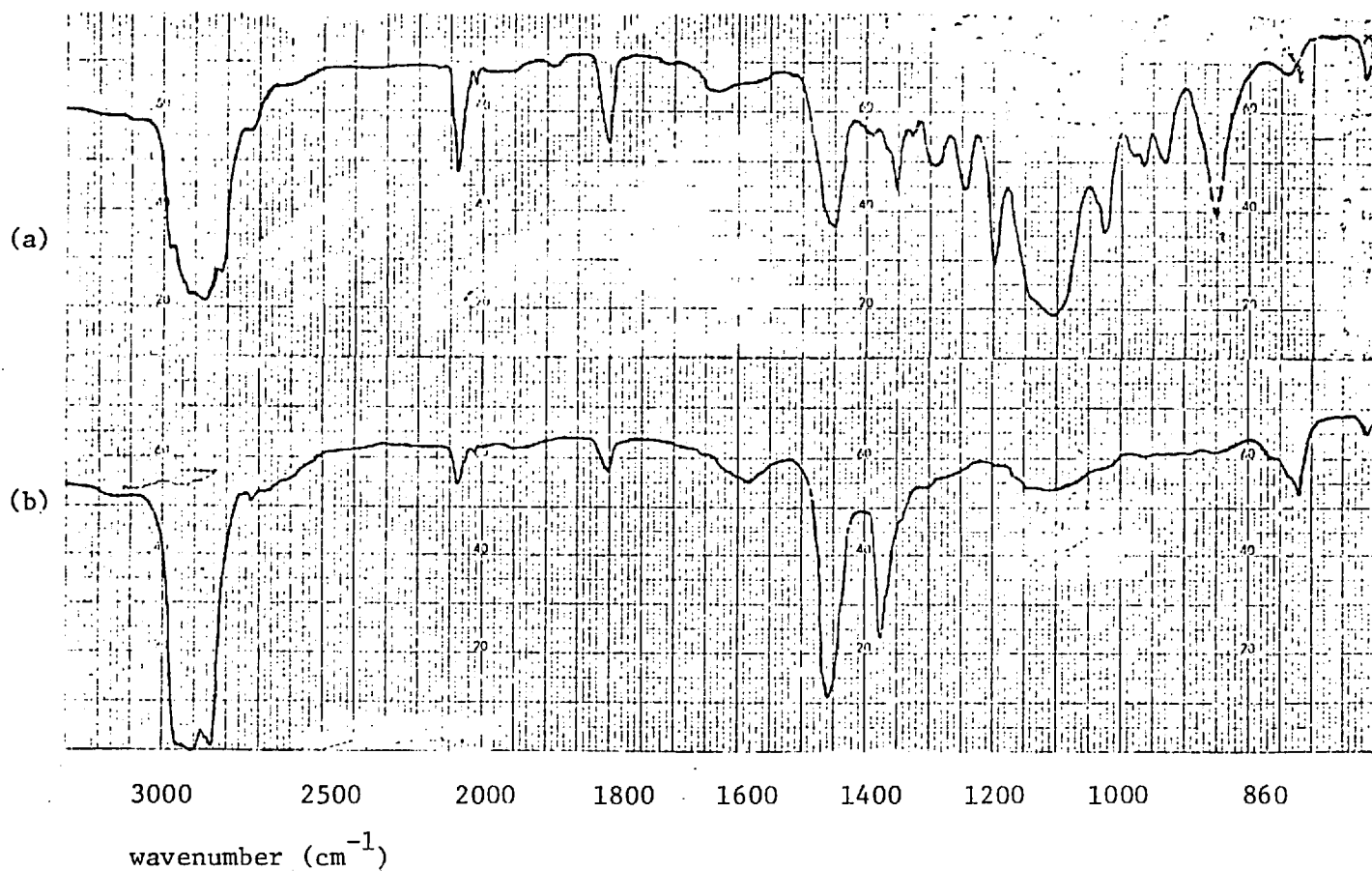


Figure 6. a) i.r. spectrum of the yellow diglyme solution  
(in KBr plates) after reaction.  
b) i.r. spectrum of the yellow-oil obtained by  
adding petrol to the diglyme reaction solution.

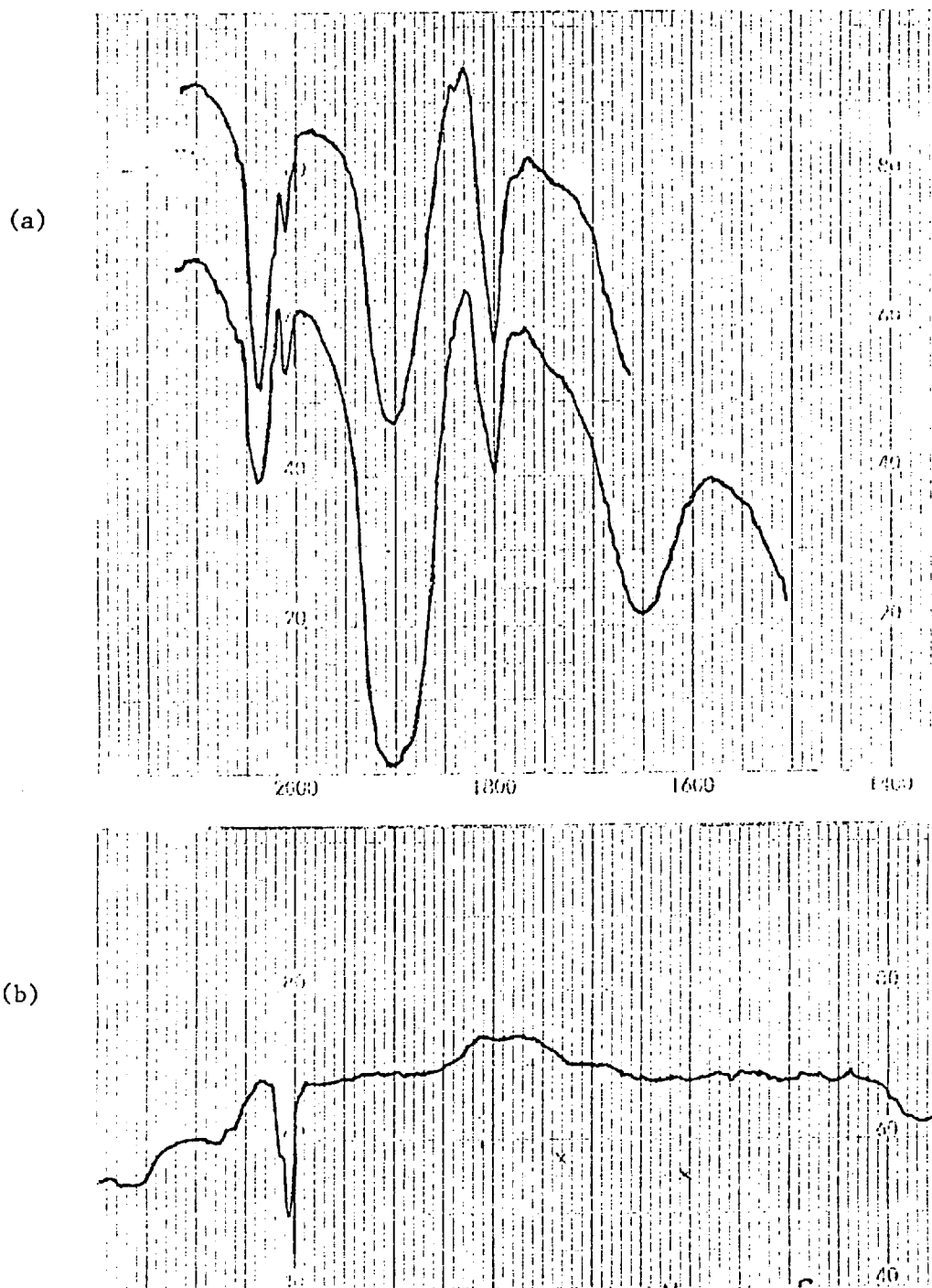


Figure 7. a) i.r. spectrum of the reaction solution of  $\text{Co}_2(\text{CO})_8$  in ethylene glycol (KBr plates)  $1900 \text{ cm}^{-1}$   $\text{Co}(\text{CO})_4$   
 b) i.r. spectrum of the yellow-gas obtained from the ethylene glycol reaction solution.

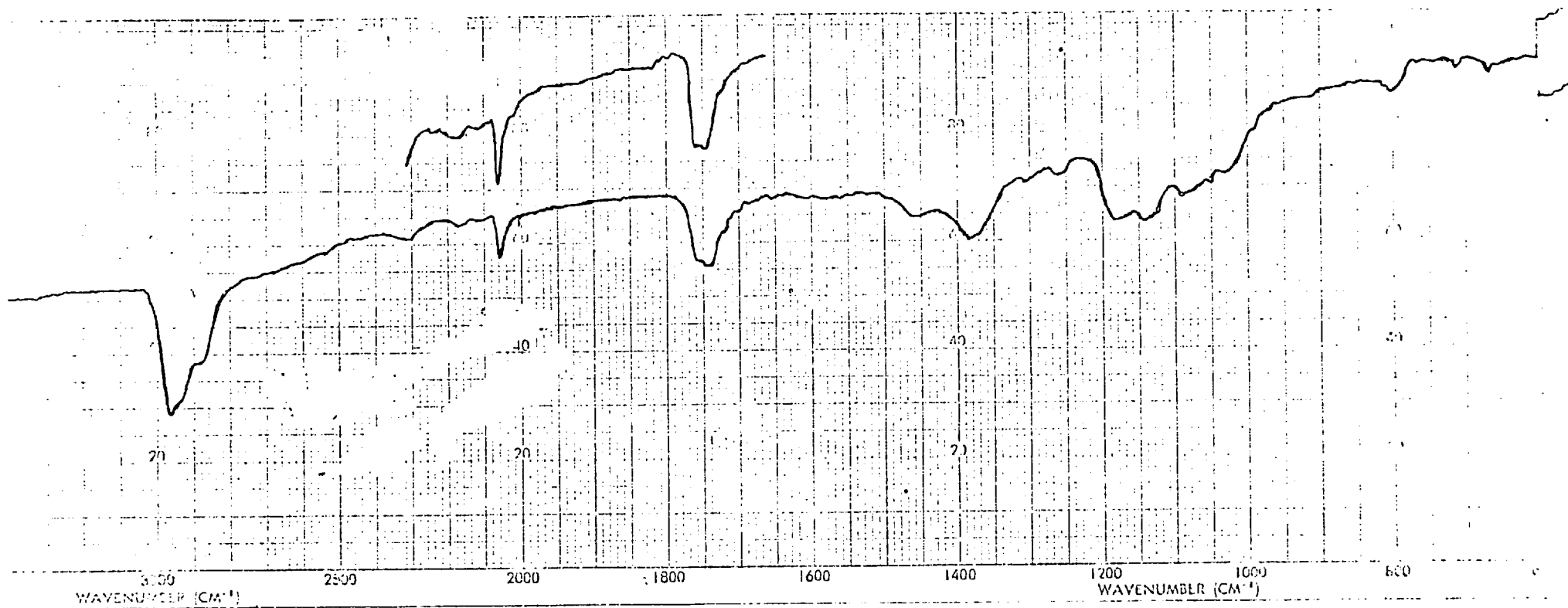


Figure 8. I.r. spectrum of the volatile cobalt complex obtained from the reactions in  $\text{H}_2$  rich mixtures ( $\text{H}_2/\text{CO} - 2:1$  and  $3:1$ ).

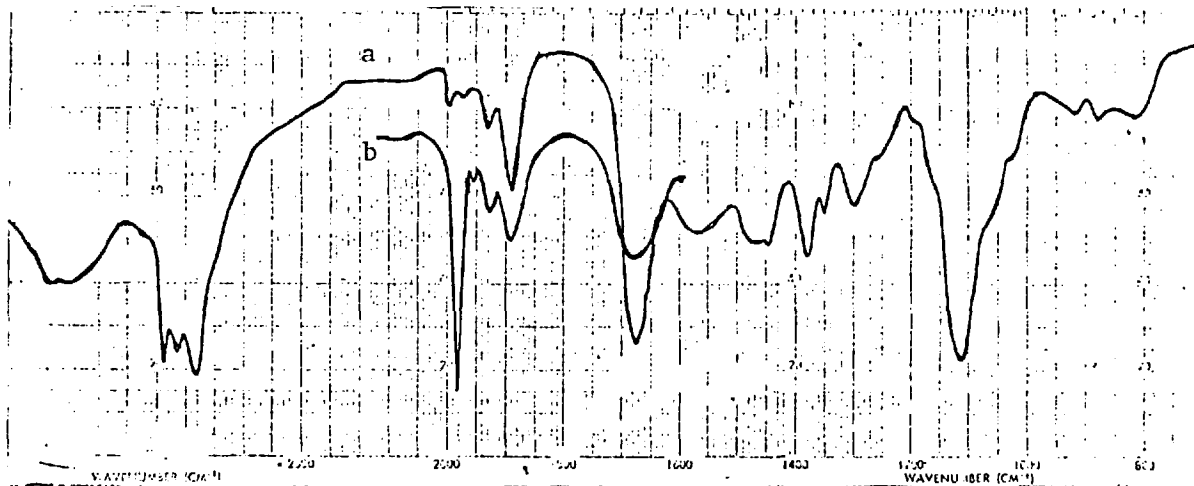


Figure 9. i.r. spectrum of the reaction solution using  $\text{Cr}(\text{CO})_6$  in  $\text{EtOEtNH}_2$ .

a) immediately after reaction showing strong absorption for ketonic group  $\text{Cr}-\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{C}-\text{N}$  at  $1675 \text{ cm}^{-1}$ .

b) same solution after 1 day: the absorption at  $1675 \text{ cm}^{-1}$  decreases while  $\text{Cr}(\text{CO})_6$  is formed ( $1980 \text{ cm}^{-1}$ ).

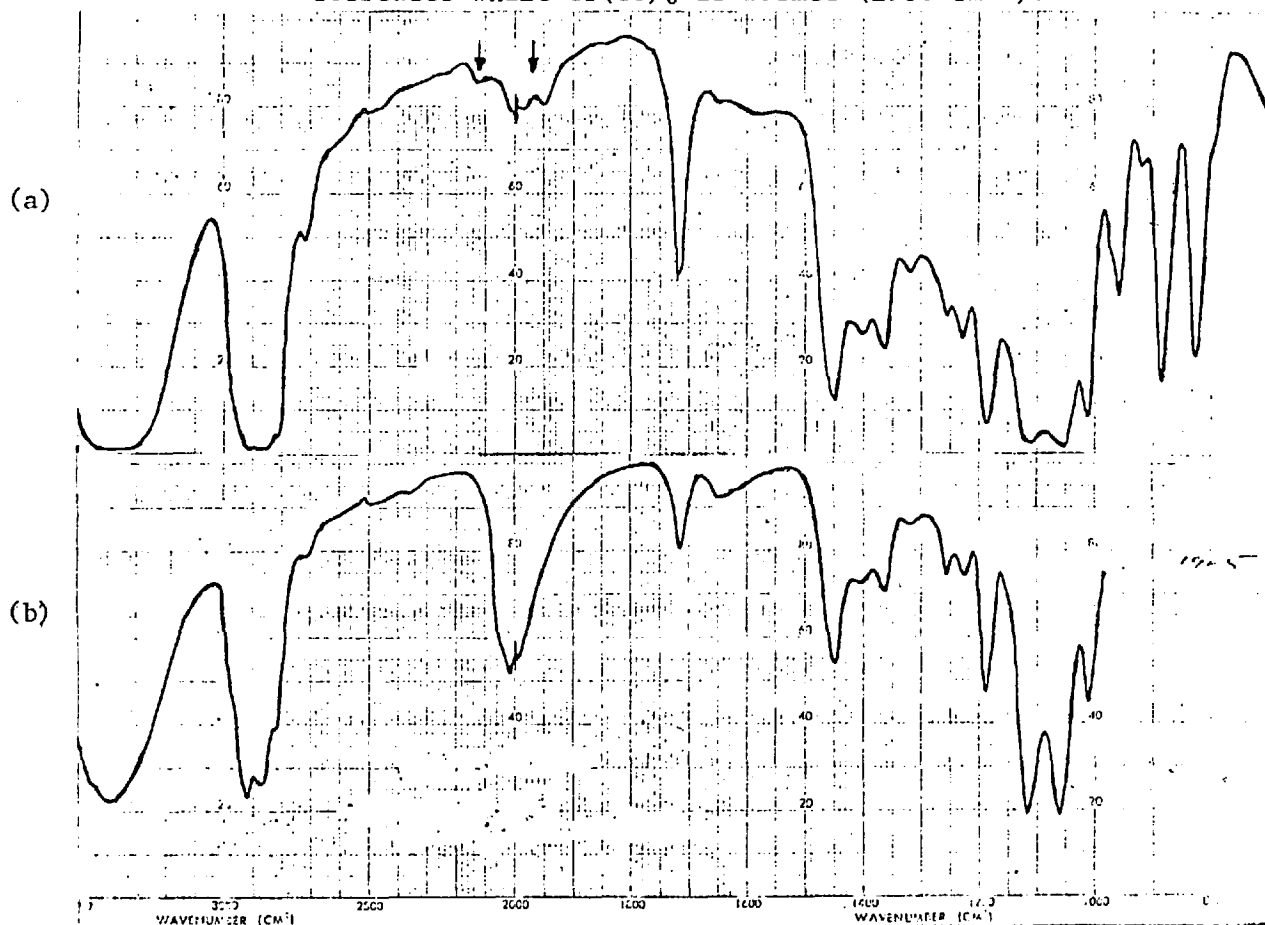


Figure 10. i.r. spectrum of the reaction solution using  $\text{Ru}_3(\text{CO})_{12}$  in 2-methoxyethanol.

a) Immediately after reaction showing only ketonic absorption of  $\text{Ru}-\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{C}-\text{EtOMe}$  at  $1720 \text{ cm}^{-1}$ . No  $\text{Ru}_3(\text{CO})_{12}$  is observed ( $\downarrow$  solvent).

b) The same solution after 10 hrs; disappearance of the absorption at  $1720 \text{ cm}^{-1}$  (for  $\text{Ru}-\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{C}-\text{OR}$ ) and formation of  $\text{Ru}_3(\text{CO})_{12}$ .

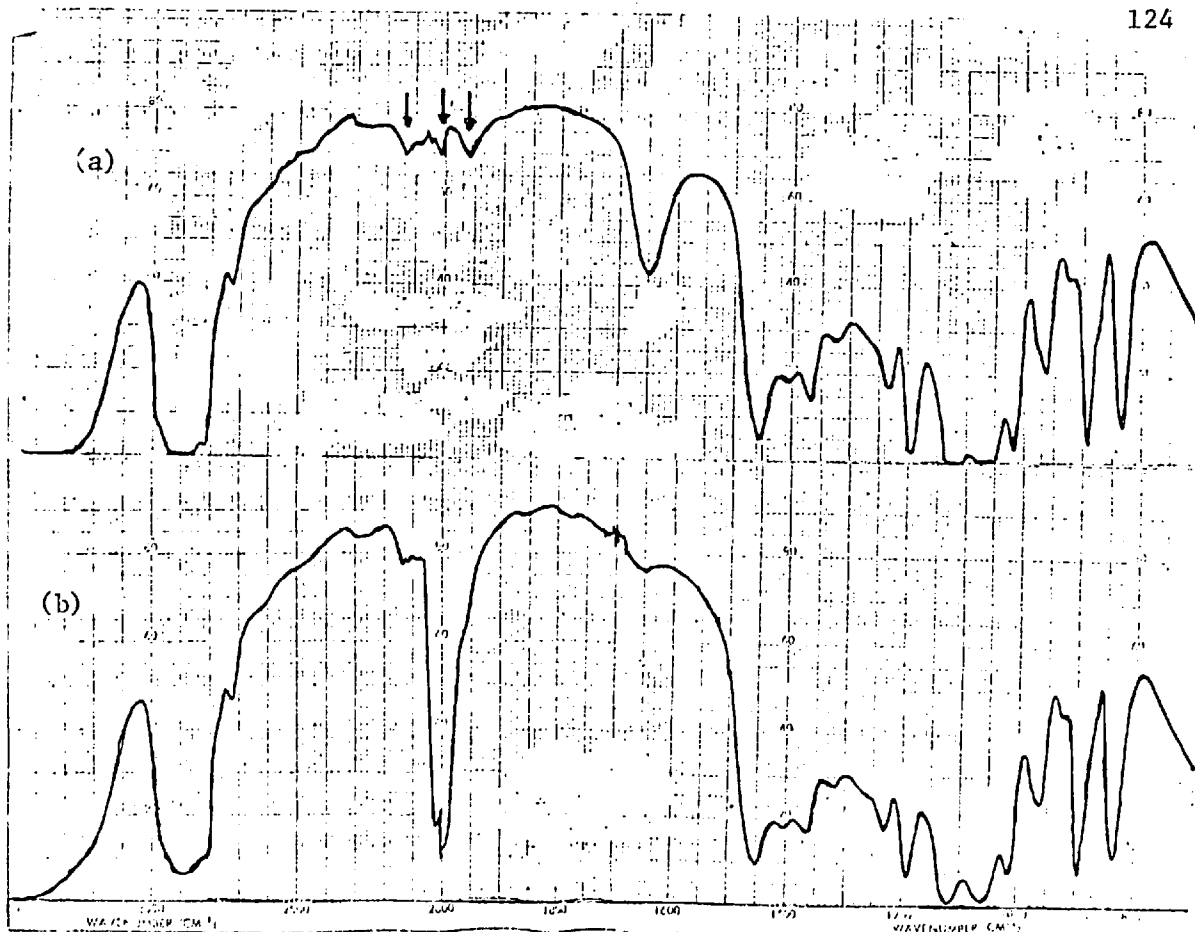


Figure 11. i.r. spectrum of the reaction solution using  $\text{Fe}(\text{CO})_5$  in 2-methoxyethanol.

- a) solution immediately after reaction showing only the absorption at  $1650\text{ cm}^{-1}$  ( $\downarrow$  solvent).
- b) same solution after 24 hrs;  $\text{Fe}(\text{CO})_5$  is re-formed.

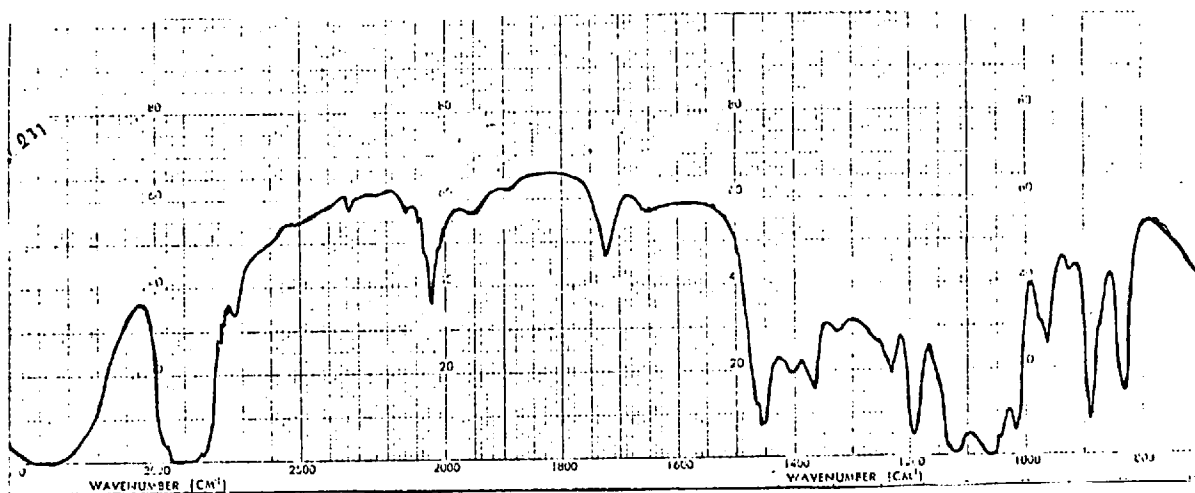


Figure 12. i.r. spectrum of the 2-methoxyethanol reaction solution with  $\text{Os}_3(\text{CO})_{12}$  showing the absorptions for  $\text{Os}$  carbonyl hydrides and the ketonic  $\text{Os}-\text{C}-\text{OR}$  ( $1720\text{ cm}^{-1}$ ).

$$\begin{array}{c} \text{Os}-\text{C}-\text{OR} \\ || \\ \text{O} \end{array}$$

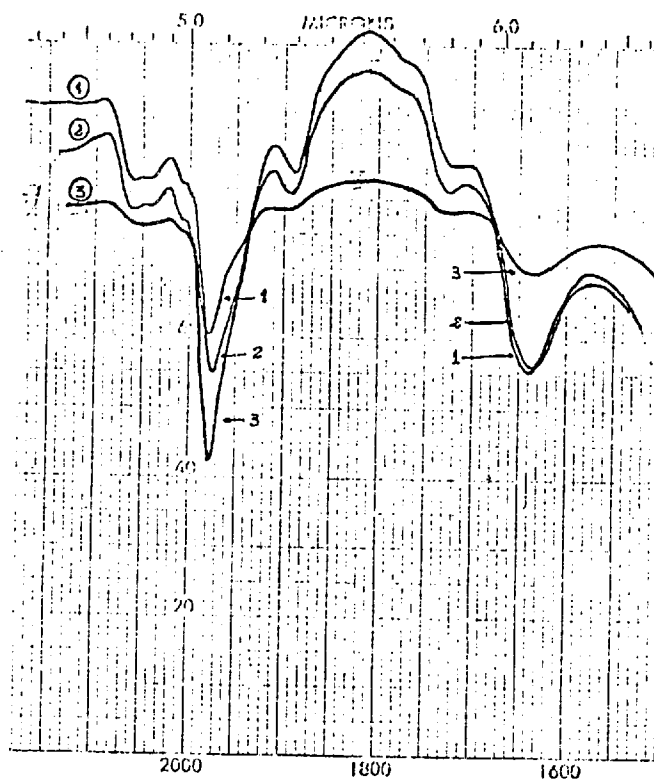


Figure 13. i.r. spectra of the 2-methoxyethanol reaction solution with  $\text{Cr}(\text{CO})_6$ . The spectra 1, 2 and 3 were recorded at different times showing the reformation of  $\text{Cr}(\text{CO})_6$  from the ketonic  $\text{Cr}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{OR}$  ( $1640 \text{ cm}^{-1}$ )

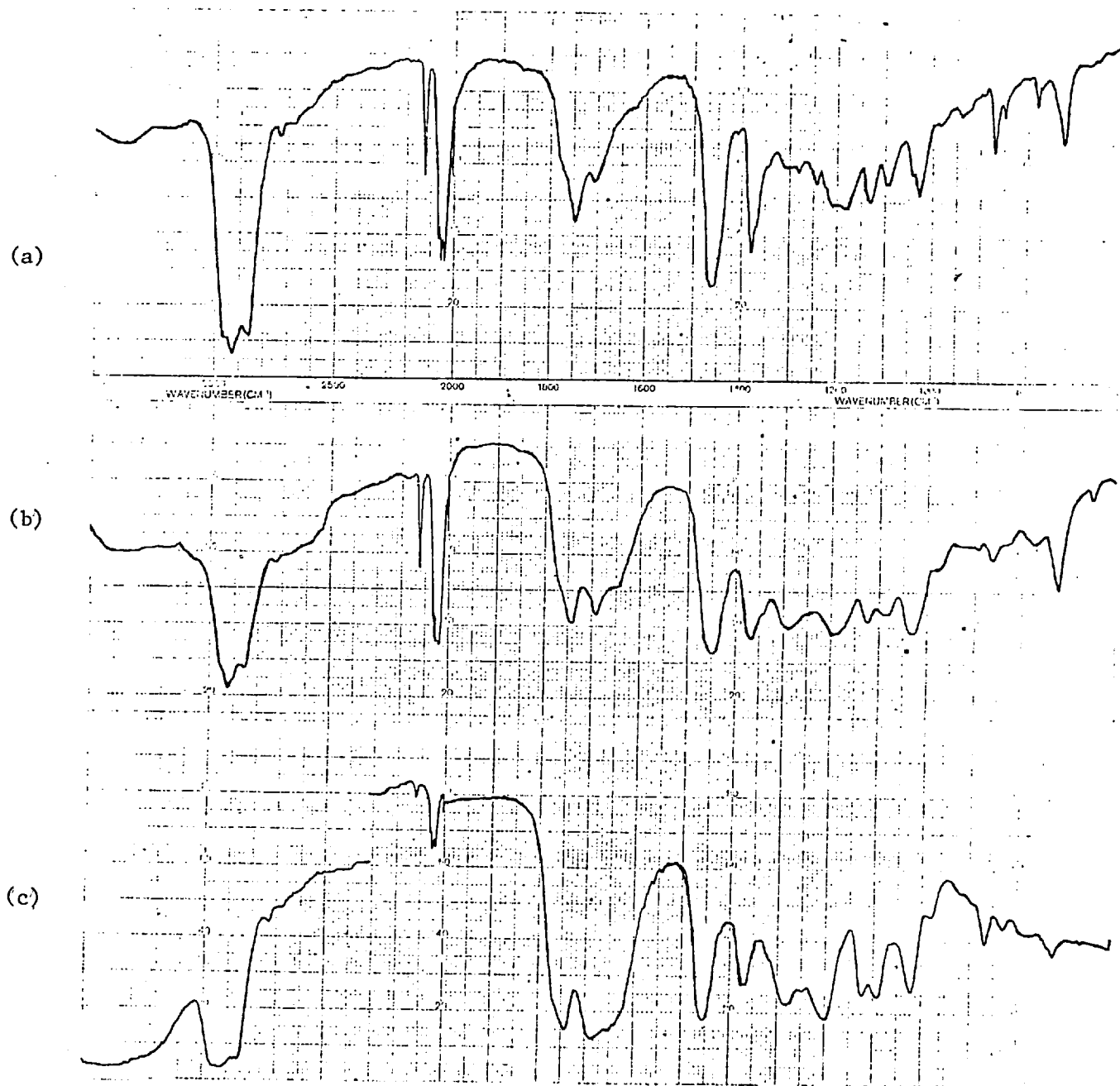
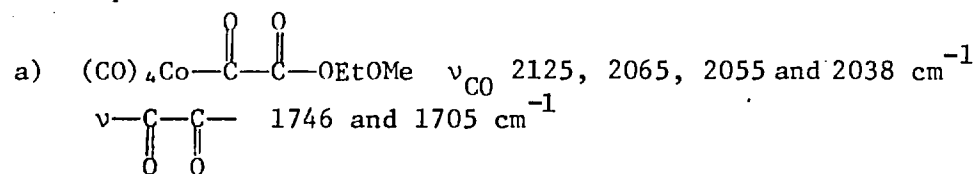


Figure 14. i.r. spectrum of



b) and c) show decomposition of (a) at room temperature forming a carboxylate ( $1600-1700 \text{ cm}^{-1}$ ) type complex.

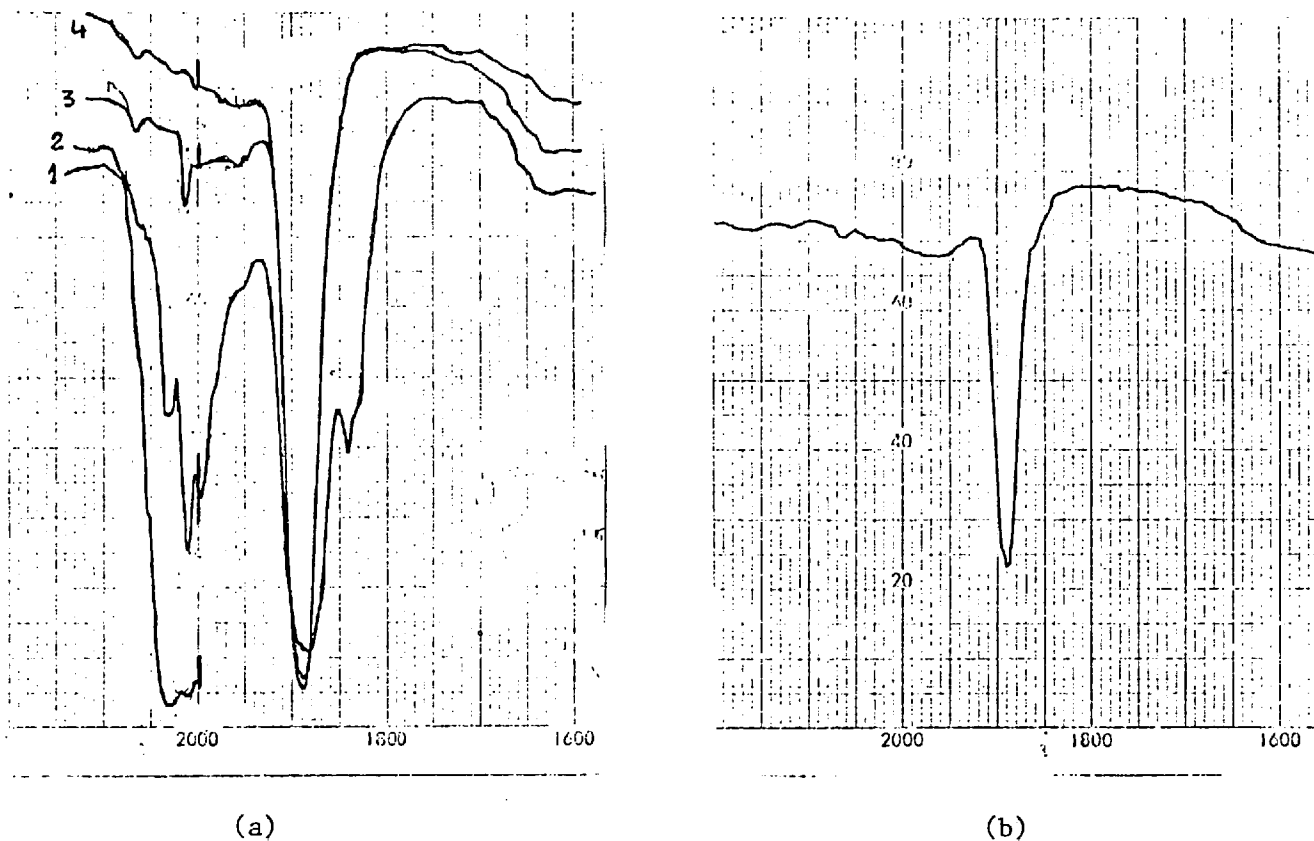


Figure 15. a) i.r. spectra of the rearrangement of  $\text{Co}_4(\text{CO})_{12}$  in diglyme,  
 1 - black  $\text{Co}_4(\text{CO})_{12}$ ; 2 - green intermediary; 3 - red solution  
 intermediary; 4 - red solution final diglyme  $\text{Co}[\text{Co}(\text{CO})_4]_3$ .  
 b) i.r. spectrum of cobalt carbonyl in all glyme solutions.



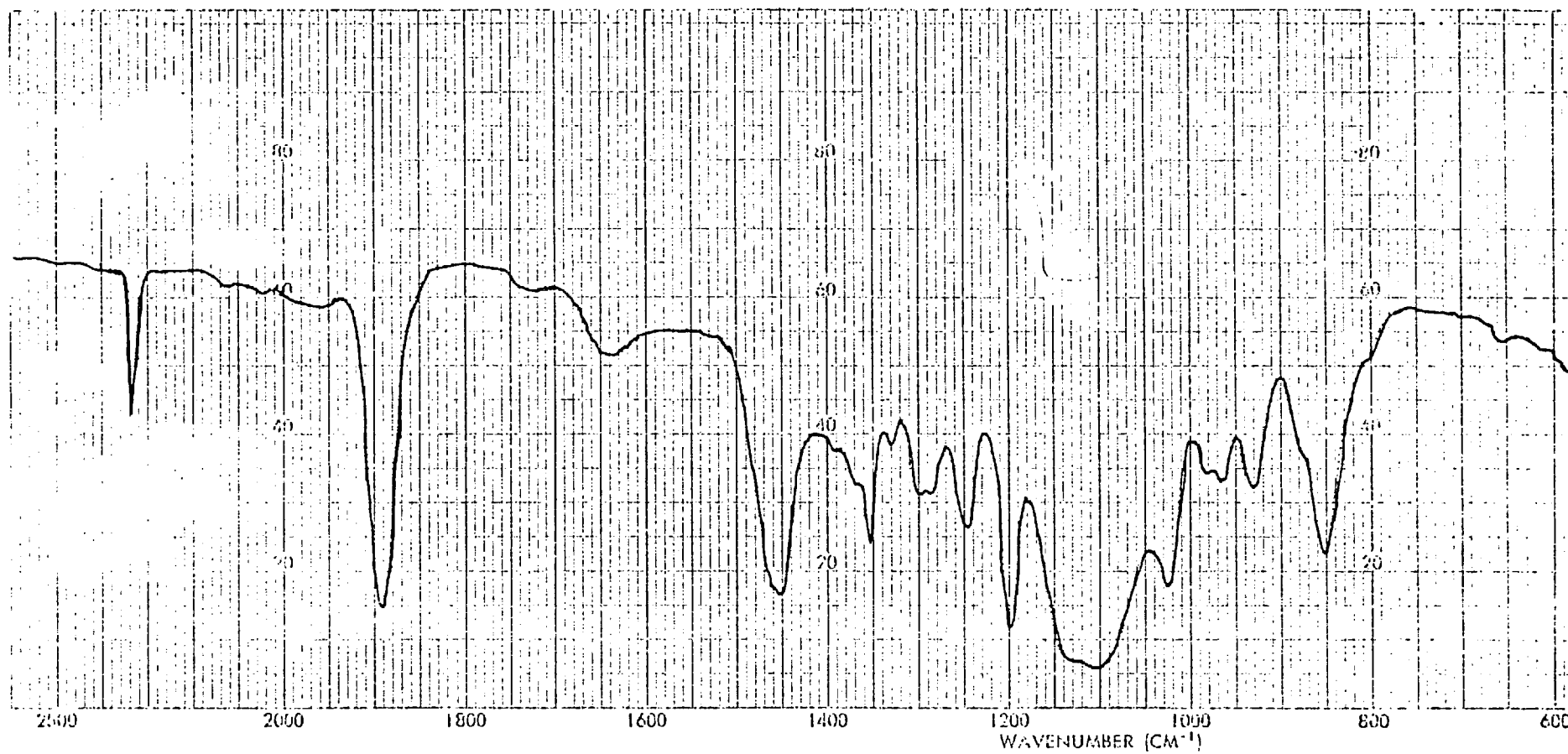


Figure 16. i.r. spectrum of the diglyme reaction solution using  $\text{NaCo}(\text{CO})_4$ . The absorption at  $2340 \text{ cm}^{-1}$  is assigned probably to  $\text{Na}^+ \text{H}^- \text{H} - \text{Co}(\text{CO})_4$ .

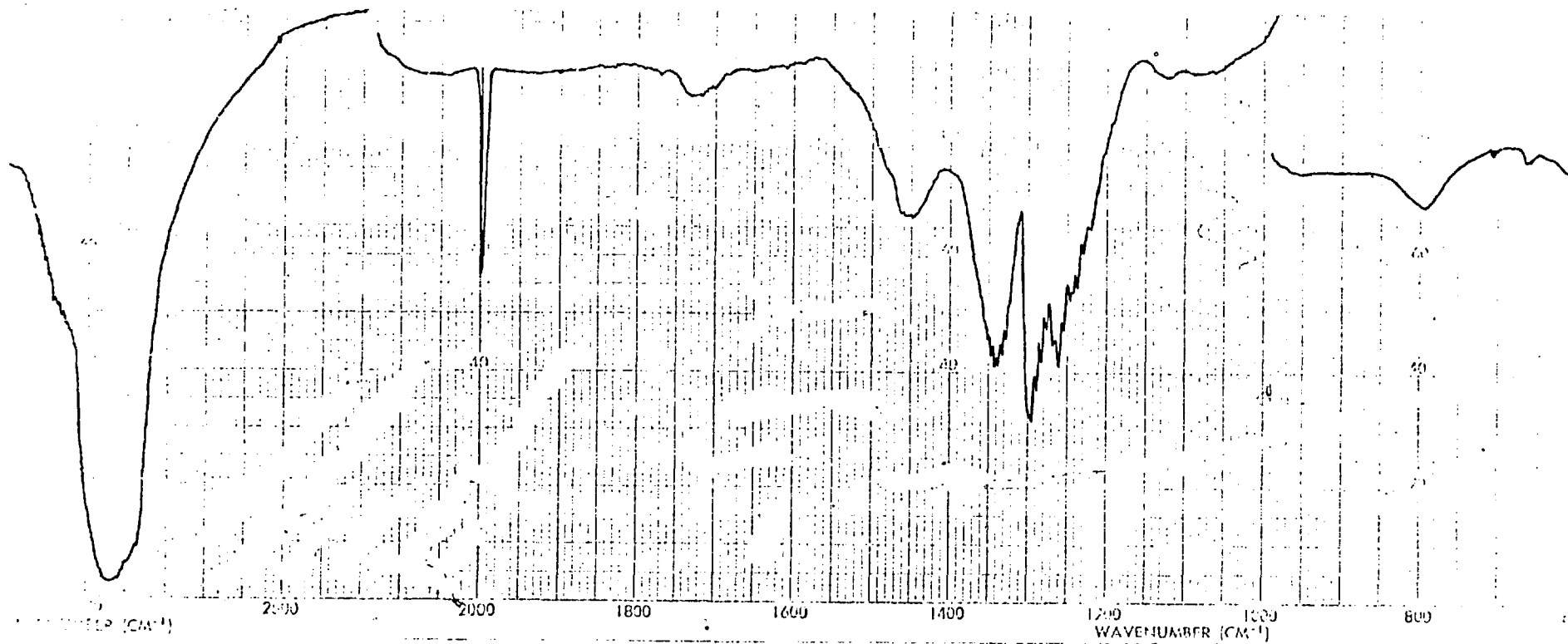


Figure 17. i.r. spectrum of the gas formed in the reaction  $\text{Co}_2(\text{CO})_8$  in diglyme.

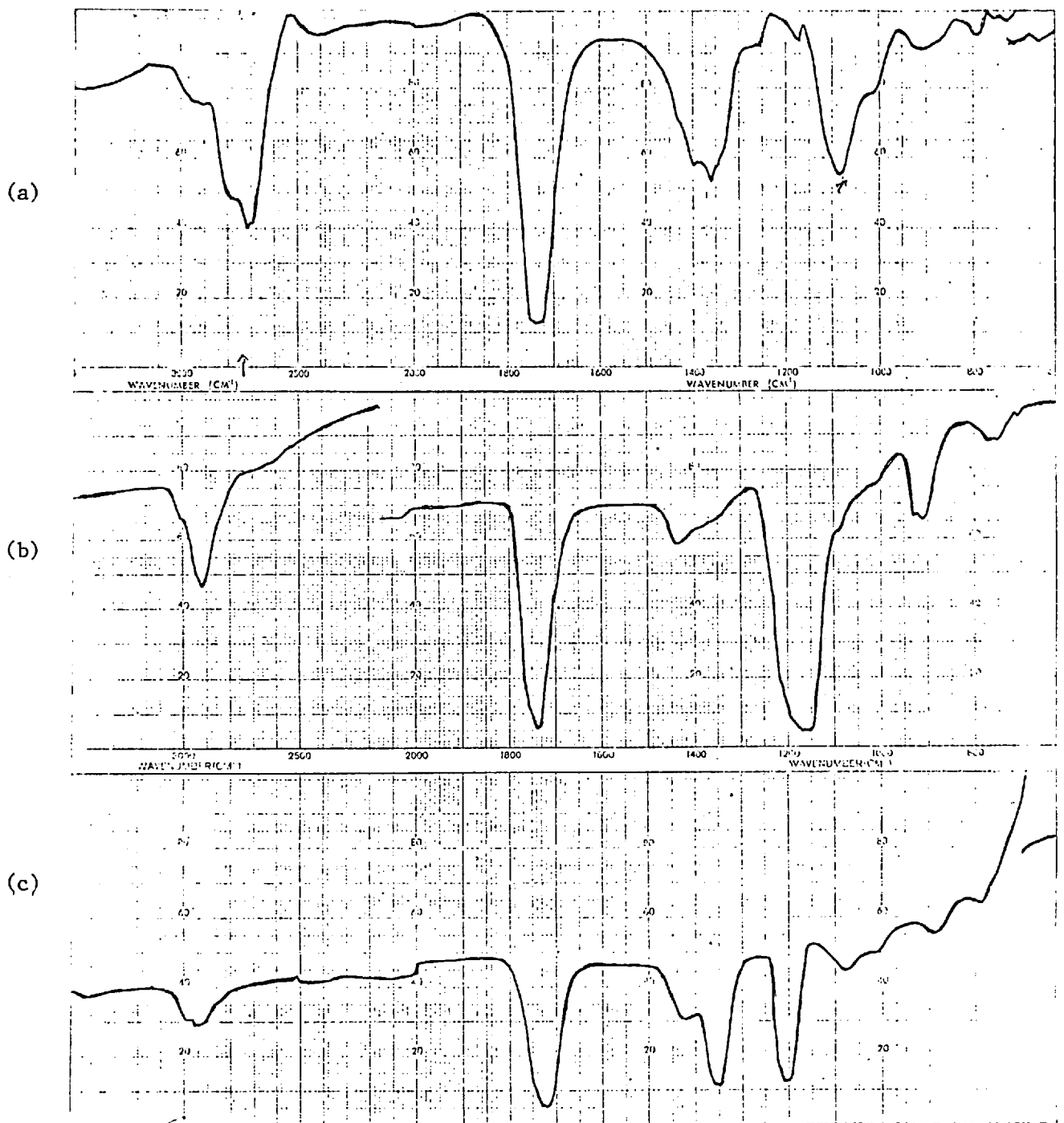


Figure 18. i.r. spectra in the gas phase of

- a) acetaldehyde
- b) methylformate
- c) acetone

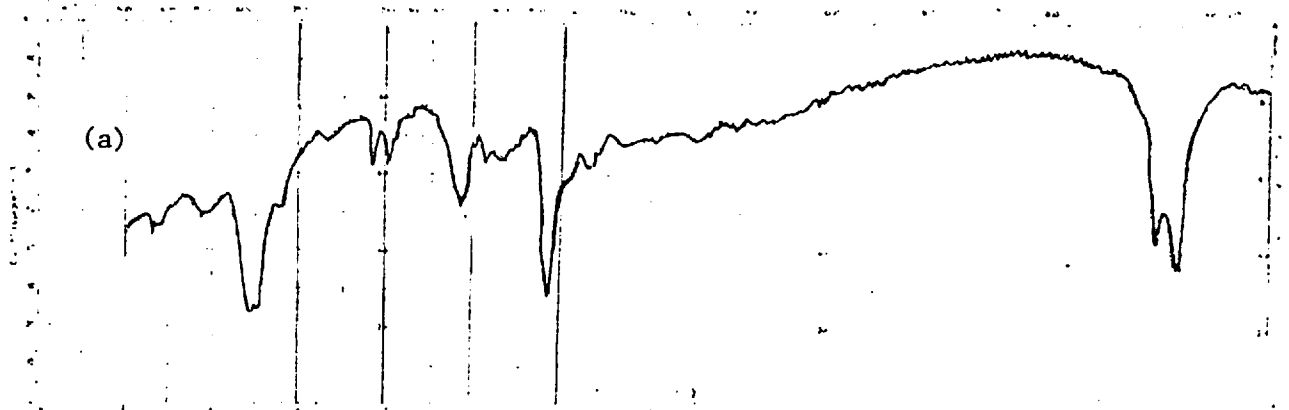


Bild 1 IR-Spektrum einer hochmolekularen Fraktion des bei 132°C erhaltenen Syntheseproduktes (dunkles Zwischenprodukt)

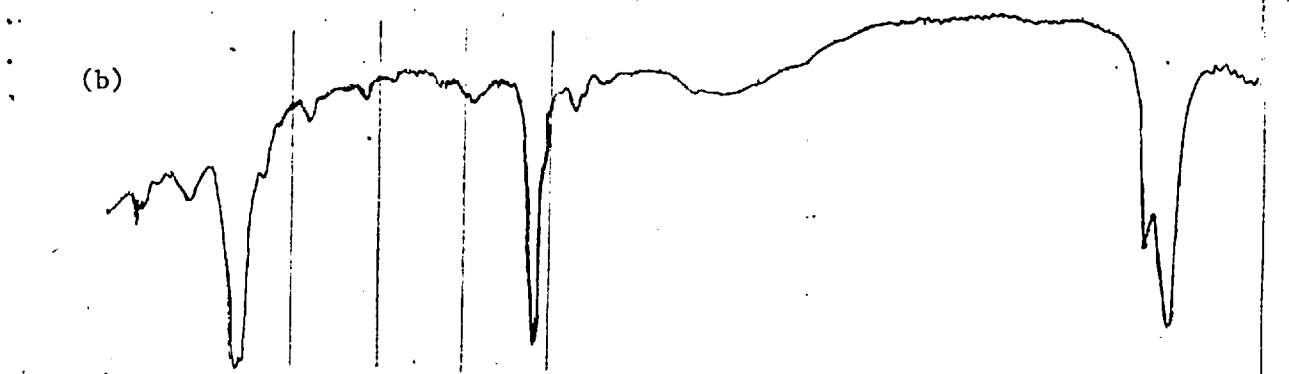


Bild 2 IR-Spektrum einer hochmolekularen Fraktion ( $M_w = 81700$ ) des bei 132°C erhaltenen und nachträglich mit Wasserstoff behandelten, rein weißen Polyäthylens

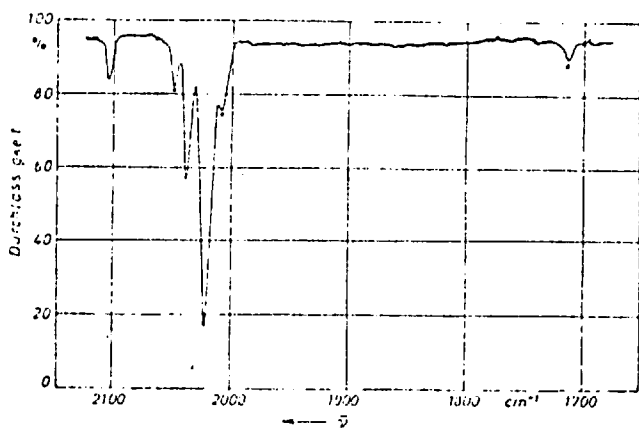


Bild 2 Infrarotspektrum des  $\text{CH}_3\text{Co}(\text{CO})_4$  in Hexanlösung  
x = Absorptionsbanden des  $\text{CH}_3\text{COCOC}(\text{CO})_4$ , das in geringer Menge als Verunreinigung vorhanden ist

(c)

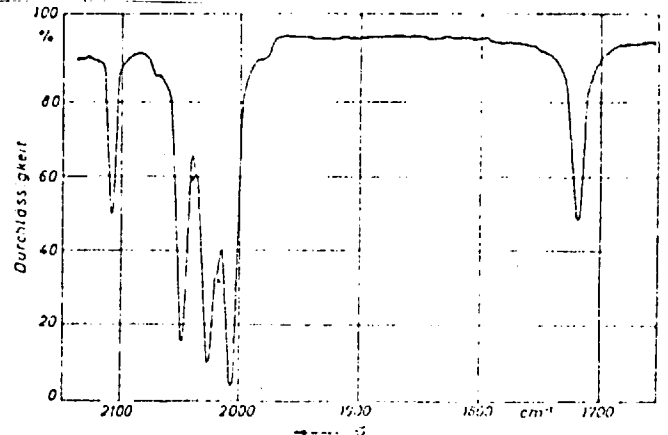


Bild 3 Infrarotspektrum des  $\text{CH}_3\text{COCOC}(\text{CO})_4$  in Hexanlösung  
x = Absorptionsbanden des  $\text{CH}_3\text{Co}(\text{CO})_4$ , das in geringer Menge als Verunreinigung vorhanden ist

(d)

Figure 19. a) and b) reproduced from: Von Helmut Pichler and B. Firnhaber, Brennstoff Chemie, 1963, 33.

Reaction with  $\text{RuO}_2$  and  $\text{CO}/\text{H}_2$ . Spectrum (b) corresponds to the product obtained; a) shows the mixture composition after reaction. At  $1725\text{ cm}^{-1}$  we can observe the absorption characteristic for CO activated.

c) and d) reproduced from: V.L. Marko, G. Poor, G. Almazy and P. Szabo, Brennstoff Chemie, 1963, 184; c)  $\text{CH}_3\text{Co}(\text{CO})_4$ ; d)  $\text{CH}_3\text{COCOC}(\text{CO})_4$  showing at  $1726\text{ cm}^{-1}$  the ketonic CO.

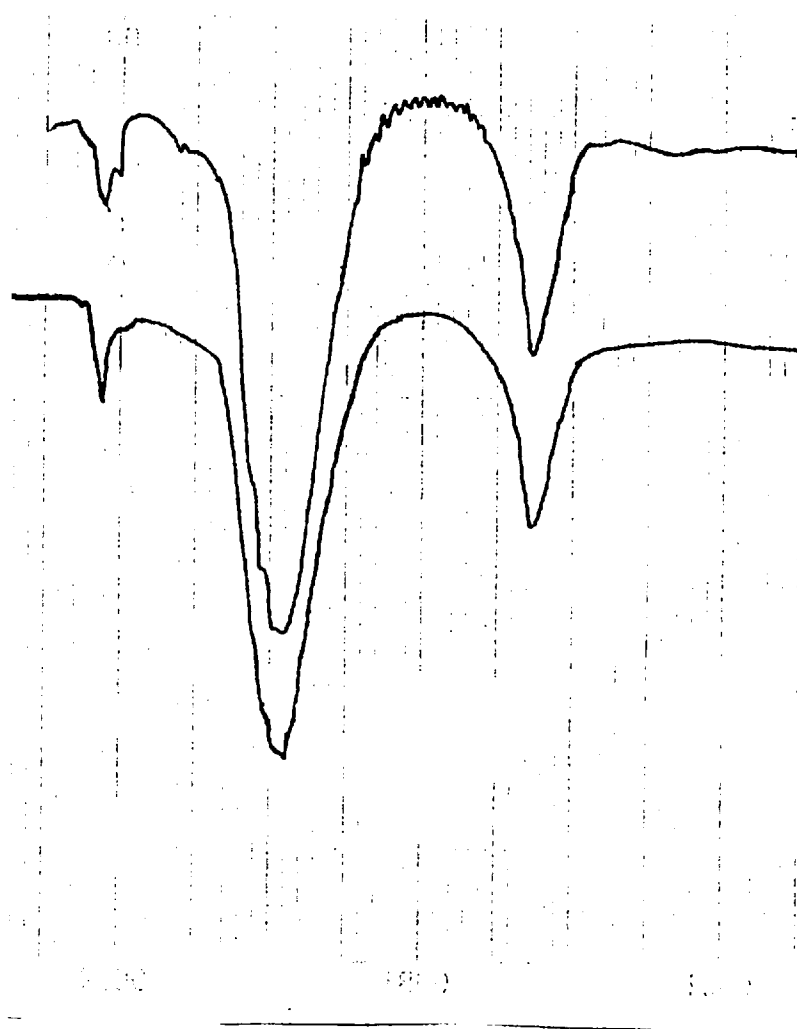


Figure 20. Black crystals obtained on cooling the diglyme solution after reaction with  $\text{CO}/\text{H}_2$  (1:1) and  $\text{Co}(\text{CO})_8$ .

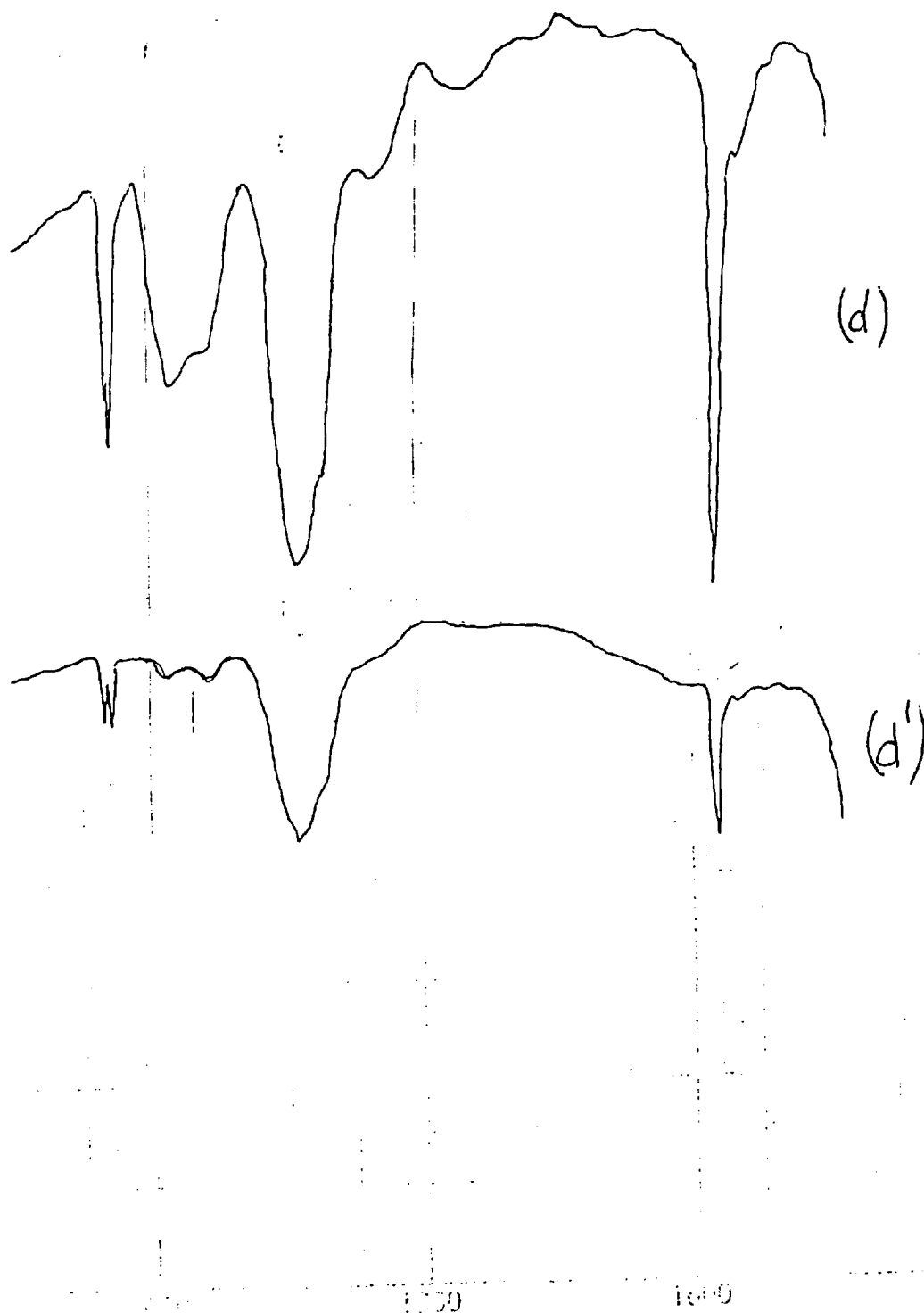


Figure 21. i.r. of the unstable crystals  
[(d), (d'), Scheme III-2]

APPENDIX 1

Minimum rates and approximate activation energy.

- a)  $\text{Co}_2(\text{CO})_8$  in diglyme; 150 atm. and  $200^\circ\text{C}$ .

Conversion rate:

$$8 \times 10^{-4} \text{ moles EtOH/mole } \text{Co}_2(\text{CO})_8/\text{sec}$$

or  $2.4 \times 10^{-3} \text{ moles CO/mole } \text{Co}_2(\text{CO})_8/\text{sec}$

- b) Activation energy using  $\text{Co}_2(\text{CO})_8$  in 2-methoxyethanol

approx. 8 kcal/mole

- c)  $\text{Ru}_3(\text{CO})_{12}$  in 2-methoxyethanol; 180 atm. and  $190^\circ\text{C}$ .

Conversion rate:

$$1.9 \times 10^{-3} \text{ moles CO/g atom Ru/sec}$$

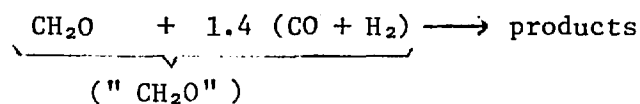
- d) Hydroformylation of paraformaldehyde using  $\text{Co}_2(\text{CO})_8$  in diglyme;

140 atm. and  $125^\circ\text{C}$ .

Conversion rate:

$$1.2 \times 10^{-2} \text{ moles "CH}_2\text{O" /moles } \text{Co}_2(\text{CO})_8/\text{sec}$$

based on equation:



- e) Comparative value.

Hydroformylation of propene at  $165^\circ\text{C}$ .

Conversion rate:

$$4 \times 10^{-2} \text{ moles propene/moles } \text{HCo}(\text{CO})_4/\text{sec}$$

REFERENCES

1. J.F. Harrod and J. Halpern, *Canad. J. Chem.*, 1959, 37, 1933.
2. M. Iguchi, *J. Chem. Soc., Japan*, 1939, 60, 1287; *ibid.*, 1942, 63, 634.
3. G.L. Eichhom, *Advances in Chemistry Series*, 1963, 37, 37.
4. B.R. James, "Homogeneous Hydrogenation", John Wiley and Sons, New York, 1973.
5. John S. Bradley, in *Homogeneous Catalysis*, Vol. 3, Minoru Tsutsui, ed., Plenum Press, New York, 1979, p. 165.
6. R.L. Pruett and W.E. Walker, U.S. Patent 3,833,634 (1974); *ibid.*, U.S. Patent 3,957,857 (1976); W.E. Walker and E.S. Brown, Jr., U.S. Patent, 3,968,136 (1976).
7. P.M. Treichel and R.L. Shubkin, *Inorg. Chem.*, 1967, 6, 1328.
8. Juan M. Manriquez, Donald R. McAlister, Robert D. Sanner, and John E. Bercaw, *J. Am. Chem. Soc.*, 1976, 98, 6733.
9. L.I. Shoer and J. Schwartz, *J. Am. Chem. Soc.*, 1977, 99 5830.
10. a) J.A. Gladysz, G.M. Williams, Wilson Tam, and Dennis Johnson, *J. Organometallic Chem.*, 1977, 140, C-1;  
b) J.A. Gladysz and J.C. Selover, *Tetrahedron Letters*, 1978, 319;  
c) Wilson Tam, Wai-Kwok Wong, and J.A. Gladysz, *J. Am. Chem. Soc.*, 1979, 101, 1589.
11. F. Fischer and H. Tropsh<sup>c</sup>, *Brennstoff. Chem.*, 1923, 4, 276.
12. C. Masters, in *Advances in Organometallic Chemistry*, Vol. 17, F.G.A. Stone and R. West, eds., Academic Press, New York, pp. 61-103.



13. a) C.R. Eady, B.F.G. Johnson, J. Lewis and T. Matheson,  
J. Organometallic Chem., 1973, 57, C-82;  
b) C.R. Eady, B.F.G. Johnson and J. Lewis, J. Organometallic  
Chem., 1972, 37, C-39.
14. E. Carmona-Guzman and G. Wilkinson, J. Chem. Soc., Dalton,  
1977, 1716.
15. a) G. Mestroni, R. Spogliarich, A. Camus, F. Martinelli and  
G. Zassinovich, J. Organometallic Chem., 1978, 157, 345;  
b) G. Mestroni, G. Zassinovich and A. Camus, J. Organometallic  
Chem., 1977, 140, 63.
16. M.L.H. Green, J.A. McCleverty, L. Pratt and G. Wilkinson, J. Chem.  
Soc., 1961, 4854.
17. a) R.L. Pruett, Annals New York Academy of Sciences, 1977, 295, 239;  
b) Jose L. Vidal and W.E. Walker, Inorg. Chem., 1980, 19, 896.
18. S. Martinengo, P. Chini, V.G. Albano, and F. Cariati,  
J. Organometallic Chem., 1973, 59, 379.
19. a) R. Whyman, J. Chem. Soc., Chem. Comm., 1970, 270;  
b) *ibid.*, 1970, 1194; c) P. Chini, S. Martinengo and G. Garlaschelli,  
J. Chem. Soc., Chem. Comm., 1972, 709;  
d) G.D. Mercer, J. Shing Shu, T.B. Rauchfuss and D.M. Roundhill,  
J. Am. Chem. Soc., 1975, 97, 1967.
20. J.W. Rathke and H.M. Feder, J. Am. Chem. Soc., 1978, 100, 3623.
21. W. Keim, M. Burger and J. Schlupp, Journal of Catalysis, 1980, 61, 359.
22. German Patent, 24,279,54 (1974).

23. a) W. Kaminsky, J. Kopf, H. Sinn and H.J. Vollmer, *Angew. Chem., Internat. Ed.*, 1976, 15, 630;  
b) A. Andresen, H.G. Cordes, J. Herwig, W. Kaminsky, A. Merk, R. Mottweiler, J. Pein, H. Sinn, and H.J. Vollmer, *Angew. Chem., Internat. Ed.*, 1976, 15, 632.
24. A. Lee Galyer and G. Wilkinson, *J. Chem. Soc., Dalton*, 1976, 2235.
25. Jacky R.M. Kress, M.J.M. Russel, Marcel G. Wesolek, and John A. Osborn, *J. Chem. Soc., Chem. Comm.*, 1980, 431.
26. Brian R. James, A.W. Addison, M. Cairns, D. Dolphin, N.P. Farrell, D.R. Paulson and S. Walker in "Homogeneous Catalysis", Vol. 3, M. Tsutsui ed., Plenum Press, New York, 1979, p. 751.
27. C.D. Chang and A.J. Silvestri, *J. Catalysis*, 1977, 47, 249.
28. C.D. Chang, A.J. Silvestri and R.L. Smith, U.S. Patent 3,928,483 (1975).
29. a) P. Sabatier and J.B. Senderens, *Hebd. Seances Acad. Sci.*, 1902, 134, 514;  
b) Badische Anilin und Soda Fabrik, German Patents 293,787 (1913), 295,202 and 295,203, (1914);  
c) H.H. Storch, N. Columbic, and R.B. Anderson, "The Fischer-Tropsch and Related Synthesis", Wiley, New York, 1951.
30. F. Haber and R. Rossignol, U.S. Patent, 971,501 (1910) to Badische Anilin und Soda Fabrik.
31. A.E. Shilov, Le Bel Lectures, University of Strasbourg, 1978.
32. D.F. Evans, *J. Chem. Soc.*, 1959, 2003.
33. W. Hieber and R. Wiesboeck, *Chem. Ber.*, 1958, 91, 1156.
34. I. Wender, H.W. Sternberg, and M. Orchin, *J. Am. Chem. Soc.*, 1952, 74, 1216.

35. a) W. Hieber and R. Werner, Chem. Ber., 1957, 90, 286;  
b) W. Hieber and E.H. Schubert, Z. Anorg. Allgem. Chem., 1965, 338, 37.
36. F. L'Eplattenier and F. Calderazzo, Inorg. Chem., 1967, 6, 2092.
37. J.R. Moss and W.A.G. Graham, J. Chem. Soc., Dalton, 1969, 800.
38. Japanese Patent 76,128,903 to Mitsubishi.
39. U.S. Patent, 4,133,966 (1979) to Gulf Research and Development Company.
40. G. Giordano, S. Martinengo, D. Strumolo, and P. Chini, Gazzetta Chimica Italiana, 1975, 105, 613.
41. J.L. Dawes and J.D. Holmes, Inorg. Chem. Letters, 1971, 7, 847.
42. H.P. Podall and A.P. Giraitis, J. Org. Chem., 1961, 26, 2587.
43. B.F.G. Johnson, J. Lewis and P.A. Kilty, J. Chem. Soc., A, 1968, 2859.
44. I. Wender, H.W. Sternberg, M. Meltin, and M. Orchin, Inorg. Synth. 1957, 5, 190.
45. P.E. Cattermole and A. G. Osborne, Inorg. Synth., 1977, 17, 115.
46. P. Chini and S. Martinengo, Inorg. Chim. Acta, 1969, 3, 299.
47. Made from  $\text{Co}_2(\text{CO})_8$  in THF in the presence of Na/Hg (1%).
48. S.J. Rhoads and R.E. Michel, J. Am. Chem. Soc., 1963, 85, 585
49. P. Chini, J. Chem. Soc., Chem. Comm., 1967, 29.

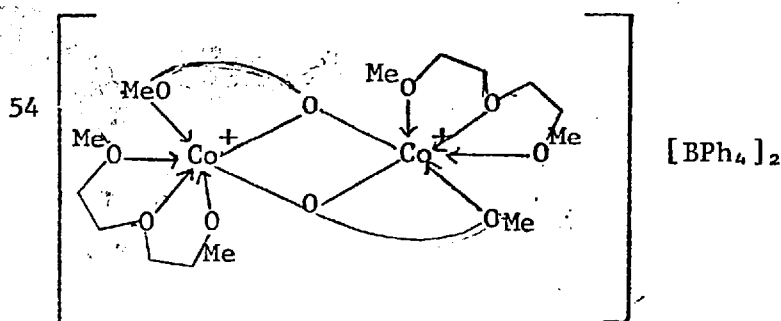
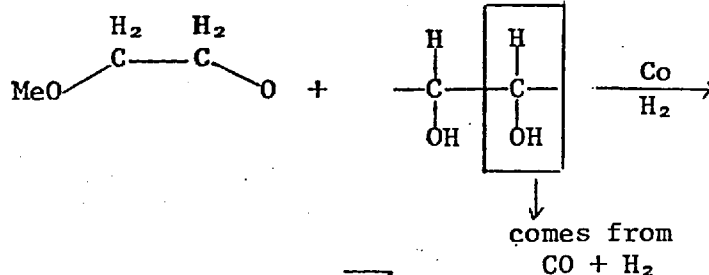
ERRATUM

PAGE

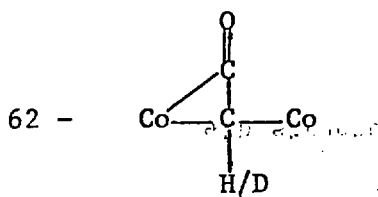
37 - 3rd line ..... (1.8 moles/ $\text{Co}_2(\text{CO})_8$ /18 hours),

47 - (X) 7th line ..... yields C-1 units

48 - 2nd line



54a -  $[\text{Co}_2(\mu\text{-OCH}_2\text{CH}_2\text{OCH}_3)_2(\text{diglyme})_2][\text{BPh}_4]_2$



87 3rd and 4th structures: add H to the first  $(\text{CO})_5\text{Mn}$ —

H

111 - 3rd line:  $[\text{Co}(\text{C}_2\text{H}_4\text{O})]_n$  .....

125 - 2nd line: with  $\text{Cr}(\text{CO})_6$  .....