Studies of the cobalt catalysed homologation reaction of methanol

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STUDIES OF THE COBALT CATALYSED HOMOLOGATION REACTION OF METHANOL

by

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To my family and friends

"The great tragedy of Science - the slaying of
a beautiful hypothesis by an ugly fact".

J.H. Huxley

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MEMORANDUM

The work described in this thesis was carried out in the Chemistry Department of the University of Durham and at British Petroleum Research Centre, Sunbury-on-Thames between October 1979 and July 1982. It has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

ABSTRACT

The reaction of methanol with synthesis gas to form ethanol in the presence of a cobalt catalyst has been known for many years. The problems relating to the commercial development of this reaction arise from the severe physical conditions required, the low yield of ethanol produced, and wide distribution of products obtained.

The objectives of the study were: (i) to assess the influence of physical conditions (pressure, temperature, gas composition) on the reaction, (ii) to examine the effect of promoters and ligand stabilisers on the system, and (iii) to identify any catalytic intermediates observed under reaction conditions. This work employed three major investigative techniques: high pressure infra-red studies, autoclave reactions and basic atmospheric pressure nitrogen line chemistry.

A coordinated study of the reactions of the system's components with each other was performed while the complexity of the system was gradually increased. The effects of changing physical parameters such as temperature, pressure, synthesis gas composition etc. were also investigated. The influences of promoter and ligand type on the reaction were also studied.

The species observed to be present in the reacting system by high pressure infra-red spectroscopy are related to the proposed mechanism for the reaction. The effect on the reaction of promoters (iodine or iodide) and stabilising ligands (phosphine, arsine or stibine) is discussed in relationship with the chemical and physical properties of the intermediates. The role of solvents in the homologation reaction is considered with regard to the possibility of phase transfer taking place between a carbon monoxide-rich methanol layer and hydrogen-rich hydrocarbon layer.

The results from the high pressure autoclave studies are used to determine the most efficient conditions for synthesis of ethanol in terms of the catalyst composition and physical reaction conditions. The high pressure infra-red studies enabled intermediate species to be identified and a reaction mechanism is proposed incorporating this new information.

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ABBREVIATIONS

Ph=C_6H_5

PPN=$(C_6H_5)_3P=N=P(C_6H_5)_3$

R = Alkyl

Me = CH_3

Et = CH_3CH_2

THF = Tetrahydrofuran

Ac = $CH_3C=O$

CHAPTER ONE

INTRODUCTION

1.1. Background Information

Synthesis gas (carbon monoxide and hydrogen) is an extremely attractive feedstock for industrial-scale production of chemicals.[1,2] The success of these processes rests ultimately upon the availability of cheap synthesis gas. At present, it can be produced from coal (or residual petroleum) by steam-oxygen gasification or from natural gas by steam reformation over a heterogeneous nickel catalyst. Thus its production is dependent on no one natural resource. Besides, direct synthesis of chemicals may be achieved from synthesis gas, e.g. by traditional Fischer-Tropsch processes; also the up-grading of other readily available feedstocks, e.g. olefins or methanol by hydroformylation or carbonylation reactions (oxo processes) can also yield valuable chemicals. The conversion of olefins to aldehydes or alcohols has been practised industrially for over thirty years. More recent developments have included the commercialisation of methanol carbonylation processes to give acetic acid.

Homogeneous methanol carbonylation reactions are strongly dependent upon the synthesis gas composition (the H_2:CO ratio) and the transition metal catalyst employed. When pure carbon monoxide is used, the reaction product is acetic acid or its methyl ester, methyl acetate.[3] This reaction is catalysed by cobalt at high pressure (800 Atm) or rhodium at low pressure (40 Atm). A different product distribution is obtained (using a cobalt catalyst) when hydrogen is introduced into the feed gas. This reaction is referred to as methanol homologation, and the major product is generally ethanol.

The homogeneously catalysed homologation of methanol to ethanol has been known for many years. Homologation is in general defined as "a reaction by which a member of an organic class of compounds is converted into a new compound containing one additional carbon atom bonded at the site of the original functional group";[4] a more specific definition involves use of carbon monoxide as the source of homologating carbon in the creation of one additional methylene unit.

The homologation of methanol would provide a pathway for production of ethanol from more economical starting materials, than those used by conventional methods of hydration of ethylene. Also it would permit production and reproduction of a more standardised product in more easily predictable yields. The reaction portends also to be the alternative to the cracking of petroleum as a route to ethylene, via a subsequent heterogeneously catalysed dehydration step.

Years of intense effort have been spent on the methanol homologation reaction at numerous industrial and government laboratories since it was first reported. Although this reaction is thermodynamically sound and has been successfully attempted, large amounts of by-products such as aldehydes, esters, acids and gaseous hydrocarbons are concurrently produced.

1.2. Introduction to Methanol Homologation

The reaction studied here is the conversion of methanol into ethanol using a catalyst based upon cobalt carbonyl, under high pressures of synthesis gas and high temperature.

The basic reaction has been known for a number of years but several commercial limitations are associated with it. The reaction conditions need to be fairly severe and hence expensive, the yield of the required product is not high, the selectivity to ethanol is poor. Many products are formed though some of the by-products can be easily hydrolysed to ethanol. The production of these materials, especially acetaldehyde, acetates and formates, adversely affects the yield of ethanol and produces complex separation problems, which together, destroy most of the economies made possible by the inexpensive raw materials.

The original experiment in the homologation of methanol was first reported by Brooks,[5] but his paper was more concerned with the production of esters than alcohols. The first reports involved with alcohol formation are generally credited to Wender[6] and co-workers. These experiments investigated the homologation of benzyl alcohol, iso-butyl alcohol, t-butyl alcohol and n-propyl alcohol. Later[7] Wender published a more specific account of the conversion of methanol to ethanol in fairly high yields. From these early experiments it was found that the order of reactivity of starting alcohols was tertiary > secondary > primary. However methanol was found to be anomalous, in that it reacted faster than secondary alcohols.

The conditions used by Wender were severe (185°C, 5100 psi, 8 hrs.) and the yield of ethanol was ∿ 38%. The fact that no appreciable quantities of the higher alcohols appeared in the reaction products showed that ethanol itself would only react very slowly under these conditions. It was also found unnecessary to use $CO_2(CO)_8$ as the catalyst in the reaction; any salt of cobalt yielding the carbonyl under the reaction conditions would serve as an effective catalyst.

For several years the homologation technique did not generate a great deal of interest;[8-10] later however, several patents were published, mainly from 1961 onwards.[11-16] One granted to Commercial Solvents[12] showed the first use of halogen promoters for the cobalt catalyst. Whether the claimed specificity and yields were due to the very high pressures used, or the particular promoters is not made clear.

Some of the major research in the field of homologation chemistry to date has been performed by the petroleum companies[17-22] and some of the most comprehensive reports and patents have been published by the Royal Dutch Shell team.[23] These relate to production of ethanol from methanol, carbon monoxide and hydrogen in the presence of a non-polar solvent with a catalyst system consisting of a tertiary phosphine, cobalt and a halide (iodide or bromide). Cobalt was preferred in the ionic form, but the use of cobalt metal to react "in situ" with synthesis gas to form the desired catalytic species was also allowed. Examples of the cobalt sources used are cobalt acetate, formate or carbonate. The halide promoter, used to complete the catalyst, can be either provided in ionic form or in molecular form (as I_2 or Br_2). Clearly the preferable source of ionic halide is the cobalt halide, as this provides both the cobalt and halide used in the reaction catalyst. However the halide can be provided in ionic form using cations that are inert with regard to the homologation reaction. Typical forms therefore include KI, KBr, NaI, NaBr, LiI and LiBr.

In these reports the cobalt was thought to be in a reduced state but its exact valency was not known; it was regarded as existing as a cobalt-phosphine-halide species. The catalytic precursor was prepared either by first combining the reagents and then adding them to the reaction vessel, or alternatively by adding the individual components to the reaction vessel and allowing the catalyst to form under reaction conditions. Frequently the introduction of CO and H_2 was staged; that is the gases were introduced initially with a relatively low hydrogen to carbon monoxide ratio (the gases could be diluted if necessary with an inert gas), and shortly thereafter the hydrogen to carbon-monoxide ratio was increased. In general reaction vessel residence times are limited to those necessary to achieve satisfactory conversion, in order to minimise the formation of by-products.

Studies by Koermer[24] et al. indicate that in batch systems, the reaction is not so selective to ethanol as was previously reported. (Over twenty different compounds have been identified in the final mixture.) Attempts to improve the selectivity or activity of the cobalt catalyst by addition of various ligands or co-catalysts were not successful.

The homologation reaction is generally investigated as a batch reaction but some information is available concerning continuous flow[24] systems. A different approach was used in the continuous process unit to avoid problems inherent in the batch reactor. Due to long heating and cooling times there is necessarily a long residence time in the batch process which could lead to the many by-products. The concentration increase of reaction products and water will alter the reaction medium and hence possibly alter the course of the reaction. The continuous flow results obtained indicate that the same range of products as observed in the batch process is present; however the relative amounts, as reflected by molar selectivities have changed slightly. The concentration of ethanol and materials easily hydrolysed to ethanol has increased. This represents a significant increase in selectivity to the required products over batch unit operation. The major unwanted by-products from the continuous run are unchanged.

More recent work by Japanese[25-28] scientists has shown that iodine and iodide are promoters for the reaction, although the product distribution was not significantly affected. The results obtained indicate that iodide is slightly more effective than iodine, especially at high conversion levels. Pressures up to 6000 psi result in an increase in total conversion, but above this pressure very little change is noted. The ratio of hydrogen to carbon monoxide in the synthesis gas has an effect upon the reaction rate: the formation of ethanol is expected to be favoured in the presence of an excess of hydrogen. In fact the yield and conversion do not increase as much as expected, and the best CO/H_2 ratio is unity. High temperature ($> 220^{o}C$) affects the reaction adversely by increasing the proportion of unwanted products (methane and C_3 and C_4 higher oxygenated compounds). Low temperature also adversely affects the reaction as the yield of acetaldehyde increases and the rate of reaction decreases sharply.

An attempted improvement[29] to the basic system was to have essentially an alcoholic solution of cobalt carbonyl in contact with a solid phase heterogeneous hydrogenation catalyst such as rhenium metal. Rhenium was found to be useful in its ability to increase the efficiency of the homologation of methanol. Many systems containing metals other than rhenium were found to be ineffective for enhancing the cobalt catalysed reaction. It is a critical aspect of this combined catalytic system that the cobalt carbonyl species does not have prolonged contact with the rhenium metal in the absence of carbon monoxide pressure, as this will cause decomposition and deactivation of the cobalt species.

Other single metal systems have been examined as homogeneous catalysts for this reaction but none have been very successful. Generally, catalysts which possess high activity tend to give a wide spectrum of products. This not only complicates the recovery of the required products, but results in wastage of reactants to commercially uninteresting by-products.

The homologation of methanol to ethanol has also been investigated in a parallel fashion by workers in the field of heterogeneous[30-31] catalysis. But, to date, there is no commercially viable procedure for converting simple alcohols into their higher homologues, using this method of catalysis. Chief amongst the reasons for this has been the failure of heterogeneous catalyst formulations to withstand the elevated temperatures and pressures inherent in these processes without substantial loss of activity, in a short period of time. As a result these catalysts usually have an effective life of only a few hours, which is far too short to justify their employment in commercial continuous processes. Recent investigations have produced moderate yields, and the range of products obtained is smaller than that produced with the homogeneous catalyst system, thus making separation and purification that much simpler. However despite these advantages the stability of the heterogeneous catalyst is far too poor for the method to be a serious competitor for the homogeneous system.

Many proposed mechanisms for the methanol homologation reaction parallel the mechanism proposed for olefin hydroformylation. An aldehyde is an intermediate product that is subsequently hydrogenated. The main difference between the two processes (hydroformylation vs. homologation) is believed to be the initial activation of the reactants by a hydridocobalt carbonyl species to form an alkyl-cobalt carbonyl. Iodine is thought to function as a promoter of the homologation reaction by forming methyl iodide, which is believed to react faster than methanol with hydridocobalt carbonyl to give methyl cobalt carbonyl. A hydridocobalt carbonyl iodide has also been suggested as a potential catalyst intermediate in iodide-promoted systems.

The study undertaken is a systematic investigation of the methanol homologation reaction, to provide information on the basic chemistry, in order to obtain a deeper understanding of the catalytic process, to determine the parameters most influencing conversion and selectivity, and to provide an assessment of proposed catalytic intermediates and mechanisms. The variation of physical reaction conditions has been studied as have the effects of ligand modifiers and solvents. Low pressure synthesis of model catalytic compounds and possible reaction intermediates have also helped in the assessment of the detailed reaction process.

CHAPTER TWO

EXPERIMENTAL

2.1. Techniques

2.1.1. Manipulations of moisture sensitive compounds

All purifications of solvents by distillation, or solution reactions at either room temperature or under reflux, were performed under an atmosphere of nitrogen. This was obtained from the supply line and passed through a tower at 400°C containing copper wire (to remove oxygen) and several drying agents, (concentrated sulphuric acid, potassium hydroxide, 3A molecular sieve and phosphorus pentoxide). A constant pressure of nitrogen was maintained in the system by connecting one outlet to an oil bubbler. The line supplied dry nitrogen directly to the vacuum line so that apparatus could be evacuated and refilled with an inert atmosphere. The vacuum line, fitted with a mercury diffusion pump was able to develop a vacuum of better than 10^{-3} torr.

More complex manipulations (e.g. preparation of moisture sensitive materials for infra-red spectroscopy or analysis) were done in a dry nitrogen glove box. Fresh phosphorus pentoxide was kept in the entry port and inside the box as a precaution against moisture being introduced. The nitrogen atmosphere in the box was recycled continuously through drying tubes also containing phosphorus pentoxide.

2.1.2. Physical techniques

Infra-red spectroscopy

Infra-red spectra (4000 - 250 cm^{-1}) of nujol mulls prepared under nitrogen were recorded, using KBr plates, on a Perkin-Elmer 577 or 457 prism grating spectrometer. If the moisture sensitivity of a compound was low, a better spectrum was often obtained from a KBr disc of the sample. Discs were prepared in a die with a hydraulic press at 2 GPa (maximum) pressure. Solution spectra were recorded using a Perkin-Elmer solution cell with a 0.1 mm path and NaCl, KCl or CaF_2 windows. High pressure solution spectra were recorded on a Perkin-Elmer 257 spectrometer, modified to accept high pressure bombs. The modifications to the spectrometer consist of an adjustment of the light path by four extra concave mirrors to enable two high pressure bombs to be inserted into the sample and reference beams. The system is similar to that used by Whyman[32] except that here an extra bomb was included in the reference beam. The bombs themselves are based on an I.C.I. design and are used with CaF_2 windows. Spectra were recorded in the region 2300 - 1200 cm^{-1}. The windows were found to extrude[33] slowly and eventually crack under high pressure.

Mass spectrometry

Mass spectra were obtained using an A.E.I. MS9 mass spectrometer at 70 eV with an accelerating potential of 8 KeV and with a source temperature of 80^o - 220^o. The samples were mounted on an inert ceramic material and introduced on a direct insertion probe.

^{31}P N.M.R. spectroscopy

Nuclear magnetic resonance spectra were recorded using an F.T. spectrometer constructed in this department and which has been described in detail elsewhere.[34] The machine utilises a 1.4τ magnet from a Perkin-Elmer R10 and is controlled by a Varian 620/L computer. This stores and accumulates the free induction decay produced by a powerful R.F. pulse. After the required number of scans have been completed the computer processes the accumulated F.I.D.'s to give the spectrum. The sweep width can be varied from 40 to 800 ppm to observe resonances in the range -400 to +1100 ppm.

Spectra were run at 307.2 K, the stationary samples being contained in 8.4 mm external diameter tubes. Chemical shifts were measured relative to external 85% H_3PO_4, with the upfield direction taken as positive. Sample tubes were filled by syringe against a counter current of nitrogen and, where necessary sealed under nitrogen.

Raman spectroscopy

Raman spectra were recorded using a Cary 82 spectrometer with a Spectra Physics 125 (632.8 nm exciting line) or a Spectra Physics 164 (514.5 nm exciting line) laser.

UV/visible spectroscopy

These were recorded on a Unicam SP8000 or Unicam SP800 recording instrument using 1 cm glass or silica cells where appropriate.

Chromatography

Liquid samples were analysed on a Varian 3700 series instrument. The column used was constructed from $^1/4$ inch (OD) stainless steel tubing and was nine feet long. The column was packed as follows; the first six feet (taken from the detector end) contained Poropak N and the last three feet Poropak Q. During use the Varian was programmed as follows:

t = 0 to 15 minutes 170°C

t = 15 minutes, increase temperature to 185°C (at 50°C/min.).

The carrier gas composition was as follows:

Nitrogen	60 psi - 30 mls/min.
Hydrogen	40 psi - 30 mls/min.
Air	60 psi - 300 mls/min.

These particular conditions were devised by adjusting the various physical parameters to give the best possible separation of methanol, acetaldehyde and ethanol.

As regards analysis, an internal standard was not usually used, since the samples themselves were generally too complex. Instead modified

Sternberg[35] factors have been used which relate the peak area directly to the weight percentage by means of the following expression:

$$\% W_i = \frac{f_i \times \text{area}_i}{\Sigma_i f_i \times \text{area}_i} \times 100 \quad \text{where } f_i = \text{Sternberg factor.}$$

Each weight percentage was then normalised to take account of the weight of catalyst in solution and the percentage of water in the sample. From the percentage by weight of each component the number of moles of each component were calculated and hence percentage yields and selectivities were found:

$$\% \text{ molar yield of product} = \frac{\text{moles of methanol converted to product}}{\text{moles of methanol put in}} \times 100$$

$$\% \text{ molar selectivity of product} = \frac{\text{moles of methanol converted to product}}{\text{moles of methanol consumed}} \times 100$$

When a series of very similar systems were being examined, it was often found for routine monitoring purposes to be simpler and more convenient to make direct comparison between the areas obtained rather than use the Sternberg factors as the results were found to be sufficiently accurate.

2.1.3. Analytical methods

Carbon, hydrogen and nitrogen

Carbon, hydrogen and nitrogen were determined by microcombustion with a Perkin-Elmer 240 Elemental Analyser. The reliability of the machine was found to be variable.

Metals, arsenic and antimony

Metals, arsenic and antimony were determined by Atomic Absorption Spectrophotometry using a Perkin-Elmer 403 instrument.

Phosphorus and halogens

Phosphorus and halogen analyses were carried out by the departmental analyst. For phosphorus and chlorine, a weighed sample was decomposed by fusion in a nickel Parr bomb. The residue was acidified with concentrated nitric acid and made up to 100 mls with distilled water. For phosphorus a suitable aliquot was treated with ammonium molybdate/ammonium vanadate reagent and the absorbance measured at 420 μm using a Unicam SP500 spectrophotometer. Chlorine was determined by potentiometric titration against M/100 silver nitrate solution using Ag/AgCl electrodes in an acetone medium.

Bromine and iodine were determined iodometrically following a Schoniger oxygen flask combustion.

Water analysis

Water was determined by Karl-Fischer[36] analysis.

2.2. Preparation and purification of starting materials

2.2.1. Solvents

Methanol: - the AnalaR reagent was reacted with magnesium ribbon (1 gm. per 100 ml.) until no further effervescence was observed, then distilled under nitrogen onto an activated, 3A molecular sieve. When a scrupulously dry solvent was required, "Spectrosol" grade methanol was used.

Ethanol and dichloromethane were distilled under nitrogen onto activated 3A molecular sieve.

THF, toluene, pentane and hexane were all dried over sodium wire and stored under nitrogen.

Hexadecane and octadecane were the best available commercial grade materials available and were used without purification.

Acetone was AnalaR grade and was distilled under nitrogen onto activated 3A molecular sieve.

Petroleum ether was used without purification.

Dioxane was dried over sodium wire and freshly distilled before use.

Water was distilled, then boiled 'in vacuo' for 15 minutes to expel dissolved CO_2, prior to storage with a soda-lime guard tube.

Other solvents were obtained in the best commercial grade available and used without purification.

2.2.2. Gases

Nitrogen and hydrogen were provided by British Oxygen Company, carbon monoxide and synthesis gas mixtures supplied by Air Products; all gases were used directly from the cylinders without purification.

2.2.3. Starting materials

Carbonyl species

Dicobalt octacarbonyl and $PPNCo(CO)_4$ were generously provided by British Petroleum Company and purchased from Strem Chemicals. Dicobalt octacarbonyl was recrystallised from hexane before use. $[Co(CO)_3PPh_3]_2$ was supplied by Strem Chemicals and used without purification.

Ligands

The phosphine ligands and triphenylarsine and triphenylstibene were all obtained from British Drug Houses and checked by infra-red and melting point before use.

Salts

Cobalt chloride, nitrate and acetate were all supplied by British Drug Houses and used after recrystallisation from water. Cobalt carbonate was provided by British Petroleum Company and used without purification. PPNCl was obtained from Strem Chemicals and used without purification.

CHAPTER THREE

AN EXAMINATION OF THE BASIC COBALT/METHANOL REACTION SYSTEM

3.1. Introduction

This chapter is concerned with the basic reactions between cobalt containing species and methanol. The reactions are studied at a variety of temperatures and pressures, including high pressures and high temperatures in an infra-red autoclave cell. The main purpose of the chapter is to report the effects of temperature, pressure, catalyst form and catalyst composition on the reaction, and to identify some major catalytic species "in situ" at high pressures. These species are compared and contrasted with those cobalt compounds produced in low pressure experiments.

3.2. Low Pressure Study of the Dicobalt Octacarbonyl/Methanol Reaction

3.2.1. Experimental

(a) Methanol and dicobalt octacarbonyl at room temperature.

When crystals of $Co_2(CO)_8$ (0.3 g, 1 mmol) were stirred with dry methanol (30 ml) a dark red/brown solution was formed rapidly. No significant change in colour was noted for about 1 hour, when a gradual loss of colour occurred and finally, after 3 hours, a pale pink solution remained. This pink solution persisted unchanged for 40 hours. The solution was then gently evaporated to dryness in vacuo, leaving a black solid, which was found to be very pyrophoric when brought into contact with air.

The reaction system was sampled and studied throughout, using solution infra-red spectroscopy in the carbonyl stretching region (2200 - 1600 cm^{-1}). The initial red/brown solution showed infra-red absorptions at $2076_{(m)}$, $2041_{(m)}$ and $1905_{(s)}$ $cm.^{-1}$ These were found to change, within 10 minutes, to absorptions at $2041_{(m)}$, $2018_{(m)}$ and $1905_{(s)}$ cm^{-1}, which persisted for the rest of the solution experiment. The absorptions are assigned as follows: the peak at 2041 cm^{-1} is due to the methanol solvent and causes problems, as it partly obscures the region of interest. The two absorptions at $2018_{(w)}$ and $1905_{(s)}$ cm^{-1} can be assigned to the ion $Co(CO)_4^-$. The temporary peak at $2076_{(m)}$ cm^{-1} is one of those assigned to the terminal CO-stretching frequency of molecular dicobalt octocarbonyl. The solid infra-red spectrum of the final black solid showed only one peak at $1890_{(s)}$ cm^{-1} again believed to be due to $Co(CO)_4^-$.

(b) Methanol and dicobalt octacarbonyl at 50°C.

The reaction was repeated with $Co_2(CO)_8$ (0.6 g, 2 mmol) and methanol (40 ml) at 50°C, to assess the influence of temperature. On warming, the initial red/brown solution was found to convert far more rapidly to the pink solution. Again the black solid remained on evaporation to dryness. The reaction at 50°C was exactly the same as that at room temperature, except that at the elevated temperature, the reaction was substantially faster. This was supported by infra-red study of the system which showed the same spectra as before

(c) Dicobalt octacarbonyl in methanol and hexane.

When dicobalt octacarbonyl (0.3 g, 1 mmol) was stirred rapidly in a mixture of hexane (20 ml) and methanol (20 ml), the solvent mixture became dark red, i.e. the partition between the two solvent layers could not be detected. After two hours the intensity of colour in both layers was noted to be lessening. However after 4 hours the hexane layer was completely clear and the methanol layer was pale pink. The hexane layer was separated from the methanol layer using a syringe and evaporated to dryness but there was no residue. On evaporation of the methanol layer a brown/black solid was produced which redissolved in methanol to reform the pink solution.

Infra-red spectral examination of the system yielded the following information. The hexane layer showed an initial series of peaks, $2074_{(s)}$,

$2067_{(m,sh)}$, $2058_{(m)}$, $2046_{(s)}$, $2034_{(m,sh)}$, $2027_{(s)}$, $1898_{(m)}$, $1866_{(m)}$, $1857_{(m)}$ cm^{-1}. These are due to molecular dicobalt octacarbonyl (peaks reported at $2074_{(s)}$, $2067_{(m,sh)}$, $2058_{(m)}$, $2046_{(m,sh)}$, $2034_{(m,sh)}$, $2027_{(s)}$, $1866_{(m)}$, $1857_{(m)}$ cm^{-1} [37,38]) and cobalt tetracarbonyl anion (peak reported at $1900_{(vs)}$ [38]), both present in the hexane. (The peak at 1898 cm^{-1} is assigned to the $Co(CO)_4^-$ ion.) With time all these absorptions were found to gradually disappear, until finally no carbonyl absorptions remained. The methanol layer initially showed bands at $2041_{(m)}$ and $1900_{(s)}$ cm^{-1}, but as time passed the peak at 1900 cm^{-1} became much more intense and a third weaker peak developed at 2018 cm^{-1}. No further change in solution spectra was noted. The black solid produced on evaporating the methanol showed a peak at 1895 cm^{-1} in its infra-red spectrum,[39] and on adding methanol to this black solid, the pink solution formed again showed peaks at 2018 cm^{-1}, 2041 cm^{-1} and 1900 cm^{-1}. Elemental analysis of the air sensitive black solid gave C, 25.6; H, 1.6; Co, 38.3%. $[Co(CH_3OH)_6][Co(CO)_4]_2$ requires C, 28.3; H, 4.0; Co, 29.8%.

(d) Ethanol and dicobalt octacarbonyl.

Dicobalt octacarbonyl (0.3 g, 1 mmol) was stirred vigorously with dry degassed ethanol (30 ml). The cobalt carbonyl species dissolved rapidly to form a red/black solution, which slowly changed into a pale red/pink solution over about 1 hour. This was evaporated down to dryness and a black solid was obtained. The reaction was performed in ethanol solution, as it was believed that ethanol and methanol react very similarly with dicobalt octacarbonyl. The solution made up in ethanol enabled easier infra-red examination of the system, free from the intruding methanol absorption at 2041 cm^{-1}. (Ethanol has peaks at $2130_{(m)}$, $2090_{(w)}$, $1920_{(s)}$ cm^{-1}, methanol has peaks at $2221_{(m)}$, $2041_{(m)}$ cm^{-1}).

Infra-red spectra of the solution show only two non-solvent peaks at $2018_{(m)}$ and $1900_{(s)}$ cm^{-1}. The only changes observed were that they both became stronger as the red/black colour faded, and remained unchanged once the pale red/pink colour had formed. The black solid again showed a single strong peak at 1895 cm^{-1}. Elemental analysis of the black solid[39] gave C, 36.3; H, 2.3; Co, 36.3%. $[Co(C_2H_5OH)_6][Co(CO)_4]_2$ requires C, 35.5; H, 5.3; Co, 26.1%.

(e) Methanol/dicobalt octacarbonyl, gas evolution study.[40]

A series of experiments were performed, using a gas burette to measure carbon monoxide evolved during the reaction of $Co_2(CO)_8$ with methanol or ethanol. Various amounts of $Co_2(CO)_8$ were reacted with dry methanol or ethanol (saturated with CO) in a gas burette, and the amount of carbon monoxide evolved at room temperature was measured. The evolved gas volume was converted to STP and the number of moles of gas released by reaction of one mole of $Co_2(CO)_8$ was calculated.

Table 3.1.

Solvent	$Co_2(CO)_8$ gm	cm^3 CO (at STP)	mmol of $Co_2(CO)_8$	mmol of CO	Ratio $\frac{\text{Moles CO}}{\text{Moles } Co_2(CO)_8}$
MeOH	0.4179	72.5	1.222	3.238	2.65
MeOH	0.9524	165.9	2.785	7.408	2.66
MeOH	0.3871	67.2	1.132	3.000	2.65
EtOH	0.5848	103.4	1.710	4.616	2.70

The majority of the gas was evolved within the first fifteen minutes (Fig. 3.1.) and once the pink/red solution was formed the evolution of the gas was found to cease. Fig. 3.1. shows the gas evolution for the second experiment in Table 3.1.

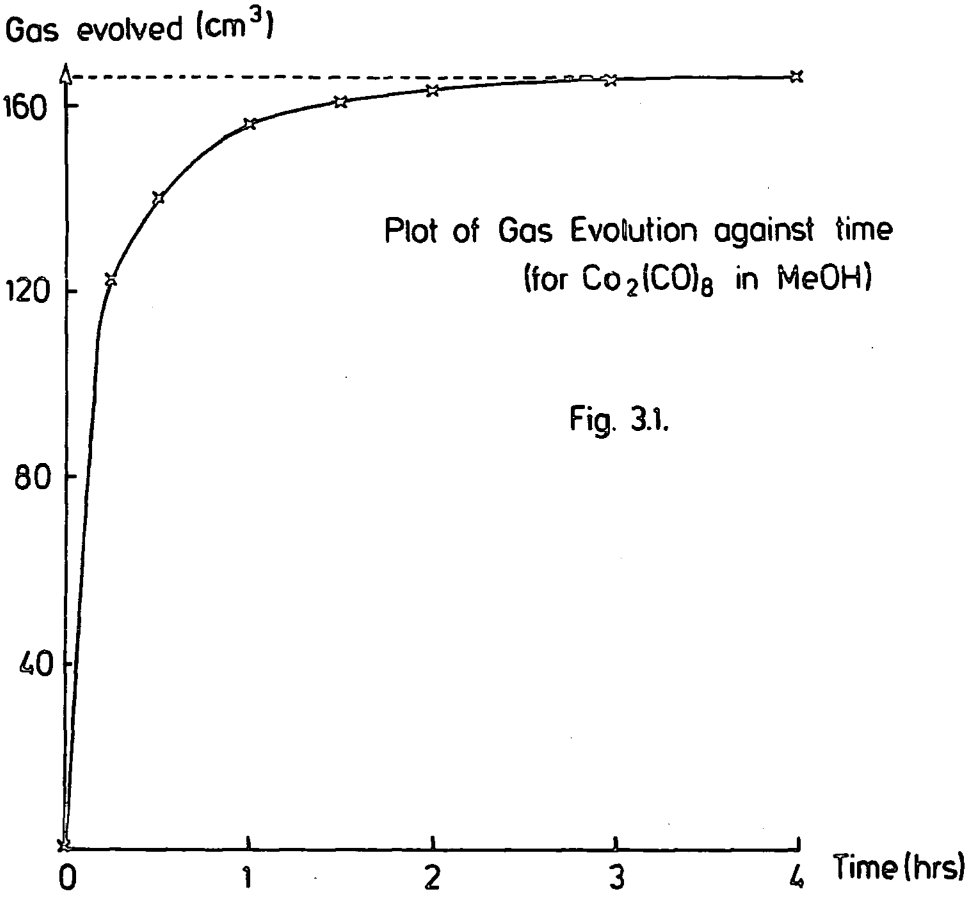


Fig. 3.1.

(f) IR, Raman spectroscopic study of $Co(CO)_4^-$.[41,42]

Several compounds containing suitable relevant counterions have been studied in solution and in the solid state, using both infra-red and Raman techniques.

PPN^+Cl^- has no observable bands in the region 2200 - 1600 cm.$^{-1}$ in its solid or solution in MeOH or CH_2Cl_2 infra-red spectra or in its solid Raman spectrum.

$PPN^+Co(CO)_4^-$ - Solid Raman spectrum shows peaks at $2004_{(m)}$, $1900_{(s)}$ and $1888_{(s)}$ cm^{-1}.

$PPN^+Co(CO)_4^-$ - Solid Infra-red spectrum has peaks at $1900_{(s)}$, $1880_{(s)}$ cm^{-1}.

$PPN^+Co(CO)_4^-$ - Solution Infra-red spectrum in CH_2Cl, has peaks at $2010_{(m)}$, and $1885_{(s)}$ cm^{-1}; solution i.r. in MeOH has a peak at $1890_{(m)}$ cm^{-1}

$(PPNCo(CO)_4^-$ is less soluble in MeOH than $CH_2Cl_2)$.

(g) UV/visible study of methanol/dicobalt octacarbonyl reaction.

UV/visible spectroscopy of the reaction solution allows the concentration of Co^{2+} species to be measured, by simple comparison with standard solutions of Co^{2+} in methanol.

$Co_2(CO)_8$ (1.231 g, 3.6 mmol) was reacted with methanol (40 ml) and allowed to form the pink solution over a four hour period. The solution was examined by UV/visible spectroscopy and was found to produce an absorption at 525 nm, which had almost exactly the same position and intensity as that produced by a 0.06 molar solution of $CoCl_2$ in methanol. This indicates that a 0.06M solution of $[Co(MeOH)_6]^{2+}$ was produced from the initial $Co_2(CO)_8$, (1.231 g in 40 ml, i.e. 0.09M). This implied that three moles of dicobalt octacarbonyl produced two moles of cobalt (II) ion on reaction with methanol.

3.2.2. Discussion

The reaction of methanol with dicobalt octacarbonyl is fairly straightforward to observe. Initially the crystals of $Co_2(CO)_8$ dissolve in the methanol in molecular form, as shown by the observance of the terminal -CO stretching frequency bands of $Co_2(CO)_8$.[37] The molecular $Co_2(CO)_8$ rapidly reacts to form the $Co(MeOH)_6^{2+}$ and $Co(CO)_4^-$ species,[40] which are apparently stable indefinitely in the absence of air. Undertaking the reaction at 50°C simply increases the rate of formation of the ionic species. With hexane present in the mixture, the reaction eventually takes the same course, but initially the dicobalt octacarbonyl dissolves in the hexane in molecular form. This is shown by the number of infra-red peaks indicating the presence of both bridged and non-bridged isomers of $Co_2(CO)_8$. The molecular dicobalt octacarbonyl slowly transfers from the hexane layer to the methanol layer where it forms the ionic species, until eventually no dicobalt octacarbonyl remains in the hexane.

This reaction with methanol is an example of a generally applicable reaction scheme in the field of metal carbonyl chemistry.[43] It involves the formation of the cobalt (II) ion and cobalt carbonyl anion from dicobalt octacarbonyl:

$$3Co_2(CO)_8 + 2nB \longrightarrow 2CoB_n^{2+} + 4Co(CO)_4^- + 8CO \qquad (1)$$

It may be considered as a homonuclear disproportionation, in which the uncharged dicobalt octacarbonyl disproportionates into a cobalt (II) cation and cobalt carbonyl anion. B can be a variety of compounds having an available unshared pair of electrons, i.e. a Lewis base. As the coordination number of cobalt (II) ion is usually 6, n is 6 for unidentate ligands and 3 for bidentate ligands, depending upon the number of functional groups with available electron pairs in B. The quantitive conversion of dicobalt octacarbonyl to cobalt cation and cobalt carbonyl anion according to the above equation, requires the liberation of $2^2/3$ moles of carbon monoxide per mole of dicobalt octacarbonyl converted, the formation of $1^1/3$ moles of cobalt carbonyl anion per mole of dicobalt octacarbonyl converted, and finally the conversion of $^1/3$ of the cobalt present in dicobalt octacarbonyl to cobalt (II) ion. The data produced here support this view for the two Lewis bases methanol and ethanol. These results support the opinion of Wender[40,44] and suggest the revision of the alternative idea that the reaction between dicobalt octacarbonyl and Lewis bases involves the displacement of one or more carbon monoxide groups of the carbonyl by the base and formation of a substituted compound, according to equation (2):[45,46,47]

$$Co_2(CO)_8 + B \longrightarrow Co_2(CO)_5.B + 3CO \qquad (2)$$

Where B = Lewis Base

It will be noted that the stoichiometry of equations (1) and (2) is approximately the same, and the analytical data previously secured to support equation (2) are also consistent with the new formulation (1). The analyses of the black solids isolated by evaporating down the pink solutions discussed earlier, fit the formulae $[Co(MeOH)^{2+}_{1.8}][Co(CO)^-_4]_2$ and $[Co(EtOH)^{2+}_{1.8}][Co(CO)^-_4]_2$. This appears to be due to loss of alcohol from the cobalt species during the removal of solvent. These results agree well with elemental analyses produced by Hieber and co-workers[48] in their investigations of the reaction of dicobalt octacarbonyl with various bases.

As the overall reaction involves transfer of electrons only between molecules of dicobalt octacarbonyl, the formation of the cobalt (II) salt of the cobalt tetracarbonyl anion from the dimer ($Co_2(CO)_8$) can be termed a homomolecular disproportionation. It is possible to visualise equation (1) as occurring stepwise as follows, where B is a Lewis base:

$$3B + 3Co_2(CO)_8 \rightleftharpoons 3[BCo(CO)_4]^+[Co(CO)_4]^-$$

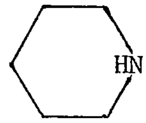
$$2[BCo(CO)_4]^+ \longrightarrow 2B + 2Co^{2+} + 8CO + 2e^-$$

$$1e^- + [BCo(CO)_4]^+ \longrightarrow B + {}^{\bullet}Co(CO)_4$$

$${}^{\bullet}Co(CO)_4 + 1e^- \longrightarrow Co(CO)_4^-$$

If the monomer $Co(CO)_4^{\circ}$ dimerised to dicobalt octacarbonyl, it would again follow the stepwise reaction sequence shown above.

With weak bases such as methanol or ethanol $[BCo(CO)_4]^+$ will decompose rapidly at room temperature. Experimental evidence for the existance of the salt has been obtained from two sources. The reaction between $Co_2(CO)_8$ and alcohols or water was studied by Tucci.[49] Strong evidence from ion-exchange and radioisotope techniques has been gathered for formation of the cationic species $[Co(CO)_4ROH]^+$ during the reaction. The alcohol complex was found to be stable only below 0^oC. Further evidence to support the existence of the $[Co(CO)_4B]^+$ species rests upon the use of a strong Lewis base, piperidine to form a relatively stable compound believed to be



$[$ HN $Co(CO)_4]^+[Co(CO)_4]^-$.[40]

Although kinetic data on this reaction are lacking, it is instructive to regard the first step of the homomolecular disproportionation as a typical organic displacement reaction, initiated by a base:

$$B: + [Co(CO)_4]:[Co(CO)_4] \longrightarrow$$

Initial state

$$\underset{\delta+}{B:} \text{----} Co(CO)_4 \text{----} \underset{\delta-}{:Co(CO)}{}_4$$

Transition state

$$\longrightarrow [BCo(CO)_4]^+[Co(CO)_4]^-$$

In the symmetrical cobalt carbonyl anion, the cobalt atom possesses the rare-gas electronic configuration, and its formation is believed to provide the driving force for the reaction. The cobalt in the cation also possesses rare-gas electronic configuration; however its lower symmetry probably makes it less stable than the anion. The relative stabilities of various cations will depend upon the basicity and geometry of the entering group. With weaker bases, the cation has less stability and decomposes rapidly. The attacking base may be neutral (alcohol, amine or olefin) or it may be an anion (Cl^-), in which case, the complex corresponding to the cation above would still possess the rare-gas electronic configuration, but would be the neutral entity, $Co(CO)_4Cl$. This species has been reported[50] in the literature and is thought to be unstable at room temperature and has not been well characterised.

3.3. High Pressure Study of the Cobalt/Methanol System

3.3.1. Experimental

The investigation consisted of several series of experiments to determine the effects of catalyst type, concentration, physical reaction conditions and solvent upon the homologation of methanol. The study was performed in the same bombs used for the high pressure infra-red work and the analysis of final products was routinely completed by G.L.C. Suitable conditions for the homologation reaction were suggested by colleagues at B.P. Research Centre, Sunbury, and these were used as a basic starting point for investigating the reaction variables.

A general example of an experiment is as follows: cobalt acetate hydrate (1.7 g, 6.8 mmol) and methanol (18 ml) were placed in the bomb, which was then sealed and purged with nitrogen. The bomb was pressurised with a mixture of 1:1 (CO/H_2) synthesis gas to a pressure of 140 Atm, and stirred as quickly as possible. The temperature was raised to the selected level (between 170 - 220°C) and the gas pressure would rise to about 200 Atm. The reaction was then allowed to take place for a set period of time (usually 2 or 8 hrs.) and the pressure was maintained at 200 Atm by occasionally injecting more synthesis gas of the same composition into the system, to replace that consumed by the reaction. When the run was complete the system was allowed to cool to room temperature overnight, the bomb was depressurised the next day and samples taken for analysis.

The results of varying the reaction parameters of the basic unpromoted system are discussed here with reference to the yield and selectivity of selected products (ethanol, methyl acetate, ethyl acetate, acetaldehyde).

Where:

$$\% \text{ Molar Yield} = \frac{\text{Moles of reactant converted to product}}{\text{Moles of reactant fed}} \times 100$$

$$\% \text{ Molar Selectivity} = \frac{\text{Moles of reactant converted to product}}{\text{Moles of reactant consumed}} \times 100$$

Catalyst

The catalyst used in these experiments was cobalt (II) acetate tetrahydrate. This is believed to be the most suitable source of cobalt (II) for the commercial process of homologation, if it eventually becomes economical, because the acetate is an easily available, relatively cheap and soluble salt of cobalt, and does not contain troublesome counterions. The catalyst for the reaction is believed to be a cobalt carbonyl type species. The standard method for preparing dicobalt octacarbonyl is to heat a cobalt salt in a non-aqueous medium above $100^{o}C$, in a superatmosphere (> 100 Atm) of carbon monoxide and hydrogen. Hence under the conditions of reaction the cobalt carbonyl catalyst should be formed "in situ" from the cobalt (II) acetate. The cobalt (II) acetate was used without any purification.

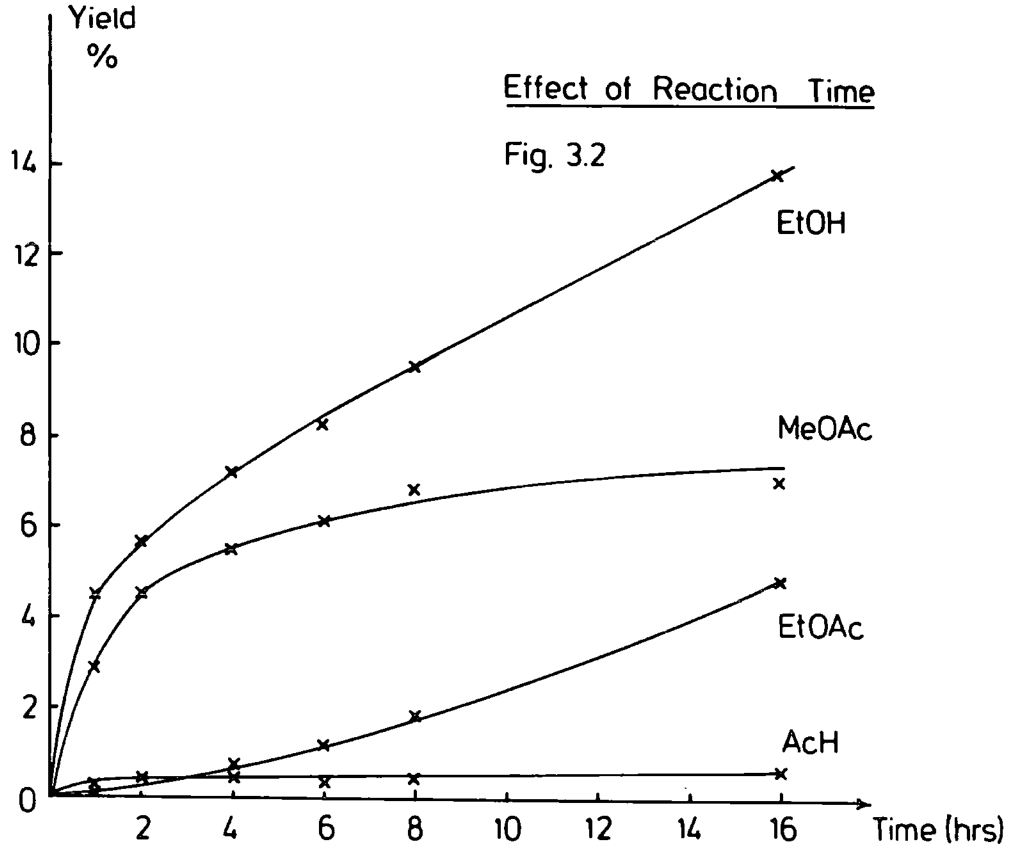
3.3.2. Discussion

(a) Influence of reaction time (Table 3.2.).

A yield of 14% ethanol was obtained from the reaction when run for 16 hours (Fig. 3.2.). The yield of ethanol was found to increase steadily with increase in reaction time. It seemed likely that higher yields of ethanol could be obtained at even longer reaction times, but these were impractical to investigate. The major by-products formed in the reaction were methyl acetate and ethyl acetate. Acetaldehyde was also generated as a by-product. The ethanol yield obtained at 8 hour reaction time was comparable to that produced using a dicobalt octacarbonyl catalyst starting

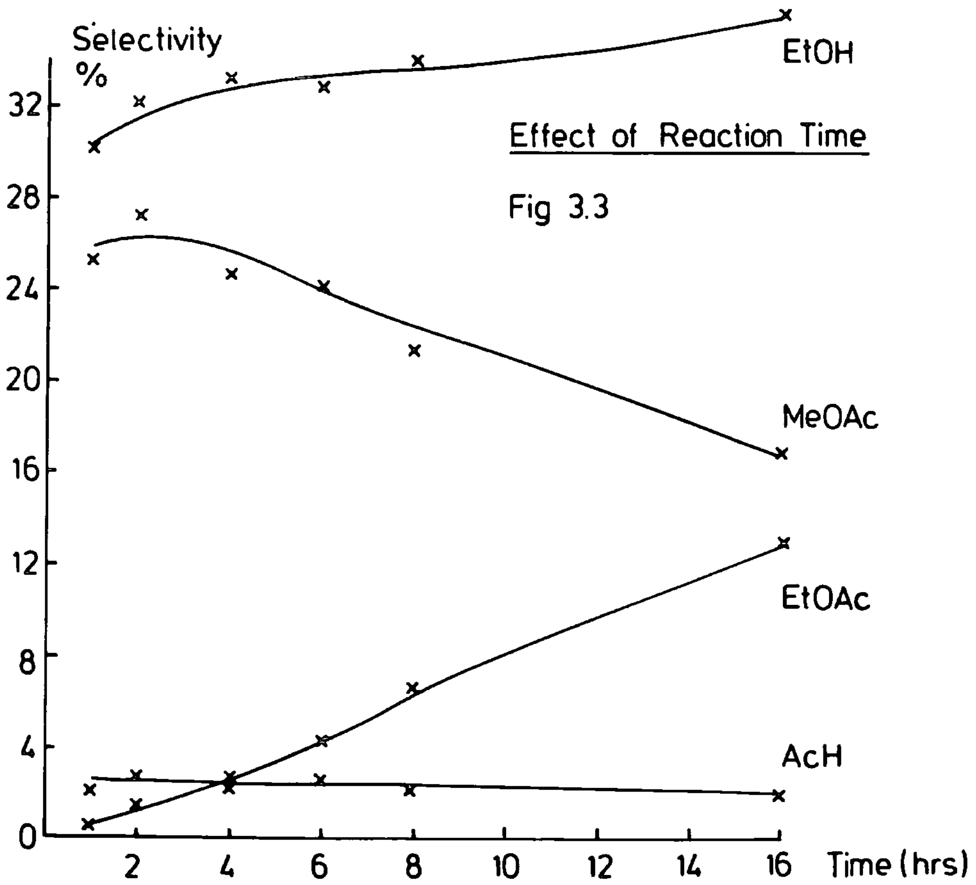
Table 3.2.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	Reaction Time (hr.)	Temperature (^oC)	Pressure (Atm)	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
1	0.56	7.0×10^{-3}	1	185	200	Yield	4.5	2.8	0.1	0.3
						Selectivity	30.2	25.2	0.5	2.0
2	0.56	7.0×10^{-3}	2	185	200	Yield	5.7	4.5	0.3	0.4
						Selectivity	32.2	27.2	1.4	2.7
3	0.56	7.0×10^{-3}	4	185	200	Yield	7.2	5.5	0.8	0.5
						Selectivity	33.4	24.6	2.6	2.2
4	0.56	7.0×10^{-3}	6	185	200	Yield	8.2	6.1	1.2	0.3
						Selectivity	32.8	24.0	4.3	2.6
5	0.56	7.0×10^{-3}	8	185	200	Yield	9.5	6.8	1.9	0.4
						Selectivity	34.0	21.3	6.6	2.0
6	0.56	7.0×10^{-3}	16	185	200	Yield	13.8	7.0	4.8	0.6
						Selectivity	36.4	17.0	13.0	1.8
5'	0.56	3.5×10^{-3} $Co_2(CO)_8$	8	185	200	Yield	9.4	6.7	2.0	0.3
						Selectivity	33.1	22.4	7.0	1.9



Effect of Reaction Time

Fig. 3.2



Effect of Reaction Time

Fig 3.3

material, instead of the $Co(OAc)_2 4H_2O$ catalyst, indicating that the same catalyst system was probably involved.

The concentration of the various products provided some useful information. The yield of ethanol increased with time; the selectivity to ethanol (Fig. 3.3.) also increased but only slowly in comparison with the yield. The yield of methyl acetate increased with time but this increase slowed down as the amount of ethanol in the system became significant and competed with the methanol in the formation of esters; hence the appearance of the ethyl acetate yield graph. Conversely the acetaldehyde yield remained relatively constant throughout the series of reaction times, indicating that it had reached an equilibrium value and therefore would not increase further in concentration; hence the selectivity to acetaldehyde decreased as the other reaction products built up.

(b) Influence of catalyst/methanol ratio (Table 3.3.).

The ratio referred to here is the molar proportion of (cobalt atoms / methanol molecules) expressed as a percentage. Hence a ratio of 1% would relate to a solution of 1.4 g of $Co(OAc)_2 4H_2O$ in 18 ml of methanol.

The yield of ethanol was found to remain relatively constant regardless of the catalyst/methanol ratio within the range 0.5 - 3.2% (Fig. 3.4.). The higher concentrations showed a slight improvement in yield; however this increase was small as the solubility of the catalyst is probably the limiting factor. (A 3% solution requires 4.2 g $Co(OAc)_2 4H_2O$ in 18 ml MeOH.) At concentrations lower than 0.125%, the reaction was effectively found to cease as no products could be detected. The yield of the other products was found to follow approximately the same pattern as that of the ethanol yield. The selectivities of the products were not found

Table 3.3.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	Reaction Time (hr.)	Temperature (^oC)	1:1 Pressure (Atm)	Ratio % Moles Co on MeOH	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
5	0.56	7.0×10^{-3}	8	185	200	1.25	Yield	9.5	6.8	1.9	0.4
							Selectivity	34.0	21.3	6.6	2.0
7	0.56	2.8×10^{-3}	8	185	200	0.5	Yield	9.6	6.2	2.0	0.6
							Selectivity	32.5	24.6	6.8	2.2
8	0.56	3.5×10^{-3}	8	185	200	0.625	Yield	9.7	6.4	2.1	0.6
							Selectivity	33.1	24.0	7.1	2.4
9	0.56	15.0×10^{-3}	8	185	200	2.68	Yield	12.1	8.0	3.5	0.4
							Selectivity	34.5	20.8	11.2	1.4
10	0.56	17.5×10^{-3}	8	185	200	3.13	Yield	12.3	8.2	4.0	0.5
							Selectivity	34.6	20.2	12.0	1.5
11	0.56	11.0×10^{-3}	8	185	200	1.96	Yield	11.1	7.6	2.8	0.6
							Selectivity	34.0	21.0	9.0	1.7
26	0.56	1.75×10^{-3}	8	185	200	0.313	Yield	8.0	4.8	1.6	0.4
							Selectivity	32.0	24.9	6.6	2.0
27	0.56	0.7×10^{-3}	8	185	200	0.125	Yield	5.0	2.3	0.2	-
							Selectivity	31.6	27.1	6.5	-

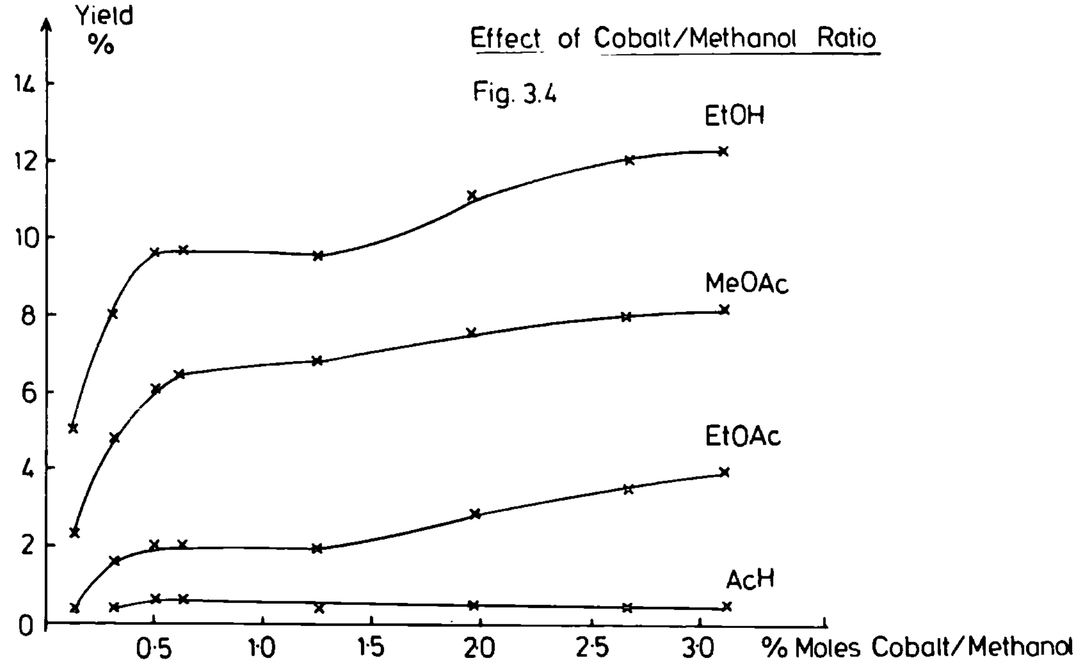

Effect of Cobalt/Methanol Ratio

Fig. 3.4

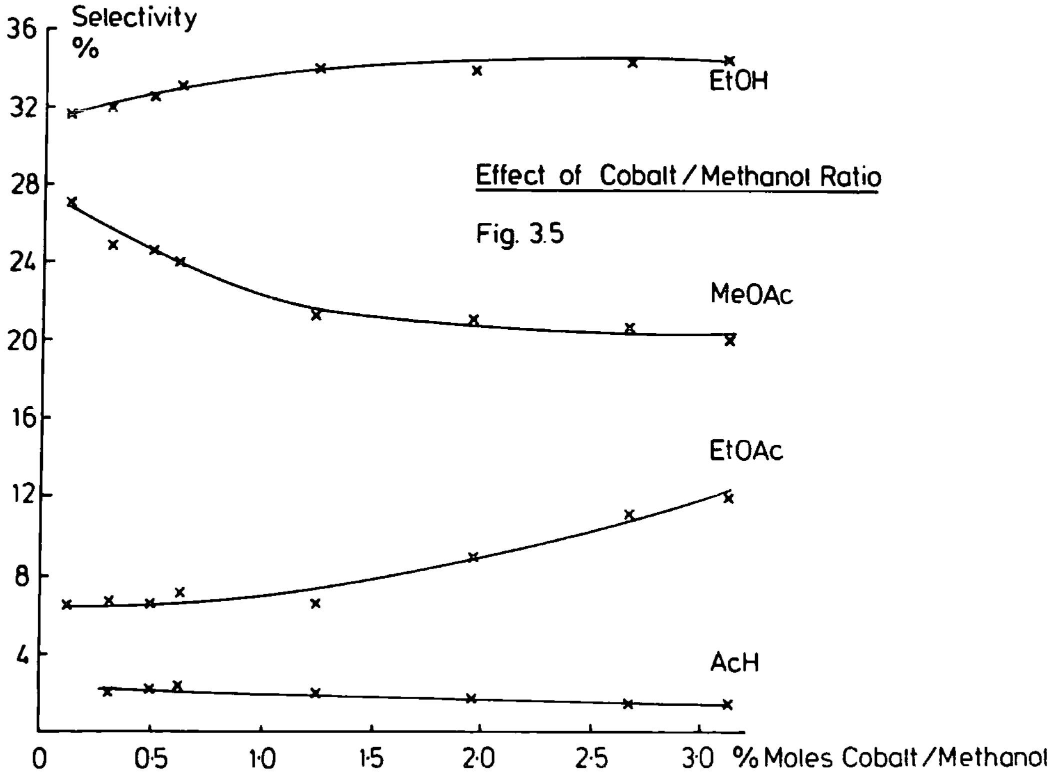

Effect of Cobalt/Methanol Ratio

Fig. 3.5

to change substantially regardless of the catalyst/methanol ratio (Fig. 3.5.).

(c) Influence of temperature (Table 3.4.).

The effect of changes of the reaction temperature on the reaction products is shown in the graph in Fig. 3.6. The yield of ethanol passed through a maximum (9 - 10%) at 185°C, falling sharply to 2% at 225°C. The decrease in ethanol yield with increased reaction temperature was accompanied by a decrease in yield of all the other major products, and in the conversion of methanol itself. At high reaction temperatures (195 - 225°C) a grey-black deposit was noted on the walls of the high pressure bomb; this was believed to be deposited metallic cobalt. It seemed therefore that the conversion of methanol to products is less at high temperatures due to cobalt metal plating out, as the catalyst is thermally unstable under these conditions.

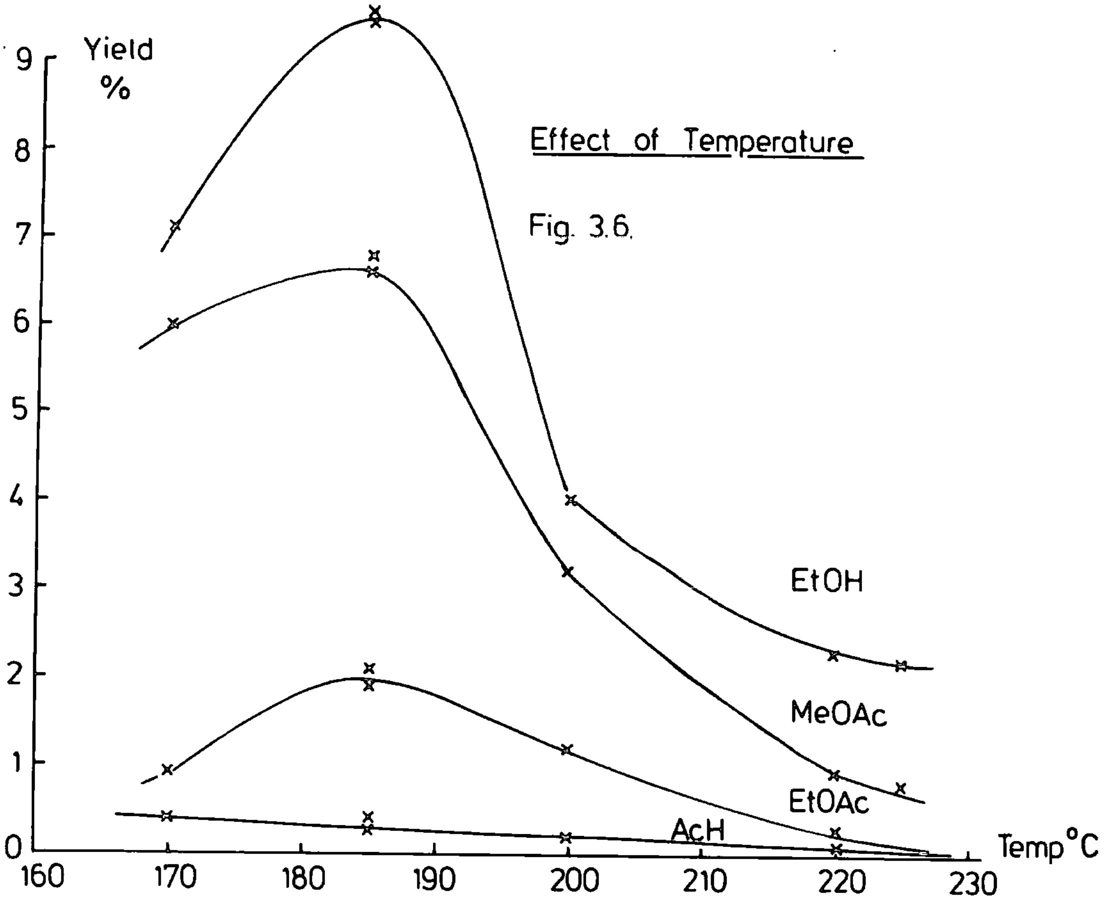
At lower temperatures (170 - 180°C) the yields of all products were found to be reduced compared with yields at 185°C. This can be considered to be due to the reaction being substantially slower at these lower temperatures or because only a fraction of the cobalt has been converted into active catalyst.

Thus the unpromoted reaction seems to have very stringent limitations upon the temperature range within which it is relatively efficient. The temperature must be kept within the range 175 - 190°C if it is to maximise the production of active catalyst and minimise the thermal degradation of the catalyst to metallic cobalt.

Examination of the selectivities of the various products of the reaction (Fig. 3.7.) shows an interesting feature. The selectivities of most of the products remain fairly constant throughout the temperature range studied. However ethanol is an exception and shows a strong

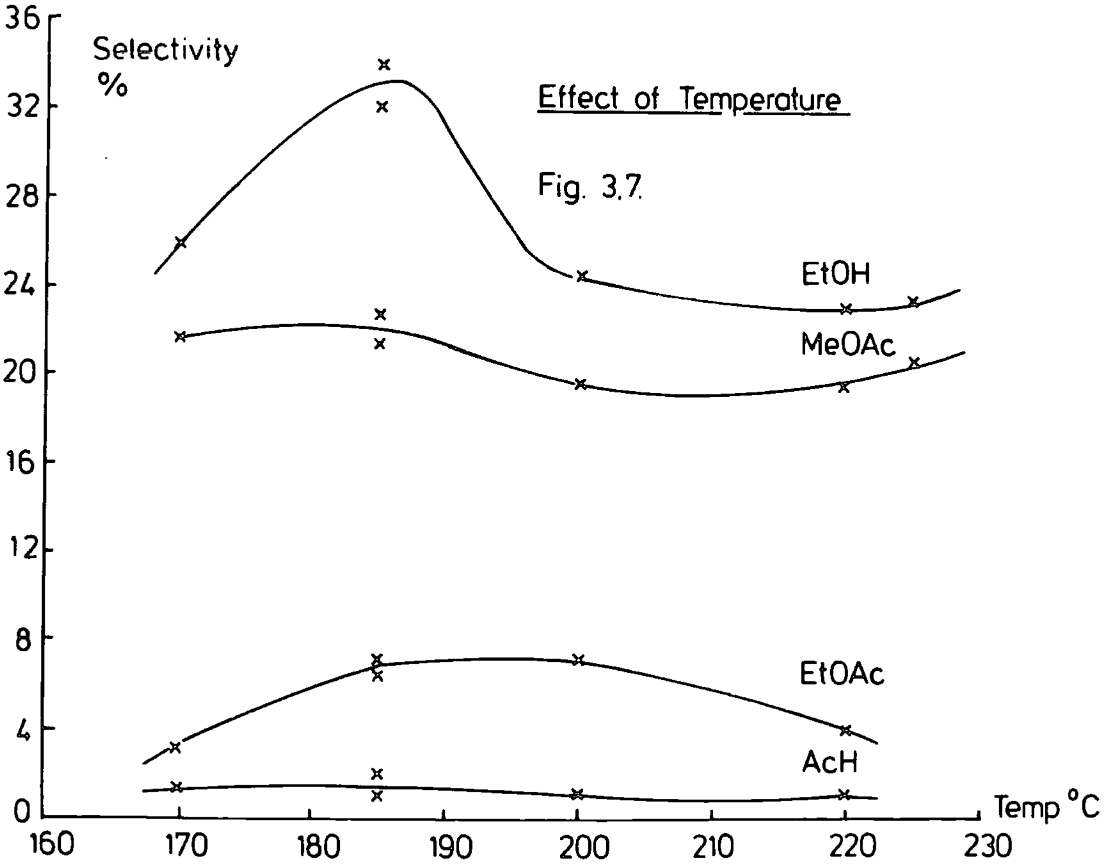
Table 3.4.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	Reaction Time (hr.)	Temperature (^oC)	Pressure (Atm)	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
5	0.56	7.0×10^{-3}	8	185	200	Yield	9.5	6.8	1.9	0.4
						Selectivity	34.0	21.3	6.6	2.0
12	0.56	7.0×10^{-3}	8	225	200	Yield	2.2	0.7	-	-
						Selectivity	23.5	20.8	-	-
13	0.56	7.0×10^{-3}	8	170	200	Yield	7.1	6.0	0.9	0.4
						Selectivity	25.9	21.6	3.2	1.4
14	0.56	7.0×10^{-3}	8	200	200	Yield	4.0	3.2	1.2	0.2
						Selectivity	24.5	19.6	7.3	1.2
15	0.56	7.0×10^{-3}	8	185	200	Yield	9.6	6.6	2.1	0.3
						Selectivity	32.1	22.7	7.1	1.0
16	0.56	7.0×10^{-3}	8	220	200	Yield	2.3	0.9	0.3	0.1
						Selectivity	23.1	19.6	4.0	1.2



Effect of Temperature

Fig. 3.6.



Effect of Temperature

Fig. 3.7.

increase in selectivity at 180 - 190°C indicating that within this very narrow temperature range the formation of ethanol is much favoured.

(d) Influence of synthesis gas pressure[51] (Table 3.5.).

The catalyst is thermally unstable unless it is under carbon monoxide such that the pressure exceeds the dissociation pressure. This dissociation pressure is temperature dependent and increases with increase in temperature.

The yield of ethanol at 200°C (Fig. 3.8a., 3.9a.) was increased from 4% to 11% by reacting the system with the synthesis gas pressure at 300 Atm instead of 200 Atm. This increased synthesis gas pressure increases the partial pressure of carbon monoxide and presumably exceeds the dissociation pressure of the cobalt carbonyl catalyst, and thus retards its thermal decomposition. Experimental limitations prevent further investigation at higher pressure than 300 Atm, but it seems likely that further increase in pressure will not increase the yield of ethanol to any great extent.

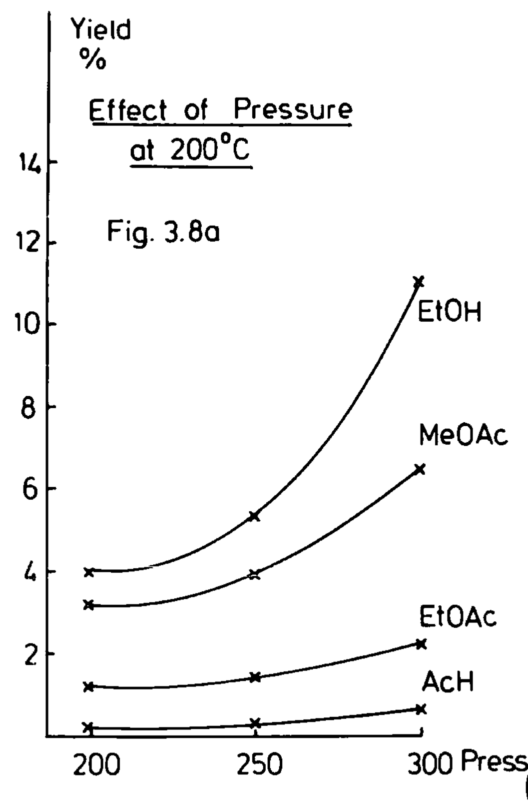
A study of lower pressure systems (at 185°C) indicated that at 100 Atm, the homologation reaction could not be detected (Fig. 3.8b., 3.9b.). As the pressure was increased the yields of all the products were found to increase, as more catalyst was stabilised, to a limit of ∿ 9.5% ethanol. Further increase in pressure seemed to have no effect upon the yield of the products. This would appear to support the earlier prediction concerning the reaction at 200°C, that increasing pressure beyond 300 Atm would not greatly improve the yields.

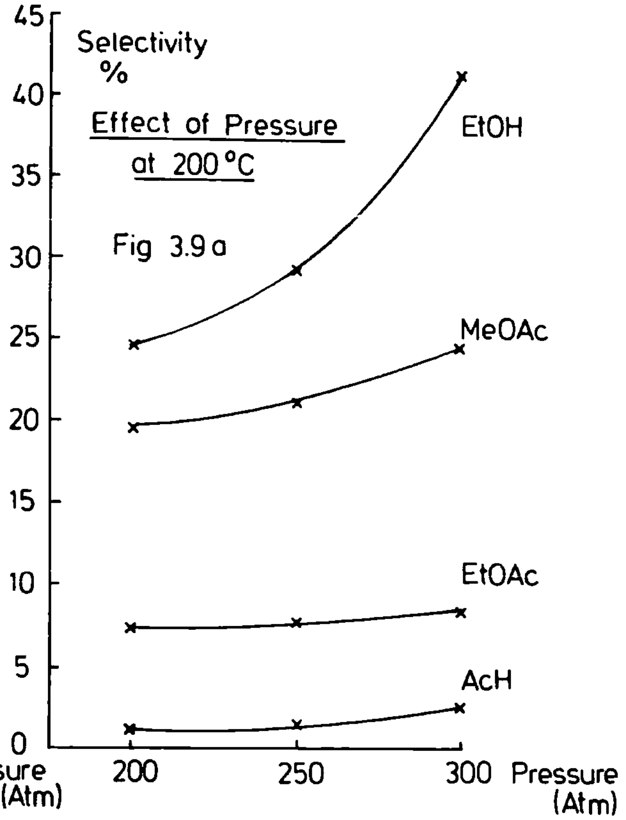
(e) Influence of carbon monoxide/hydrogen ratio (Table 3.6.).

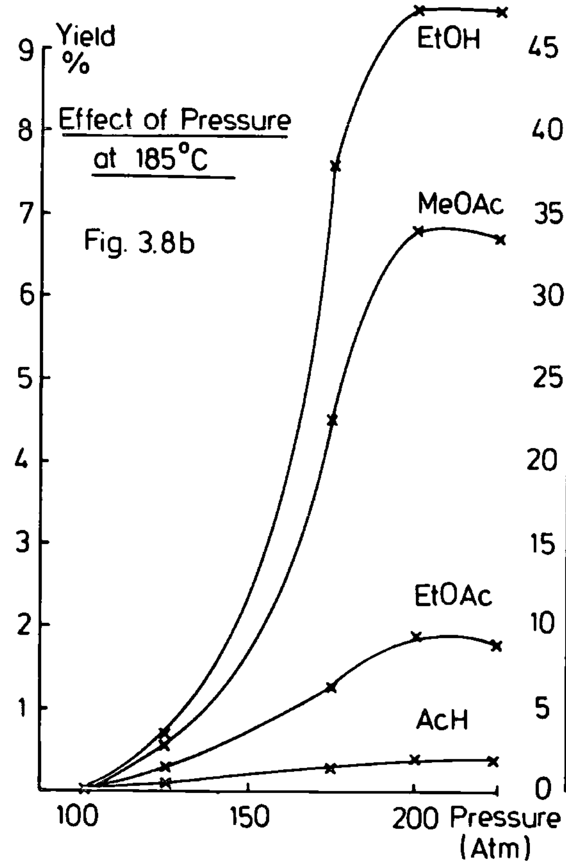
A variation in the molar ratio of carbon monoxide to hydrogen in the synthesis gas charged to the bomb, had marked effects on the product

Table 3.5.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	Reaction Time (hr.)	Temperature (°C)	Pressure (Atm)	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
14	0.56	7.0×10^{-3}	8	200	200	Yield	4.0	3.2	1.2	0.2
						Selectivity	24.5	19.6	7.3	1.2
17	0.56	7.0×10^{-3}	8	200	250	Yield	5.3	3.9	1.4	0.3
						Selectivity	29.2	21.0	7.6	1.5
18	0.56	7.0×10^{-3}	8	200	300	Yield	11.0	6.4	2.2	0.6
						Selectivity	41.3	24.4	8.2	2.5
5	0.56	7.0×10^{-3}	8	185	200	Yield	9.5	6.8	1.9	0.4
						Selectivity	34.0	21.3	6.6	2.0
19	0.56	7.0×10^{-3}	8	185	175	Yield	7.6	4.5	1.3	0.3
						Selectivity	33.1	19.6	5.6	1.3
20	0.56	7.0×10^{-3}	8	185	125	Yield	0.7	0.6	0.3	0.1
						Selectivity	30.0	22.6	9.7	4.1
21	0.56	7.0×10^{-3}	8	185	100	Yield	-	-	-	-
						Selectivity	-	-	-	-
22	0.56	7.0×10^{-3}	8	185	225	Yield	9.4	6.7	1.8	0.4
						Selectivity	33.8	21.0	6.4	2.0


Yield
%
Effect of Pressure
at 200°C
Fig. 3.8a
14
12
10
8
6
4
2
EtOH
MeOAc
EtOAc
AcH
200
250
300 Pressure
(Atm)


45
40
35
30
25
20
15
10
5
0
Selectivity
%
Effect of Pressure
at 200 °C
Fig 3.9 a
EtOH
MeOAc
EtOAc
AcH
200
250
300
Pressure
(Atm)


9
8
7
6
5
4
3
2
1
Yield
%
Effect of Pressure
at 185°C
Fig. 3.8b
EtOH
MeOAc
EtOAc
AcH
100
150
200 Pressure
(Atm)

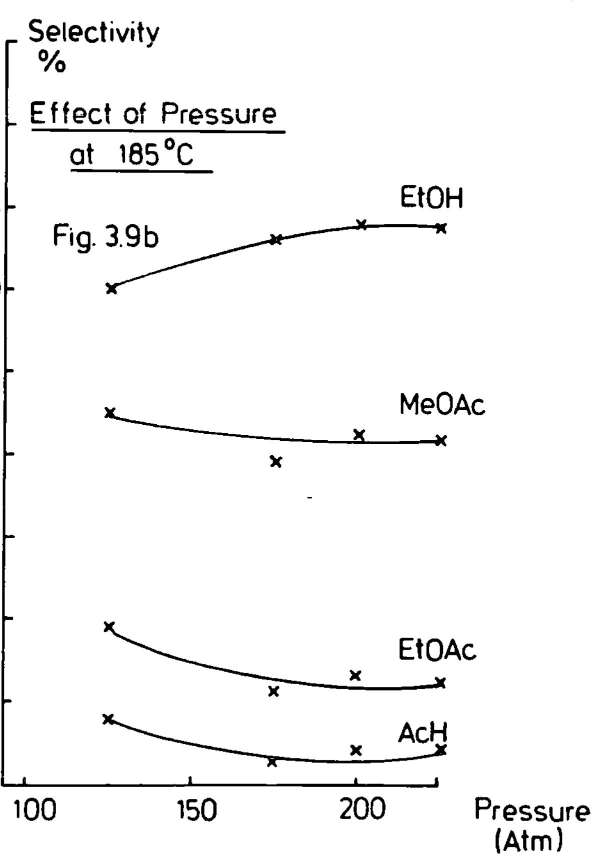
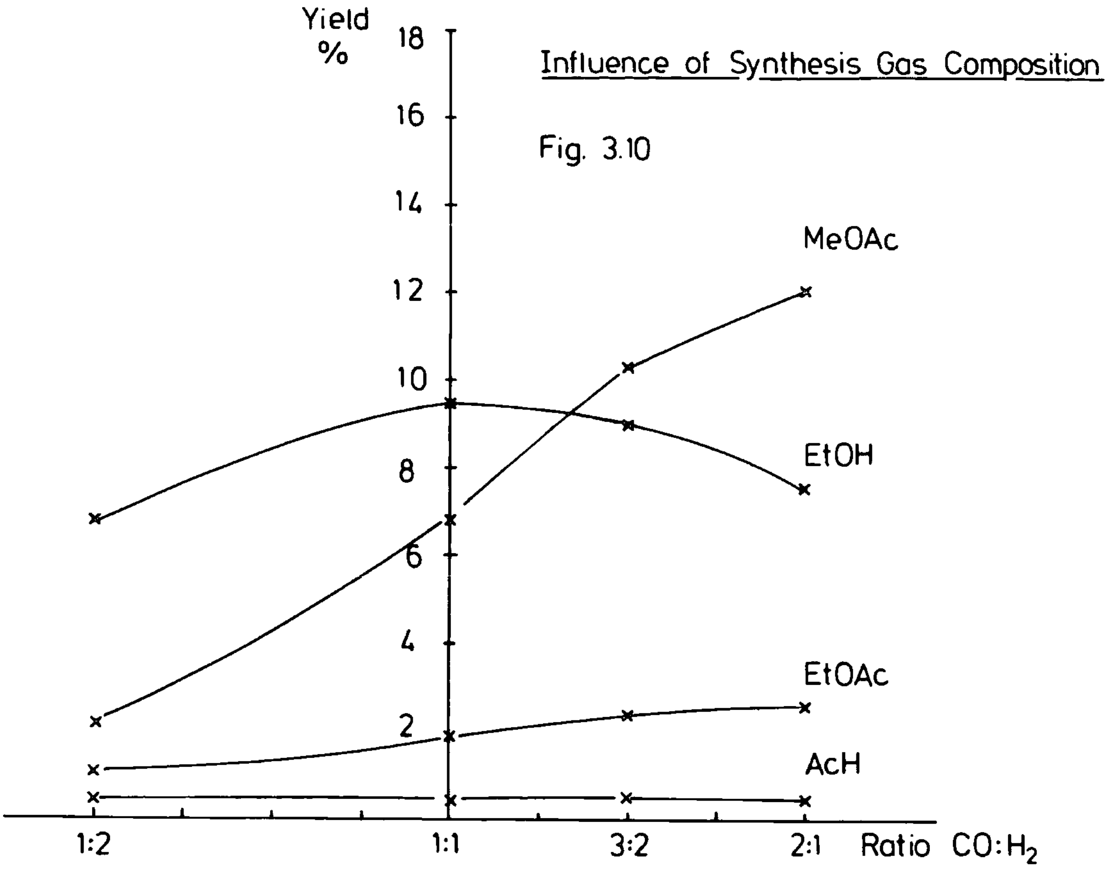

45
40
35
30
25
20
15
10
5
0
Selectivity
%
Effect of Pressure
at 185 °C
Fig. 3.9b
EtOH
MeOAc
EtOAc
AcH
100
150
200
Pressure
(Atm)

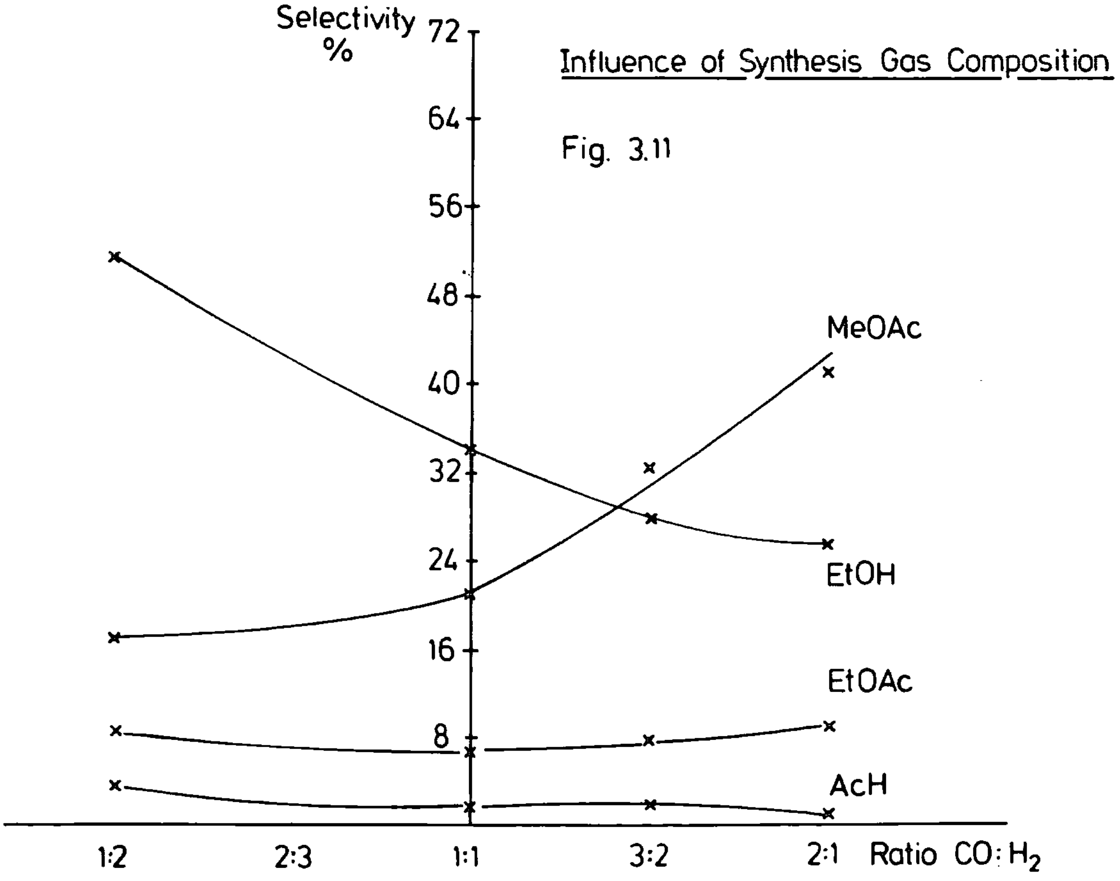
Table 3.6.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	Reaction Time (hr.)	Temperature (°C)	Pressure (Atm)	Ratio $CO:H_2$	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
5	0.56	7.0×10^{-3}	8	185	200	1:1	Yield	9.5	6.8	1.9	0.4
							Selectivity	34.0	21.3	6.6	2.0
23	0.56	7.0×10^{-3}	8	185	200	1:2	Yield	6.8	2.2	1.1	0.5
							Selectivity	51.6	17.0	8.5	3.9
24	0.56	7.0×10^{-3}	8	185	200	2:1	Yield	7.5	12.0	2.6	0.4
							Selectivity	25.6	41.0	8.8	1.4
25	0.56	7.0×10^{-3}	8	185	200	3:2	Yield	9.0	10.3	2.4	0.5
							Selectivity	29.7	32.2	8.1	1.9



Influence of Synthesis Gas Composition

Fig. 3.10



Influence of Synthesis Gas Composition

Fig. 3.11

yields (Fig. 3.10.) and selectivities (Fig. 3.11.). When the carbon monoxide content of the gas mixture was decreased, both the ethanol yield and methanol conversion were reduced. This was probably a result of catalyst decomposition due to the lower partial pressure of carbon monoxide. Conversely increase in the carbon monoxide to hydrogen ratio in the gas greatly increased the yield of methyl acetate at the expense of ethanol. The most suitable ratio for the synthesis gas mixture, to maximise the production of ethanol, appeared to be equal amounts of carbon monoxide and hydrogen. The selectivities (Fig. 3.11.) showed approximately the same pattern and confirmed that the ratio of synthesis gas required for ethanol production should not have a high proportion of carbon monoxide.

(f) Other catalysts.[51]

The effect of using different sources of cobalt for the reaction has been investigated to a small extent. The studies indicate that the best sources are of the following types: - dicobalt octacarbonyl, cobalt carbonate, naphthanate, acetate, formate and basic acetate. Those materials producing moderate activity are cobalt chloride or sulphate, whilst those possessing poor activity are the oxides of cobalt or finely divided cobalt metal.

3.4. High Pressure Infra-red Study of the Cobalt/Methanol System

3.4.1. Experimental

The infra-red study of the cobalt/methanol system was carried out in the same autoclaves that were used for the high pressure autoclave studies. The method employed was to prepare the starting materials in solution in methanol wherever possible, and to inject the solution into the sample bomb, against a counter current of nitrogen or carbon monoxide. The reference bomb would be filled with solvent in the same way. The bombs were then sealed and filled with the required gas or gas mixture to the selected pressure. The infra-red spectra were recorded regularly as the temperature was raised in steps of ∿ 30°C to the final reaction temperature; at each interval sufficient time (½ hour) was allowed for equilibrium to be reached. The system was generally permitted to remain at reaction temperature for a relatively short time, once equilibrium had been reached, to avoid complication of the spectra by peaks due to the organic reaction products, which when combined with peaks due to the catalytic species make interpretation of the spectra far more difficult. In general it was found possible to leave the reacting system at the maximum temperature for about an hour before any contamination in the infra-red spectra was noticeable, and this was believed to allow ample time for the catalyst system to reach equilibrium. The cells would then be allowed to cool to room temperature and the infra-red spectrum taken before depressurising the bombs. The resultant solution was syringed out and examined, by infra-red and chromatographic techniques, to ensure that the organic products of the homologation reaction had not built up to such a concentration, that would cause strong absorptions in the infra-red spectra and obscure the infra-red absorptions of the catalytic species.

3.4.2. Discussion

(a) Study of cobalt/methanol system under nitrogen pressure.

An examination of several cobalt carbonyl systems in methanol indicated that under nitrogen pressure (∿ 100 Atm) none of the carbonyl species were stable at elevated temperature, regardless of the pressure of nitrogen. The starting materials used were dicobalt octacarbonyl, $Co(MeOH)_6^{2+}[Co(CO)_4^-]_2$ and $PPNCo(CO)_4$. The investigation centred upon the peak at 1900 cm^{-1}, due to $Co(CO)_4^-$, which was observed as the temperature was slowly increased. The peak was found to disappear rapidly at ∿ 100°C as the $Co(CO)_4^-$ species decomposed by loss of carbon monoxide. On opening the bomb, metallic cobalt was found to be deposited on the walls.

(b) The cobalt/methanol system under carbon monoxide pressure.

The investigation again used observation of the 1900 cm^{-1} band of $Co(CO)_4^-$ as a method of following the course of the reactions. No other carbonyl bands were detected in this study as the band at 2018 cm^{-1}, also due to $Co(CO)_4^-$, was effectively masked by a methanol solvent peak.

The observation of the 1900 cm^{-1} band gave a good indication of the stability of the cobalt carbonyl species at particular temperatures and pressures. A series of reactions were performed using solutions of $Co(CO)_4^-$ to determine the pressure of carbon monoxide necessary to stabilise this species at a particular temperature. The results are presented in Table 3.7. It was found that the system was easily stabilised at lower temperatures (∿ 100°C) by a moderate pressure of carbon monoxide (10 Atm) but at higher temperatures (∿ 200°C) a much higher pressure was required to prevent decomposition to cobalt metal (170 Atm). The relationship between the carbon monoxide pressure necessary to stabilise the $Co(CO)_4^-$ and the temperature is illustrated in Fig. 3.12.

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Table 3.7.

Conc. $Co(CO)_4^-$ (moles)	Pressure CO (P_{CO} Atm)	Max. Temp. (T-273) °C	log P_{CO}	$\frac{1}{T} \times 10^3$
66.7	170	200	2.23	2.11
65.8	160	185	2.20	2.18
66.0	120	175	2.08	2.23
66.4	55	165	1.74	2.28
66.5	48	155	1.68	2.33
66.7	34	143	1.53	2.40
67.0	14	125	1.15	2.51

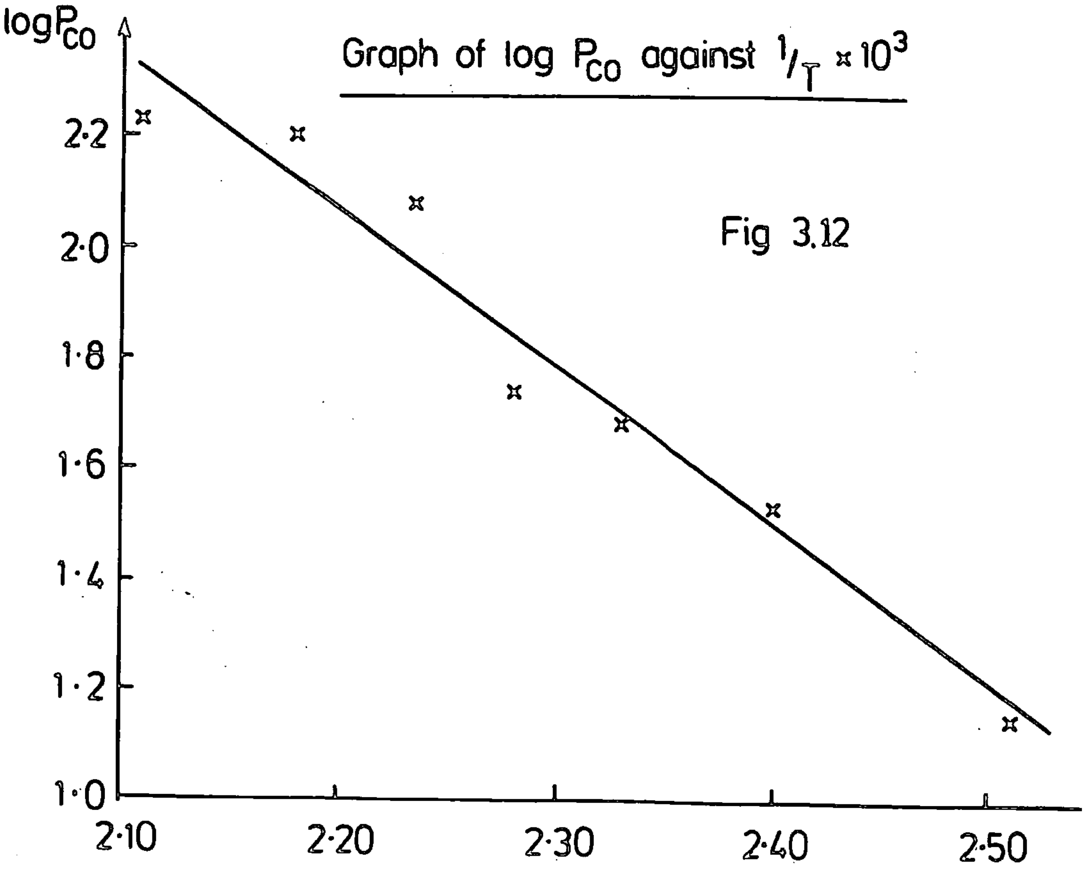


Fig 3.12

The thermal decomposition of the cobalt carbonyl anion to cobalt metal is believed to occur thus:-

$$2Co(CO)_4^- \longrightarrow 2Co\downarrow + 8CO + 2e^-$$

The cobalt (II) cation present is reduced to cobalt metal;

$$Co(MeOH)_6^{2+} + 2e^- \longrightarrow Co\downarrow + 6MeOH$$

No evidence for the reverse of these reactions was obtained; the cobalt metal remained plated out upon the walls of the cell and did not reform the carbonyl species when the temperature was reduced.

This loss of carbonyl species[52] by thermal decomposition is an important limitation upon the minimum pressure at which the reaction can be successfully run. These results indicate that in Table 3.7. the reaction performed at 200°C has insufficient partial pressure of carbon monoxide to stabilise the carbonyl species present, and hence further increase in CO pressure would give a higher yield of ethanol. Also these results show that modifying the carbon monoxide/hydrogen ratio in synthesis gas must be performed carefully to ensure the partial pressure of carbon monoxide does not fall too low.

(c) The cobalt/methanol system under synthesis gas pressure.

The reaction system under synthesis gas pressure requires a partial pressure of carbon monoxide sufficient, as proposed earlier, to stabilise the carbonyl species at reaction temperature ($\sim$ 185°C). If this partial pressure was not present the system decomposed and cobalt metal plated out onto the cell.

However if the carbon monoxide partial pressure was sufficient the carbonyl species present could be observed throughout the experiment. The only carbonyl species detected at temperatures below 160°C was the

$Co(CO)_4^-$ anion, which showed a distinct band at 1900 cm^{-1}. At higher temperatures (170 - 185°C) a second species became detectable which gave bands at $1730_{(s)}$, $2025_{(s)}$, $2110_{(w)}$ cm^{-1}. These bands can be assigned to the acyl species $CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4$. This species is believed to be an intermediate in the reaction to form ethanol. The acyl species is formed regardless of whether the reaction is started with a synthesis gas mixture, or following injection of hydrogen into a system under carbon monoxide pressure only at the reaction temperature. The partial pressure of hydrogen does not appear to affect the system. No dicobalt octacarbonyl or cobalt tetracarbonyl hydride was detected spectroscopically in the system at any stage in the reaction.

CHAPTER FOUR

AN EXAMINATION OF THE LIGAND STABILISED COBALT/METHANOL REACTION SYSTEM

4.1. Introduction

The system studied in this chapter is the ligand stabilised reaction. The ligands considered are aryl arsines and stibines, and aryl and alkyl phosphines. These materials, suggested in many patents to be useful in the homologation of methanol, are classed as stabilising ligands as they are believed to have the ability to permit the reaction to run either at higher temperatures or lower gas pressures. A secondary effect of the addition of these compounds is to alter the ratio of the various reaction products; this too may be beneficial to the reaction by suppressing unwanted materials.

4.2. Low Pressure Study of the Dicobalt Octacarbonyl/Ligand/Methanol Reaction

4.2.1. Experimental

(a) Reaction of dicobalt octacarbonyl with triphenyl phosphine in methanol.

Crystals of dicobalt octacarbonyl (0.6 gm, 2 mmol) were stirred with methanol (40 ml) and to this a solution of triphenyl phosphine (1.3 gm, 5 mmol) in 40 ml of methanol was added. The methanol solution initially went brown in colour, gas was evolved, and later, a red/brown solid began to settle out of solution. This red/brown solid settled out over a period of about three hours and finally the methanol was left only faintly brown. After all reaction had ceased, the solvent was evaporated and a red/brown solid was produced. The material was washed with pentane to remove any unreacted phosphine and analysed: Co, 14.3; H, 3.65; C, 62.0; P, 7.5%, ($[Co(CO)_3PPh_3]_2$ requires Co, 14.6; H, 3.7; C, 62.2; P, 7.7%).

Infra-red examination of the system was performed using solution spectroscopy in the carbonyl stretching frequency region. Once the phosphine solution had been added the only bands observed in the spectrum were at $2010_{(m)}$ and $1904_{(s)}$ cm^{-1}. These persisted unchanged throughout the experiment. The red/brown solid produced from the reaction was also analysed by infra-red, as a nujol mull, and showed peaks at $2000_{(m)}$, $1945_{(m)}$ and $1890_{(m)}$ cm^{-1}.

(b) Reaction of dicobalt octacarbonyl and triphenyl phosphine in ethanol.

An identical reaction was performed in ethanol to facilitate solution infra-red study as described in chapter 3. The reaction was observed to take the same course. The red/brown solid was extracted by evaporating the system to dryness under vacuum, and it was washed with hexane. This red/brown solid was treated with acetone and was found to reduce greatly in bulk and appeared to partly dissolve in the acetone forming a brown solution. Further treatment with acetone failed to dissolve any further solid.

Once the phosphine had been added, solution infra-red spectroscopy of the reaction showed peaks at $2007_{(m)}$ and $1902_{(s)}$ cm^{-1}. These then persisted unchanged throughout the experiment.

Analysis of the insoluble red/brown solid gave Co, 14.5; H, 3.8; C, 62.1; P, 7.8%. ($[Co(CO)_3PPh_3]_2$ requires Co, 14.6; H, 3.7; C, 62.2; P, 7.7%.) A solid infra-red spectrum, as a nujol mull or KBr disc, showed peaks at:- $1960_{(m)}$, $1950_{(s)}$ and $1902_{(w)}$ cm^{-1}. The mass spectrum of the solid showed no molecular ion peak but some fragmentation peaks were observed; $[Co(CO)_2PPh]_2^+$, $^m/e$ 446; $[Co_2(CO)_4P_2Ph]^+$, $^m/e$ 369; $[Co_2(CO)_4P]^+$, $^m/e$ 261; $[Co_2(CO)_3P_2]^+$, $^m/e$ 264; $[Co_2(CO)_4]^+$, $^m/e$ 230.

The infra-red spectrum of the second brown solid was taken in acetone solution and showed peaks at $2008_{(s)}$ and $1895_{(s)}$ cm^{-1}. Elemental analysis done after evaporating down the acetone solution gave Co, 14.2; H, 3.65; C, 61.7; P, 7.5%, ($[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-]$ requires Co, 14.1; H, 3.6; C, 61.6; P, 7.4%). The mass spectrum of the solid showed no molecular ion peak but some decomposition peaks were observed; $[Co(CO)_3P_2Ph_2]^+$, $^m/e$ 359; $[Co(CO)_3P_2Ph]^+$, $^m/e$ 282; $[Co(CO)_3P_2]^+$, $^m/e$ 205; $[Co(CO)_4]^+$, $^m/e$ 171; $[Co(CO)_3]^+$, $^m/e$ 143. These results indicated quite clearly that two different products had been formed but with approximately the same elemental formulation.

(c) Reaction of dicobalt octacarbonyl with triphenyl arsine in methanol.

Crystals of dicobalt octacarbonyl (0.6 g, 2 mmol) were added to 40 ml of methanol containing triphenyl arsine (1.5 g, 5 mmol). The system was stirred rapidly, gas was evolved and the solvent went dark brown. After a period of about 3 hours a brown solid was seen to precipitate from the methanol which left the solvent free of colour. The solvent was syringed off and the dark brown solid dried, by pumping under vacuum. The solid was removed, washed with hexane to remove any excess triphenyl arsine still present, and once again pumped dry, before being sent for elemental analysis. Washing with acetone had no effect upon the material. The solid infra-red spectrum was also run as a nujol mull. Analysis gave Co, 13.2; H, 3.4; C, 57.1; As, 16.0%, ($[Co(CO)_3AsPh_3]_2$ requires Co, 13.1; H, 3.3; C, 56.1; As, 16.7%). Infra-red gave peaks at:- $1965_{(sh)}$, $1945_{(s)}$ and $1900_{(sh)}$ cm^{-1}. The mass spectrum of the solid showed no molecular ion peak but several decomposition peaks were observed; $[Co_2(CO)_4As_2Ph]^+$, $^m/e$ 457; $[Co_2(CO)_4AsPh]^+$, $^m/e$ 382; $[Co_2(CO)_4As_2]^+$, $^m/e$ 380; $[Co_2(CO)_4As]^+$, $^m/e$ 305; $[Co_2(CO)_4]^+$, $^m/e$ 230.

(d) Reaction of dicobalt octacarbonyl with triphenyl stibine in methanol.

Crystals of dicobalt octacarbonyl (0.6 g, 2 mmol) were added directly to 50 ml of methanol containing triphenyl stibine (1.75 g, 5 mmol) and the system was stirred overnight. A brown solid was found to have deposited from the system and the methanol had only a faint brown tinge. The methanol was syringed off and the solid dried by pumping under vacuum. The solid was washed with pentane before being sent for elemental analysis. Washing with acetone had no effect on the material. The solid infra-red spectrum was also run as a nujol mull. Analysis gave Co, 12.0; H, 2.9; C, 50.4; Sb, 25.0%, ($[Co(CO)_3SbPh_3]_2$ requires Co, 11.9; H, 3.0; C, 50.8; Sb, 24.6%). Infra-red gave peaks at:- $1980_{(sh)}$, $1940_{(s)}$ and $1900_{(sh)}$ cm^{-1}. The mass spectrum of the solid showed no molecular ion peak but some fragmentation peaks were detected; $[Co_2(CO)_4Sb_2]^+$, $^m/e$ 474; $[Co_2(CO)_4Sb]^+$, $^m/e$ 352; $[Co_2(CO)_4]^+$, $^m/e$ 230; $[Co_2(CO)_2]^+$, $^m/e$ 174.

(e) Reaction of triphenyl phosphine with $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ in methanol.

Dicobalt octacarbonyl (0.9 g, 3 mmol) was dissolved in methanol (20 ml) and stirred at room temperature for 4 hours. After this time the characteristic pink solution of the ionic species had formed. Triphenyl phosphine (1.05 g, 4 mmol) was added to the pink solution and the system observed. No visible change was noted as the triphenyl phosphine dissolved in the methanol. After about 1 hour the solution became slightly brown and it appeared that a very fine solid was in suspension in the methanol. The system remained unchanged overnight and so the brown solid was filtered off, dried under vacuum and analysed. The filtrate still contained some brown solid and on warming to ∿ 40°C for 1 hour more brown solid was produced. The faintly brown methanol was syringed from above this solid and the residue was dried under vacuum. This brown solid was also sent for elemental analysis and examined by infra-red spectroscopy. Analysis results gave Co, 20.2; H, 3.5; C, 57.8; P, 7.2%, ($[Co(CO)_3PPh_3]_2$ requires Co, 14.6; H, 3.7; C, 62.2; P, 7.7%). Infra-red analysis of the solid as a nujol mull, in the carbonyl stretching frequency region showed peaks at:- $1960_{(m)}$, $1950_{(m)}$ and $1902_{(w)}$ cm^{-1}. The infra-red analysis agreed with the peaks for the species $[Co(CO)_3PPh_3]_2$ ($1960_{(m)}$, $1950_{(m)}$ and $1900_{(w)}$ cm^{-1}).

(f) Reaction of $PPN^+Co(CO)_4^-$ with triphenyl phosphine in methanol.

A small amount of $PPN^+Co(CO)_4^-$ (0.35 g, 0.5 mmol) was dissolved in methanol (80 ml), triphenyl phosphine (0.13 g, 0.5 mmol) was added to this solution and the system was rapidly stirred. The buff coloured solution of the PPN^+ salt initially became pale yellow on addition of the triphenyl phosphine and then slowly began to go cloudy. The solution was stirred for 2 hours and the cloudiness was seen to be due to a very fine brown solid, suspended in the methanol. The system remained unchanged overnight. It was then warmed to approximately 50°C for 2 hours, but no further change in colour was observed. The brown solid was filtered off and washed with hexane and acetone before drying under vacuum and analysis and infra-red examination. Analysis gave Co, 14.4; H, 3.75; C, 62.6; P, 7.6%, ($[Co(CO)_3PPh_3]_2$ requires Co, 14.6; H, 3.7; C, 62.2; P, 7.7%). The infra-red showed peaks at $1968_{(m)}$, $1944_{(s)}$ and $1897_{(m)}$ cm^{-1}.

The methanol was evaporated down to dryness and a white material was produced. This was washed with hexane to extract any unreacted triphenyl phosphine and the volume of white solid was found to be substantially reduced. The hexane washings were themselves evaporated down and a white solid was produced, believed to be triphenyl phosphine. Analysis gave C, 82.6; H, 6.0; P, 11.6%, (PPh_3 requires C, 82.4; H, 5.7; P, 11.8%). The infra-red also agreed with PPh_3.

The hexane insoluble white solid was found to be soluble in acetone but infra-red showed mainly peaks due to $PPN^+Co(CO)_4^-$, which obscured the spectrum of a second unidentified material.

The reaction was observed using solution infra-red spectroscopy of the carbonyl stretching frequency region. Initially a peak at 1900 cm^{-1} was observed but on addition of the triphenyl phosphine the peak was observed to weaken slowly. This weakening continued as the system was warmed, to a limit where no further reduction in intensity was observed.

(g) Reaction of $PPN^+Co(CO)_4^-$ with triphenyl phosphine in CH_2Cl_2/ methanol.

A solution of $PPN^+Co(CO)_4^-$ (0.71 g, 1 mmol) was made up in 25 ml of dichloromethane and triphenyl phosphine (0.13 g, 0.5 mmol) was added to this light brown solution. No change of colour was noted on the addition or dissolution of the phosphine. The system was allowed to stir rapidly for three hours before any further examination was made. The solution colour was unchanged after this period and so to encourage reaction the solution was warmed to approximately 50°C, but still no change was observed. The system was then allowed to return to room temperature, before the addition of a small amount of methanol (5 ml). The solution was noted to slowly darken and became browner and this darkening continued with further stirring. A very fine red/brown solid deposited from the solution, and as time passed, this continued and the colour of the solution became red/brown. The system was filtered under vacuum to remove the solid which was found to include particles of a white solid. After washing first with hexane and then with acetone, the brown solid was analysed. Found Co, 14.5; H, 3.7; C, 61.9; P, 7.6% ($[Co(CO)_3PPh_3]_2$ requires Co, 14.6; H, 3.7; C, 62.2; P, 7.7%). The infra-red spectrum gave peaks at $1970_{(m)}$, $1944_{(s)}$ and $1898_{(m)}$ cm^{-1}. The hexane washings, on evaporation, produced unreacted triphenyl phosphine. Elemental analysis gave C, 82.1; H, 5.6; P, 11.6% (PPh_3 requires C, 82.4; H, 5.7; P, 11.8%).

The solution infra-red spectrum of the methanol/dichloromethane mixture showed no carbonyl peaks, but showed peaks due to the ion PPN^+.

The reaction was followed as usual by infra-red spectroscopy in the carbonyl stretching region. Initially a strong peak at 1900 cm^{-1} and a weak one at 2018 cm^{-1} were observed both due to the ion $Co(CO)_4^-$. These persisted unchanged through the warming and cooling of the solution. However on adding the small amount of methanol, the peaks both slowly weakened in intensity until neither could be detected at all.

The pH of the system was recorded after the methanol was added to the dichloromethane and gave a value of 7.4. As the brown solid was formed the pH of the system slowly changed to a final value of 10.1.

(h) Reaction of dicobalt octacarbonyl with triphenyl phosphine in dioxan.

Crystals of dicobalt octacarbonyl (1.0 g, 3 mmol) were dissolved in dioxan (50 ml) producing a red/black solution. A solution of triphenyl phosphine (2.1 g, 8 mmol) also in dioxan, was then added slowly to this system over a period of ½ hour with rapid stirring. Gas was evolved steadily as the phosphine solution was added and the red/black colour faded slowly. After an hour had elapsed the system was cooled to 0°C on an ice-bath to encourage deposition of products and this precipitate was filtered off as a light brown solid. This material was washed with petroleum ether (30 - 60^{o}), to remove any excess triphenyl phosphine, before drying under vacuum. Elemental analysis of the light brown solid gave Co, 14.2; H, 3.6; C, 61.8; P, 7.3% ($[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-]$ requires Co, 14.1; H, 3.6; C, 61.6; P, 7.4%) (2.35 g of brown solid were produced, a yield of 90%). The infra-red spectrum as a nujol mull showed carbonyl peaks at $2009_{(m)}$ and $1887_{(s)}$ cm^{-1}.

A small amount of this brown solid (0.8 g) was stirred as a suspension in toluene (40 ml). This mixture was then warmed upon an oil bath to ∿ 60^{o}C for ∿ ½ hour and then allowed to cool to room temperature. The system was then filtered and the brown residue washed with petroleum ether (30 - 60^{o}) before drying under vacuum. Elemental analysis of the solid gave Co, 14.7; H, 3.8; C, 62.2; P, 7.6% ($[Co(CO)_3PPh_3]_2$ requires Co, 14.6; H, 3.7; C, 62.2; P, 7.7%). The carbonyl stretching frequency region showed peaks at $1960_{(sh)}$, $1950_{(s)}$ and $1900_{(m)}$ cm^{-1}. These two phosphine substitution products have similar elemental composition but markedly different infra-red spectra.

4.2.2. Discussion

Several publications have appeared on the reaction of dicobalt octacarbonyl with compounds containing phosphorus, arsenic and antimony, particularly triaryl- and trialkyl phosphines.[53-55] It is now established that, with trialkyl- and triaryl-phosphines ionic compounds are obtained (I) together with covalent substitution products (II):

$$\underset{\text{I}}{[Co(CO)_3(PR_3)_2^+][Co(CO)_4^-]} \qquad \underset{\text{II}}{[Co(CO)_3PR_3]_2}$$

The relative amounts of the ionic compounds and the substitution products may change depending upon the conditions used, especially upon the temperature of the reaction system.[56] At temperatures of approximately

50^oC formation of the substitution products is favoured, and at lower temperatures (∿ 0^oC) formation of the ionic products is favoured.

However the ionic compounds from triphenyl arsine and triphenyl stibine $[Co(CO)_3(AsPh_3)_2^+][Co(CO)_4^-]$ and $[Co(CO)_3(SbPh_3)_2^+][Co(CO)_4^-]$ are very unstable, and at 0^oC the substitution products are formed according to the equation[57] below:

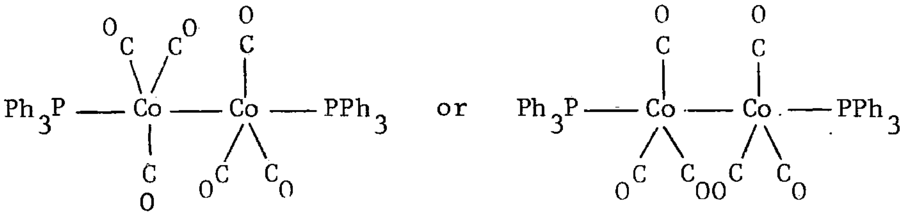
$$[Co(CO)_3(XR_3)_2^+][Co(CO)_4^-] \xrightarrow{\geqslant 0^oC} [Co(CO)_3XR_3]_2 + CO$$

Where X represents P, As or Sb.

However if the reaction of dicobalt octacarbonyl and triphenyl arsine or stibine is performed at a temperature of -5^oC the ionic species is found to be stable[57]:

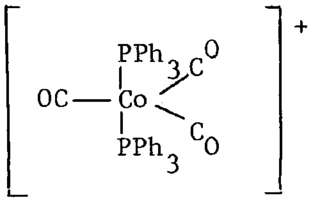
$$Co_2(CO)_8 + 2XR_3 \xrightarrow{< -5^oC} [Co(CO)_3(XR_3)_2^+][Co(CO)_4^-] + CO$$

The infra-red spectra of $[Co(CO)_3PPh_3]_2$ and $[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-]$ have been studied.[42] The substitution product does not show any infra-red stretching mode attributable to bridging carbon monoxide, therefore a structure having a cobalt-cobalt bond is suggested.

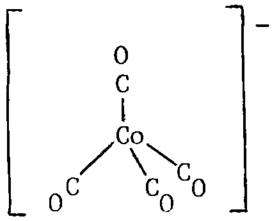


Staggered   Eclipsed

It is not possible to differentiate between the staggered form, of symmetry D_{3d}, and the eclipsed form, of symmetry D_{3h}, on the number of infra-red active CO stretching vibrations, because both forms give rise to the same number, though the staggered forms are normally adopted. For the cation the following axial trans structure has been proposed;



The anion of course has the familiar tetrahedral structure:



Some reports[58,59] have indicated that monosubstituted derivatives of dicobalt octacarbonyl can be formed by direct reaction with triphenyl phosphine, arsine or stibine. These derivatives are usually characterised by a high frequency carbonyl stretching band at $\sim$ 2080 cm^{-1}, in contrast to the simple spectra of the disubstituted derivatives, which characteristically possess a very strong band, usually in the region of 1950 cm^{-1}, accompanied by a weaker band at 1920 cm^{-1}. However the monosubstituted derivative[15] unstable with respect to the disubstituted derivative and dicobalt octacarbonyl:

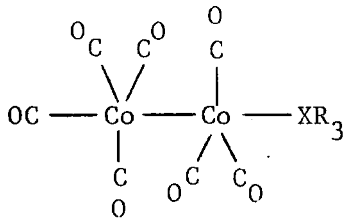
$$2Co_2(CO)_7XPh_3 \longrightarrow Co_2(CO)_8 + Co_2(CO)_6(XPh_3)_2$$

Studies of the formation of these monosubstituted derivatives[60] and their inherent instability, as regards forming the disubstituted derivative and dicobalt octacarbonyl, indicate that they are formed in equilibrium reactions which lead to the disubstituted products:

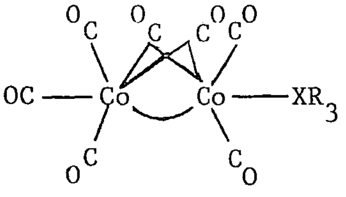
$$Co_2(CO)_8 \underset{-XR_3}{\overset{+XR_3}{\rightleftharpoons}} Co_2(CO)_7XR_3 + CO \underset{-XR_3}{\overset{+XR_3}{\rightleftharpoons}} Co_2(CO)_6(XR_3)_2 + CO$$

and they only exist in solution under a pressure of about one atmosphere of carbon monoxide.

These triphenyl phosphine, arsine or stibine monosubstituted derivatives are generally prepared in hexane solution. Any disubstituted species formed immediately precipitates from the solution due to their very low solubility. The structures of the monosubstituted species have been determined by infra-red study of their hexane solutions, and the results indicate that the triphenyl phosphine species exists predominantly as the unbridged structure (III), whereas the arsine and stibine analogues exist progressively more in the carbonyl bridged form (IV):



III



IV

The disubstituted forms have also been studied in detail by one group of workers,[61,62] and their results show that equilibria exist in solution between the bridged and non-bridged isomers for most of the $[XR_3Co(CO)_3]_2$ systems. However in the solid form the compounds with XR_3 as triphenyl phosphine, arsine or stibine are believed only to exist in the non-bridged form due to their very low solubilities. Studies[63] of the equilibrium between the bridged and non-bridged isomers of $[XR_3Co(CO)_3]_2$ show that in solution formation of the non-bridged form is favoured by higher temperatures, polar solvents, bulky ligands and a higher electron density upon the cobalt.

In general dicobalt octacarbonyl reacts with triphenyl phosphine to form two disubstituted compounds the ionic disubstituted compound, favoured by room or low temperatures and polar solvents, and the true disubstituted covalent compound, favoured by higher temperatures and non-polar solvents.

Dicobalt octacarbonyl reacts with two moles of triphenyl phosphine at $0^{o}C$ or below, in polar solvents, to evolve one mole of carbon monoxide, and form the salt, bis-(triphenyl phosphine)-tricarbonyl cobalt (I) tetracarbonyl cobaltate (-I).

$$Co_2(CO)_8 + 2PPh_3 \longrightarrow [Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-] + CO$$

Studies of the reaction[64] indicate that it takes place via a series of three stages. First the dicobalt octacarbonyl reacts directly with triphenyl phosphine and the complex formed then evolves carbon monoxide in a slower reaction. Finally another molecule of triphenyl phosphine must be added rapidly to form the ionic product:

$$Co_2(CO)_8 + PPh_3 \longrightarrow Co_2(CO)_8.PPh_3$$

$$Co_2(CO)_8PPh_3 \longrightarrow Co_2(CO)_7PPh_3 + CO$$

$$Co_2(CO)_7PPh_3 + PPh_3 \longrightarrow [Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-].$$

The reaction of dicobalt octacarbonyl with triphenyl phosphine in methanol produces a red/brown solid of composition Co, 14.3; H, 3.65; C, 62.0; P, 7.5% intermediate between $[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-]$ and $[Co(CO)_3PPh_3]_2$ which analyse as Co, 14.1; H, 3.6; C, 61.6; P, 7.4% and Co, 14.6; H, 3.7; C, 62.2; P, 7.7% respectively. This result implied that the solid was a mixture of the two species and its solid infra-red spectrum supported this belief. This infra-red spectrum exhibited bands assignable to the known carbonyl stretching frequencies of both species: the salt produced peaks at $2008_{(m)}$ and $1895_{(s)}$ cm^{-1}, and the dimer, peaks at $1960_{(sh)}$, $1945_{(s)}$ and $1900_{(w)}$ cm^{-1}. The solution infra-red analysis only showed peaks due to the salt, presumably because the dimer was insoluble in the methanol.

Further study of the system with ethanol as the solvent showed a very similar reaction and identical solution infra-red spectra. However, in this case, an attempt was made to separate the two products of the reaction. The red/brown product was washed with acetone to extract the salt from the mixture. This separated the soluble from the insoluble red/brown products. The insoluble red/brown solid showed solid infra-red peaks corresponding well with those for $[Co(CO)_3PPh_3]_2$ and its elemental composition also agreed with this assignment. The soluble red/brown solid in acetone solution showed the carbonyl frequencies associated with salt $[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-]$ and gave the appropriate elemental analysis for this formula.

The reaction of triphenyl arsine with dicobalt octacarbonyl in methanol was believed to follow approximately the same course. However the solid infra-red spectrum of the brown solid produced from the reaction showed no strong peak at 1900 cm^{-1} indicating that the $[Co(CO)_4^-]$ ion was probably not present. The carbonyl peaks that did appear at $1965_{(sh)}$, $1945_{(s)}$ and $1900_{(w)}$ cm^{-1} all agreed with those due to $[Co(CO)_3AsPh_3]_2$, as did the elemental analysis of the compound, Co, 13.2; H, 3.4; C, 57.1; As, 16.0%. ($[Co(CO)_3AsPh_3]_2$ requires Co, 13.1; H, 3.3; C, 56.1; As, 16.7%.)

Triphenyl stibine reacted with dicobalt octacarbonyl in methanol in an almost identical fashion. A brown solid was produced which when analysed by infra-red gave carbonyl peaks at $1980_{(sh)}$, $1940_{(s)}$ and $1900_{(sh)}$ cm^{-1}, and when analysed elementally gave Co, 12.0; H, 2.9; C, 50.4; Sb, 25.0%. ($[Co(CO)_3SbPh_3]_2$ requires Co, 11.9; H, 3.0; C, 50.8; Sb, 24.6%.)

At no time in these reactions of triphenyl phosphine, arsine or stibine with dicobalt octacarbonyl in methanol were any peaks observed in solution infra-red spectra that could be assigned to the monosubstituted derivatives $Co_2(CO)_7XPh_3$. This was believed to be a result of the polar solvents examined.

The formation of the covalent dimer only for the ligands triphenyl arsine and stibine was a result of the temperature at which the reaction was carried out. Had the temperature been < 5^oC the ionic species would have been formed, and this would have decomposed by loss of carbon monoxide to the covalent dimer on warming slightly.

The reaction of triphenyl phosphine with dicobalt octacarbonyl in dioxan illustrated this instability of the ionic substitution products at elevated temperatures.[65] Initially the reaction at room temperature produces the salt $[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-]$ as shown by the solid infra-red and elemental composition. This red/brown solid was then suspended in toluene and warmed to ∿ 60^oC. The red/brown product extracted from the toluene had changed both in infra-red spectrum and composition, and this information confirmed that the dimer had indeed been formed.

The reaction of the species $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ in methanol with triphenyl phosphine was studied and the red/brown solid produced was found to give the infra-red spectrum of the dimer, $[Co(CO)_3PPh_3]_2$, but the elemental analysis did not correspond with this species. The elemental analysis showed a much larger cobalt percentage than for $[Co(CO)_3PPh_3]_2$.

The reaction occurred essentially by the oxidation of the cobalt (-I) anion to a zero valent cobalt species:-

$$2[Co(CO)_4]^- + 2PPh_3 \longrightarrow [Co(CO)_3PPh_3]_2 + 2e^- .$$

A reduction must consequently also have taken place in the system and the only available species for reduction were the Co^{2+} ion or the methanol solvent. The Co^{2+} ion was thought more likely to be reduced and this can explain the high proportion of cobalt in the product if metallic cobalt was formed:

$$Co^{2+} + 2e^{-} \longrightarrow Co.$$

The product therefore may have contained Co + $[Co(CO)_3PPh_3]_2$ which requires Co, 20.4; H, 3.5; C, 58.0; P, 7.1%, and these percentages correspond closely to the actual values obtained, Co, 20.2; H, 3.5; C, 57.8; P, 7.2%. The infra-red spectrum thus would be unchanged from that produced by the dimer only, as was found.

The reaction of $PPN^{+}Co(CO)_4^{-}$ with triphenyl phosphine produced a red/brown solid which, from elemental analysis and solid infra-red, was identified as the dimer $[Co(CO)_3PPh_3]_2$. The reaction did not go to completion, as unreacted triphenyl phosphine and $PPN^{+}Co(CO)_4^{-}$ were extracted from the system during isolation of products. Unfortunately these materials obscured a possible second product of the reaction.

The reaction consisted essentially of the oxidation of a cobalt anion (-I) to a zero valent cobalt species:-

$$2Co(CO)_4^{-} + 2PPh_3 \longrightarrow [Co(CO)_3PPh_3]_2 + 2e^{-}$$

Consequently, a reduction must also have taken place within the system, and the only species available for reduction were the PPN^{+} ion and the methanol solvent. The PPN^{+} ion was regarded as an unlikely candidate for reduction as it is a very stable species, so the methanol was considered as the more likely.

The reaction was attempted in solution in dichloromethane, using excess of triphenyl phosphine, but was found not to take place until some methanol had been added. This implied that the methanol was an essential component in the reaction and hence was probably the species being reduced. The most likely way for reduction of methanol to occur is by the following equation:

$$MeOH + e^- \longrightarrow MeO^- + \tfrac{1}{2}H_2.$$

This implied that the full reaction proceeded thus:-

$$2PPN^+Co(CO)_4^- + 2PPh_3 + 2MeOH \longrightarrow [Co(CO)_3PPh_3]_2 + 2PPN^+OMe^- + H_2.$$

No evolved gas was noted but the quantity concerned would have been relatively small. The evidence to support the formation of the methoxide ion rests upon the large change in pH in the course of the reaction due to the basicity of the methoxide ion.

4.3. High Pressure Study of the Cobalt/Methanol/Ligand System

4.3.1. Experimental

The basic experimental details are very similar to those described in chapter 3. The study was performed in the same high pressure infra-red cell, and the analysis of products was routinely completed by G.L.C. The physical conditions used were varied in order to find their effect upon the reaction. The ligand included in the system was generally placed in the bomb together with the cobalt acetate tetrahydrate, and then methanol (18 ml) was added to the system. The bomb was purged with nitrogen before pressurising with 1:1, CO/H_2 synthesis gas to a pressure of approximately 140 Atm, and stirred as quickly as possible. The temperature was raised to the selected level (between 180 - 220°C) and the gas pressure would rise to about 200 Atm. The reaction was then allowed to run for 8 hours while the pressure was maintained at 200 Atm. When the run was complete the system was allowed to cool overnight and the bomb was depressurised slowly the next day. The liquid and solid samples were syringed from the bomb and analysed.

The results of varying some of the reaction parameters of the ligand stabilised homologation of methanol are discussed with reference to the yield and selectivity of some products.

Catalyst.

The catalyst used in these experiments consisted of cobalt acetate tetrahydrate (as in chapter 3) plus a stabilising ligand. The stabilising ligand consisted of a phosphine species PR_3 (R = alkyl, aryl), an arsine species AsR_3 or a stibine species SbR_3 (R = aryl).

4.3.2. Discussion

(a) Effect of temperature upon the cobalt/methanol/phosphine system (Table 4.1.).

The first general result of the ligand stabilised reaction which was noted, was that the addition of the ligand virtually stopped the reaction: the ligand, in this case triphenyl phosphine, caused the percentage molar yields of the four major products to fall to below 1%. However on the positive side, the addition of the phosphine appeared to substantially increase the selectivity to ethanol, mainly at the expense of formation of acetates. The most suitable temperature for running this very inefficient reaction was about 205°C (Fig. 4.1.). This showed that one of the reasons for adding phosphine ligands to the system was upheld, i.e. they had succeeded in stabilising the reaction catalyst to a higher temperature, without requiring a corresponding pressure increase. Throughout the temperature range studied (180 - 210°C) the selectivity to ethanol was improved compared with the unstabilised reaction, but the yields were conversely

Table 4.1.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	PPh_3 (moles)	Reaction Time (hr.)	Temperature (^oC)	Pressure (Atm)	Ratio Co:Ligand	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
5	0.56	7×10^{-3}	-	8	185	200	1:1	Yield	9.5	6.8	1.9	0.4
								Selectivity	34.0	21.3	6.6	2.0
28	0.56	7×10^{-3}	7×10^{-3}	8	180	200	1:1	Yield	0.075	0.03	-	-
								Selectivity	42.7	17.1	-	-
29	0.56	7×10^{-3}	7×10^{-3}	8	185	200	1:1	Yield	0.14	0.05	-	-
								Selectivity	43.8	15.0	-	-
30	0.56	7×10^{-3}	7×10^{-3}	8	190	200	1:1	Yield	0.45	0.16	-	-
								Selectivity	44.7	15.9	-	-
31	0.56	7×10^{-3}	7×10^{-3}	8	195	200	1:1	Yield	0.61	0.3	0.06	-
								Selectivity	45.1	14.8	2.9	-
32	0.56	7×10^{-3}	7×10^{-3}	8	200	200	1:1	Yield	0.84	0.38	0.1	-
								Selectivity	46.4	22.1	5.8	-
33	0.56	7×10^{-3}	7×10^{-3}	8	205	200	1:1	Yield	0.88	0.4	0.11	0.05
								Selectivity	45.0	20.4	5.6	2.5
34	0.56	7×10^{-3}	7×10^{-3}	8	210	200	1:1	Yield	0.73	0.34	-	-
								Selectivity	41.0	19.0	-	-

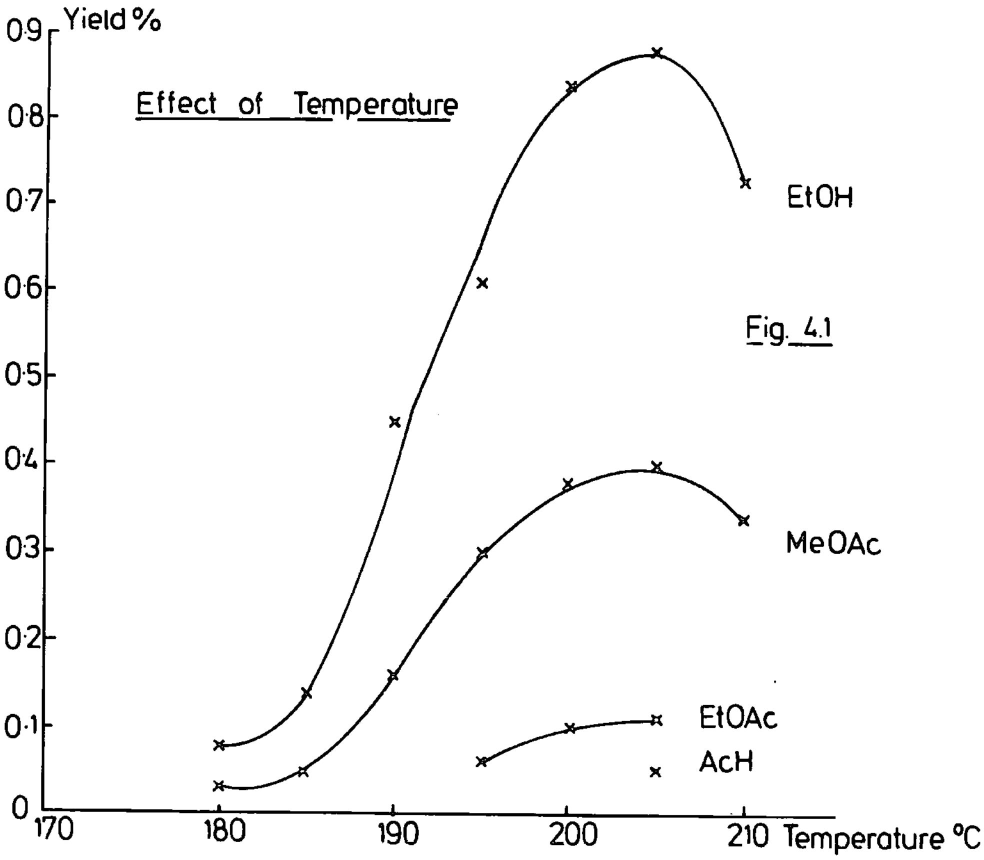

Yield %
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Effect of Temperature
EtOH
MeOAc
EtOAc
AcH
170
180
190
200
210
Temperature °C

Fig. 4.1

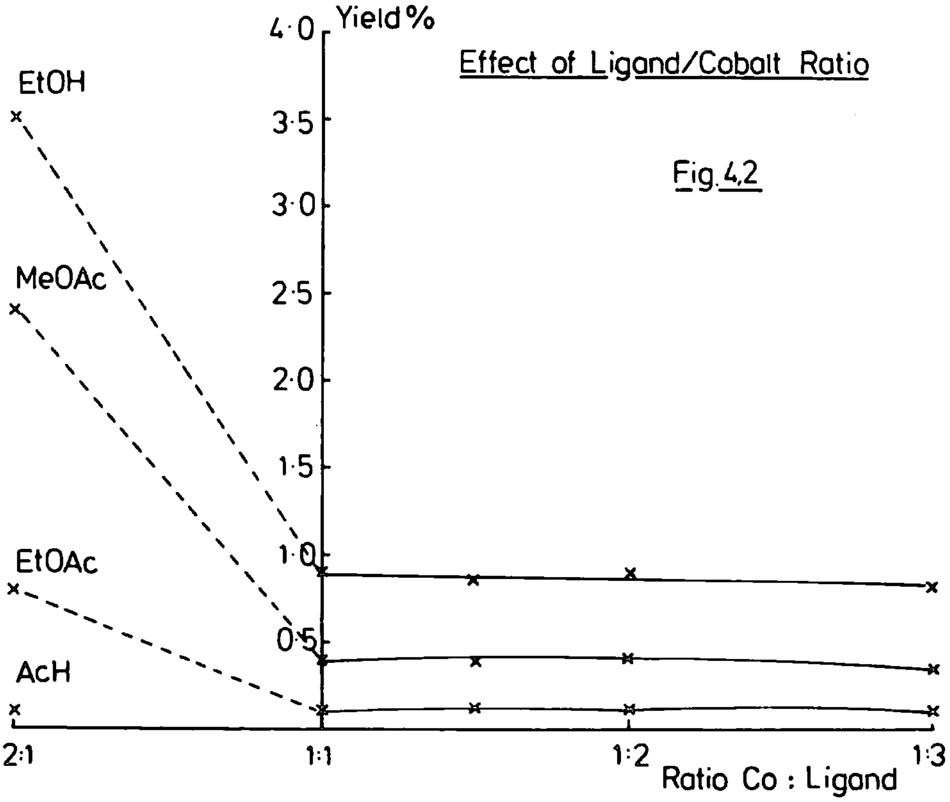

Yield %
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Effect of Ligand/Cobalt Ratio
EtOH
MeOAc
EtOAc
AcH
2:1
1:1
1:2
1:3
Ratio Co : Ligand

Fig. 4.2

much lower (Fig. 4.1.). It was found to be difficult to obtain accurate results due to the very small changes in concentration.

On opening the bombs at the end of each run the products were syringed out, and with them was extracted a red/brown solid. After filtering the mixture, the solid was dried under vacuum before being sent for elemental analysis: Co, 14.6; H, 3.6; C, 62.1; P, 7.6%. (These results correspond well with those of the dimer $[Co(CO)_3PPh_3]_2$ Co, 14.6; H, 3.7; C, 62.2; P, 7.7%.) The infra-red spectrum of the solid was run as a nujol mull or a KBr disc and shows carbonyl peaks at $1920_{(m)}$, $1950_{(s)}$ and $1900_{(w)}$ cm^{-1}.

(b) The effect of the ligand/cobalt ratio for the methanol/cobalt/ ligand system (Table 4.2.).

The study was performed with triphenyl phosphine as the ligand, and at 205^o to obtain the largest yields possible. The reaction was studied to discover the most favourable phosphine/cobalt ratio for production of ethanol. It was clearly seen from the results obtained (Fig. 4.2.) that for ratios of ligand/cobalt of unity and greater, the products were formed in approximately the same yield and selectivities. No clear effect due to the phosphine concentration could be observed. However reduction of the same ratio below unity caused the yield and selectivities to increase markedly so that they closely resembled those due to the simple unstabilised cobalt/methanol system (Table 3.2.).

These observations were explained as follows:- the lack of change in product spectrum at high ligand/cobalt ratio (i.e. $\geqslant 1$) implied that the quantity of phosphine present was not significant, provided that there was sufficient to form the relevant catalytic species. The unused remainder of the phosphine would take no part in the reaction and remain

Table 4.2.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	PPh_3 (moles)	Reaction Time (hr.)	Temperature (^oC)	Pressure (Atm)	Ratio Co:Ligand	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
35	0.56	7×10^{-3}	3.5×10^{-3}	8	205	200	2:1	Yield	3.5	2.4	0.8	0.1
								Selectivity	24.0	19.4	6.5	1.0
36	0.56	7×10^{-3}	21×10^{-3}	8	205	200	1:3	Yield	0.80	0.35	0.1	-
								Selectivity	42.7	18.9	4.8	-
37	0.56	7×10^{-3}	14×10^{-3}	8	205	200	1:2	Yield	0.9	0.41	0.12	0.03
								Selectivity	4.5	20.5	6.0	1.5
38	0.56	7×10^{-3}	10.5×10^{-3}	8	205	200	2:3	Yield	0.85	0.37	0.10	0.04
								Selectivity	46.1	20.1	5.4	2.1
33	0.56	7×10^{-3}	7×10^{-3}	8	205	200	1:1	Yield	0.88	0.4	0.11	0.05
								Selectivity	45.0	20.4	5.6	2.5

unchanged either in solution or as a solid at the bottom of the reaction vessel. The change in yields and selectivities when the ligand/cobalt ratio falls below unity was believed to occur due to presence of unstabilised cobalt catalyst. The phosphine present stabilised a fraction of the cobalt and this reacted, producing low yields of the products as before, but these relatively small quantities were effectively swamped by the conversion of much more methanol by the unstabilised portion of the catalyst, which behaved as reported in the preceding chapter.

When the experiments were concluded and the bomb opened, the mixture was syringed out and filtered to remove any solid present. The solids obtained were washed well with hexane or pentane and dried under vacuum. All the solids obtained were red/brown and all showed approximately the same elemental composition and infra-red spectra (Co, 14.5; H, 3.8; C, 62.4; P, 7.6%, carbonyl stretching peaks at $1970_{(wsh)}$, $1950_{(s)}$ and $1900_{(w)}$ cm^{-1}). These correspond well with the dimer $[Co(CO)_3PPh_3]_2$, Co, 14.6; H, 3.7; C, 62.2; P, 7.7%; infra-red carbonyl peaks at $1970_{(w)}$, $1950_{(s)}$ and $1900_{(w)}$ cm^{-1}.

The hexane or pentane washings were themselves evaporated, and for experiments with ligand/cobalt ratio > 1, a white solid was produced C, 81.9; H, 5.8; P, 11.9% believed to be PPh_3. (PPh_3 requires C, 82.4; H, 5.7; P, 11.8%.)

Therefore the effect of the ligand/cobalt ratio seemed to show that to stabilise all the cobalt present, a ratio of unity was required, and increasing this ratio further seemed to have no great influence upon the homologation. Thus it appeared that the 1:1 correspondence of cobalt to ligand was a significant ratio in this particular, albeit inefficient, homologation catalyst formulation.

(c) Effect of ligand type upon the cobalt/methanol/ligand system (Table 4.3.).

The homologation of methanol was investigated by using a series of different ligands to assess their influence upon the reaction system.

The use of different phosphine ligands seemed to cause very little change in the reaction (Table 4.3.). Possibly the tricyclohexyl phosphine was not as effective as the tri-n-butyl and triphenyl phosphines, but these discrepancies can be explained on experimental differences alone. The most interesting result of changing the ligands was the effect of replacing the phosphine ligand by one containing arsenic or antimony. In these cases the yield of ethanol was greatly reduced, and the major product of the reaction was found to be acetaldehyde. There seemed to be no particular difference between the behaviour of the arsine or the stibine ligands themselves. The formation of acetaldehyde, rather than ethanol, implies that the reduction of acetaldehyde to ethanol was hindered by the arsenic (or antimony) ligand on the cobalt. This hindrance could take the form of electronic effects or be due to steric reasons.

When the bomb was opened the mixture was syringed out and the solid filtered off, and washed with hexane. The phosphine experiments generated the species $[Co(CO)_3PR_3]_2$:

	Obtained Analyses	Calculated Analyses
R=Ph	Co, 14.7; H, 3.8; C, 62.4; P, 7.6%	Co, 14.6; H, 3.7; C, 62.2; P, 7.7%
R=n-C_4H_9	Co, 17.1; H, 7.7; C, 52.4; P, 9.1%	Co, 17.1; H, 7.8; C, 52.2; P, 9.0%
R=C_6H_{11}	Co, 13.7; H, 7.9; C, 59.4; P, 7.5%	Co, 13.9; H, 7.8; C, 59.6; P, 7.3%

The arsine and stibine experiments also produced similar products believed to be $[Co(CO)_3AsPh_3]_2$ and $[Co(CO)_3SbPh_3]_2$:

Table 4.3.

Ligand Type	Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	Ligand (moles)	Reaction Time (hr.)	Pressure (Atm)	Temp. (^oC)	Ratio Co:Ligand	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
PPh_3	33	0.56	7×10^{-3}	7×10^{-3}	8	200	205	1:1	Yield	0.88	0.4	0.11	0.05
									Selectivity	45.0	20.4	5.6	2.5
$P(C_6H_{11})_3$	39	0.56	7×10^{-3}	7×10^{-3}	8	200	205	1:1	Yield	0.80	0.39	0.1	-
									Selectivity	40.4	18.7	5.0	-
$P(C_4H_9)_3$	40	0.56	7×10^{-3}	7×10^{-3}	8	200	205	1:1	Yield	0.86	0.4	0.11	-
									Selectivity	43.7	19.5	5.3	-
$AsPh_3$	42	0.56	7×10^{-3}	7×10^{-3}	8	200	205	1:1	Yield	0.19	0.95	0.1	0.36
									Selectivity	7.6	38.2	3.0	14.6
$SbPh_3$	43	0.56	7×10^{-3}	7×10^{-3}	8	200	205	1:1	Yield	0.15	0.91	0.11	0.36
									Selectivity	5.6	35.0	4.2	13.9

Obtained Analyses	Calculated Analyses
Co, 13.0; H, 3.3; C, 56.0; As, 16.8%	Co, 13.1; H, 3.3; C, 56.1; As, 16.7%
Co, 12.1; H, 2.9; C, 60.0; Sb, 24.8%	Co, 11.9; H, 3.0; C, 60.8; Sb, 24.6%

4.4. High Pressure Infra-Red Study of the Cobalt/Methanol/Ligand System

4.4.1. Experimental

The reactions were all performed in the same cells used for the autoclave studies, but the infra-red facility was utilised to follow the course of the reaction. It was found possible in these high pressure infra-red studies to examine the systems for a much greater period of time, as the reactions were all relatively inefficient and the spectra produced were not masked by product absorptions. It was therefore possible to observe the systems for periods of about 4 hours at reaction temperature without interference bands forming in the spectra of the catalytic species under investigation .

The materials added to the cell, dicobalt octacarbonyl, ligand and methanol, were inserted in a particular order. The ligand was first dissolved/suspended in the methanol and this solution/suspension was syringed into the bomb. The bomb was then flushed with nitrogen before addition of the dicobalt octacarbonyl as a solid. The bomb was flushed once again with nitrogen, sealed and pressurised to the level selected with the appropriate gas or gas mixture.

The infra-red spectra were recorded regularly as the temperature was raised from room temperature in increments of approximately 30°C to the final selected reaction temperature; at each interval, time was allowed for the system to reach equilibrium before the spectra were recorded.

Once the system had been examined at the final reaction temperature, it was allowed to cool slowly to room temperature before the gas pressure above the system was released. The infra-red spectra were again taken at room temperature before depressurising the bomb, and once the gas had been released a standard infra-red solution spectrum of the extracted liquid was run. The solution was also examined by chromatographic methods to check that the reaction products were at a tolerable level.

4.4.2. Discussion

(a) Study of the system under nitrogen pressure only.

A series of reactions were studied with a pressure of nitrogen only above the systems. The pressure of nitrogen above the system appeared to have no detectable effect upon the reaction.

Dicobalt octacarbonyl and triphenyl phosphine in methanol were reacted under nitrogen pressure and the peaks generated by the reaction were observed with increase in temperature. The only peaks observed were at $2000_{(m)}$ and $1900_{(s)}$ cm^{-1} and could be assigned to the species $[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-]$. With increase in temperature both of these peaks were found to reduce in intensity. When the spectrum was examined at 100°C, the peaks were found to have disappeared, and they did not reappear on further heating. The bomb was cooled and opened and a red/brown solid was found to have deposited. The red/brown solid was washed with hexane and dried before elemental and solid infra-red analysis. These gave Co, 14.7; H, 3.8; C, 62.1; P, 7.6%, ($[Co(CO)_3PPh_3]_2$ requires Co, 14.6; H, 3.7; C, 62.2; P, 7.7%): carbonyl peaks at $1970_{(sh)}$, $1950_{(s)}$ and $1900_{(w)}$ cm^{-1}. These analyses showed it to be the dimer $[Co(CO)_3PPh_3]_2$.

The reaction between dicobalt octacarbonyl and triphenyl arsine (or triphenyl stibine) was also examined under the same conditions. The only peaks observed were at about the same positions in the infra-red spectra i.e. $1995_{(w)}$ and $1900_{(m)}$ cm^{-1}, but these absorptions did not even persist above 30°C. No new peaks appeared on heating the system. In the case of both the antimony and arsenic ligands, a brown solid was extracted from the bomb. These solids were analysed elementally and by solid infrared and were found to be $[Co(CO)_3AsPh_3]_2$ and $[Co(CO)_3SbPh_3]_2$. Infra-red analysis showed carbonyl stretching peaks at $1970_{(sh)}$, $1942_{(s)}$, $1900_{(sh)}$ cm^{-1}. Elemental analysis gave Co, 13.0; H, 3.2; C, 56.0; As, 16.8% and Co, 11.9; H, 3.1; C, 51.0; Sb, 24.4%. ($[Co(CO)_3AsPh_3]_2$ and $[Co(CO)_3SbPh_3]_2$ require Co, 13.1; H, 3.3; C, 56.1; As, 16.7% and Co, 11.9; H, 3.0; C, 50.8; Sb, 24.6% respectively.)

This study showed that under even high pressure (100 Atm) of nitrogen, the reaction follows the same pattern as the bench work discussed earlier. The triphenyl phosphine ligand was able to react with dicobalt octacarbonyl to form the ionic substitution product as before, and this salt was again found to decompose by loss of carbon monoxide to form the covalent dimer on warming. The triphenyl arsine and stibine ligands reacted first to form the salt but these were not stable and soon decomposed to form the insoluble covalent dimer as shown by the rapid disappearance of the peaks at 1995 and 1900 cm^{-1} even at 30°C. The pressure of nitrogen seemed to have no influence upon the system whatsoever.

(b) Study of the system under carbon monoxide pressure

A series of reactions were performed under carbon monoxide pressure of ∿ 100 Atm and investigated to reveal the species present at reaction temperature.

Dicobalt octacarbonyl was reacted with triphenyl phosphine in methanol under carbon monoxide pressure. The reaction initially produced peaks due to the salt $[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-]$ at 2000 and 1900 cm^{-1} at 30°C. As the temperature was increased the intensity of the bands reduced slightly but they still remained fairly strong. At temperatures around 160°C further weak carbonyl peaks appear at $2050_{(w)}$, $1980_{(w)}$, $1970_{(w)}$ and $1690_{(w)}$ cm^{-1}. These can be assigned to the acyl species $Me\overset{O}{\overset{\|}{C}}Co(CO)_3PPh_3$.[66] These new carbonyl peaks persist to 185°C but do not become particularly strong. When the system was allowed to cool to room temperature the peaks were found to remain. However on releasing the pressure the peaks due to the salt were found to rapidly disappear, and on extracting the mixture most of the cobalt was found to be in the form of $[Co(CO)_3PPh_3]_2$.[67]

The same study was performed with triphenyl arsine (or triphenyl stibine) as the ligand. Under high carbon monoxide pressure the peaks of the salt (at 1995 and 1900 cm^{-1}) were found to persist to the reaction temperature (185°C), instead of decomposing to the dimer and precipitating from the solution. The peaks due to this salt at 185°C however were much weaker than those with triphenyl phosphine ligand. This was believed to be due to the fact that most of the cobalt-ligand complex exist as the insoluble dimers.

Other peaks can be observed at this temperature (185°C) at $2050_{(w)}$ $1980_{(w)}$, $1970_{(w)}$ and $1690_{(w)}$ cm^{-1} but these too are substantially weaker than those produced with the phosphine ligand. On cooling all the peaks persist to 30°C, but on releasing the carbon monoxide pressure the peaks due to the salt disappear.

(c) Study of the system under synthesis gas mixture.

A series of reaction were studied under a synthesis gas pressure of 200 Atm (100 Atm H_2, 100 Atm CO) using dicobalt octacarbonyl with triphenyl phosphine (or arsine or stibine) in methanol.

A very similar result was observed with the synthesis gas as was found with the pressure of carbon monoxide only. Initially only the salt,

$[Co(CO)_3(XR_3)_2^+][Co(CO)_4^-]$, was formed as shown by the peaks at 2000 and 1900 cm^{-1}. On warming the systems all produced peaks at approximately 2050, 1980, 1960 and 1690 cm^{-1} believed to be due to the species $Me\overset{\overset{O}{\|}}{C}Co(CO)_3L$. The peaks due to this species were much stronger for the phosphine ligand than for those produced from the arsine or stibine ligand.

The only difference observed in the systems, which could be attributed to the presence of hydrogen, was a weak peak at ∿ 1970 cm^{-1}.[68] This peak was regarded as being caused by species of the type $HCo(CO)_3L$. This species normally has carbonyl stretching peaks at about $2050_{(mw)}$, $1970_{(vs)}$ and $1935_{(w)}$ cm^{-1}, and under these conditions, these weak peaks probably were too small to be seen and were masked by nearby absorptions.

All the carbonyl absorptions persist when the system was allowed to return to room temperature but on releasing the pressure, those due to the salt disappeared.

CHAPTER FIVE

AN EXAMINATION OF THE IODIDE PROMOTED COBALT/METHANOL REACTION SYSTEM

5.1. Introduction

This chapter is concerned with the influence of ionic or alkyl iodides on the cobalt catalysed homologation of methanol. The ionic and alkyl iodides have been suggested as promoters for this reaction by several authors, and halides have been proposed as useful additives for many other homogeneously catalysed reactions.[69-71] A promoter is a compound which is, in itself, not a catalyst for the reaction in question, but serves to enhance the effect of the catalyst utilised.

Iodides are believed to improve both the selectivity and yields of the major products of the reaction but accurate measurements are sparse.[72] Several possible reaction schemes have been proposed for the involvement of the iodide ion, and an objective of this work relates to the reasons for increased efficiency of the reaction when performed in the presence of the iodides.

5.2. Low Pressure Study of the Dicobalt Octacarbonyl/Iodide/Methanol Reaction

5.2.1. Experimental

(a) Reaction of $PPN^+Co(CO)_4^-$ with methyl iodide in dichloromethane at -40°C.

A small amount of $PPN^+Co(CO)_4^-$ (0.35 g, 0.5 mmol) was dissolved in dichloromethane (50 ml) and the solution cooled to -40°C in an acetone/dry ice bath. This solution was rapidly stirred as a solution of methyl iodide (1 g, 7 mmol) in dichloromethane (20 ml) was added slowly. The initial yellow solution slowly became pale red/brown, then dark brown over a period of 1 hour. The solution remained unchanged over a further 4 hour period. Cooled hexane (20 ml) at -40°C was added to the system to extract any hydrocarbon-soluble products. The system was stirred rapidly for ½ hour and then the yellow/brown hexane layer was separated from the dichloromethane layer. The hexane was evaporated off "in vacuo" at room temperature in an attempt to obtain a solid product. However, it was found that decomposition of any products formed had occurred, and only a grey/black deposit was obtained, probably cobalt metal.

The reaction was studied throughout by solution infra-red using a specially cooled infra-red cell, to prevent any decomposition of the reaction products. The infra-red spectrum of the original solution showed only two peaks in the carbonyl stretching frequency region; at $2015_{(w)}$, $1900_{(s)}$ cm^{-1}. Both of these can be assigned to the ion $Co(CO)_4^-$. On addition of the methyl iodide solution the spectra changed rapidly. The peak at 2015 cm^{-1} disappeared, the peak at 1900 cm^{-1} weakened rapidly and new peaks appeared at 2105, 2035 and 2020 cm^{-1}. Within 15 minutes the peaks due to $Co(CO)_4^-$ had completely disappeared and the only ones remaining were at $2105_{(w)}$, $2035_{(m,w)}$ and $2020_{(s)}$ cm^{-1}. After the system was extracted with hexane these peaks were found in both the hexane and the dichloromethane layers, though they were stronger in the hexane layer. These three peaks can be assigned to the species $Me\,Co(CO)_4$, ($2104_{(w)}$, $2035_{(m)}$ and $2018_{(s)}$ cm^{-1} [66,73]).

(b) Reaction of $Na^+Co(CO)_4^-$ with methyl iodide in THF at -40°C.

An amalgam of sodium and mercury was prepared by reacting sodium metal directly with liquid mercury under nitrogen atmosphere.[74] The cleanest portion of this freshly prepared amalgam was taken and reacted with dicobalt octacarbonyl (0.3 g, 1 mmol) in solution in THF (50 ml). The system was stirred for about 2 hours, until the THF was colourless.[40] Then this solution of $Na^+Co(CO)_4^-$ in THF was cooled to -40°C in an acetone/dry ice bath. A solution of methyl iodide (1 g, 7 mmol) also in THF (20 ml) was slowly added to the rapidly stirred, cooled solution. The THF slowly began to take on a brown colouration and this darkened as the methyl iodide was added. This system remained unchanged for 2 hours. The amalgam was run off from the flask and the THF solution was stirred with hexane (20 ml) to extract any non-polar species. The hexane layer was syringed off and pumped on at room temperature to encourage crystallisation; but decomposition of the material occurred.

Infra-red analysis in the carbonyl region of the system initially showed only those peaks due to dicobalt octacarbonyl: $2073_{(s)}$, $2046_{(s)}$, $2029_{(s)}$, $1866_{(m)}$ and $1858_{(m)}$ cm^{-1}. As the reaction with the amalgam took place the peaks due to dicobalt octacarbonyl slowly reduced in strength and were eventually replaced by a single peak at $1900_{(m)}$ cm^{-1}, due to $Co(CO)_4^-$. On the addition of the methyl iodide solution to the system, the spectra followed the same pattern described for the reaction using the $PPN^+Co(CO)_4^-$ salt. The species $MeCo(CO)_4$ was generated (peaks at $2105_{(w)}$, $2035_{(m)}$, $2020_{(s)}$ cm^{-1}) from the ion $Co(CO)_4^-$. This alkyl cobalt species was extracted mostly into the hexane layer but was found to decompose on evaporation of the solvent.

(c) Reaction of $PPN^+Co(CO)_4^-$ with methyl iodide in dichloromethane at room temperature.

A small amount of $PPN^+Co(CO)_4^-$ (0.7 g, 1 mmol) was dissolved in dichloromethane (50 ml) and the system was stirred rapidly. A solution of methyl iodide (1 g, 7 mmol) also in dichloromethane (20 ml) was slowly added to the $PPN^+Co(CO)_4^-$ solution. The yellow solution of $PPN^+Co(CO)_4^-$ slowly became brown as the methyl iodide was added. Within about 1 hour, the brown colour was found to have changed to a greeny brown colour. The solution was rapidly stirred and hexane (20 ml) was added to extract any non-polar species from the dichloromethane. The hexane layer became brown as well as the dichloromethane layer. Evaporation of the hexane layer only resulted in decomposition of the species.

Infra-red study of the carbonyl stretching frequency region showed that initially peaks at 2014$_{(w)}$ and 1900$_{(s)}$ cm^{-1} were present. As the methyl iodide was added to the system the spectra rapidly changed and these peaks weakened very quickly. Several new peaks were also seen to appear within 10 minutes of the addition. After 10 minutes the spectrum showed peaks at 2110$_{(w)}$, 2050$_{(m\ w)}$, 2030$_{(m)}$, 2010$_{(m)}$, 1955$_{(w)}$, 1935$_{(w)}$, 1895$_{(m)}$ and 1710$_{(w)}$ cm^{-1}. After a further 10 minutes the spectrum showed peaks at 2110$_{(w)}$, 2050$_{(m\ w)}$, 2030$_{(m)}$, 2010$_{(m)}$, 1955$_{(vw)}$, 1935$_{(vw)}$ and 1710$_{(w)}$ cm^{-1}. The two peaks at 1955 and 1935 cm^{-1} slowly disappeared within 40 minutes but the other five peaks remained unchanged and persisted throughout the experiment. These five peaks could not be assigned to the species $CH_3Co(CO)_4$ and so a new product must have formed from this reaction at room temperature. A study of possible products from these starting materials, revealed that the compound $CH_3\overset{\overset{O}{\|}}{C}Co(CO)_4$ had carbonyl stretching frequencies at 2107$_{(w)}$, 2048$_{(m)}$, 2026$_{(m)}$, 2007$_{(s)}$ and 1715$_{(m)}$ cm^{-1}.[66] These appeared to fit the peaks obtained very well and so the species formed in this reaction was believed to be the acyl species $CH_3\overset{\overset{O}{\|}}{C}Co(CO)_4$.

(d) Reaction of $PPN^+Co(CO)_4^-$ with methyl iodide in methanol at room temperature.

Crystals of $PPN^+Co(CO)_4^-$ (0.2 g, 0.3 mmol) were dissolved in methanol (50 ml) and the buff coloured solution formed was stirred rapidly. A solution of methyl iodide (1 g, 7 mmol) in methanol (20 ml) was slowly added to the system. The colour of the solution remained unchanged after addition of the methyl iodide. Hexane (20 ml) was added to the system in an attempt to extract any non-polar species present, but no change in the hexane layer was observed.

Infra-red study of the system showed only one peak due to carbonyl stretching at $1900_{(m)}$ cm^{-1}, which was assigned to $Co(CO)_4^-$. When the methyl iodide solution was added to the system the peak at 1900 cm^{-1} was seen to weaken rapidly, and disappear completely within 10 minutes. No other peaks were observed to form. The hexane layer was examined by infra-red and showed two weak peaks at 2030 and 2010 cm^{-1}. These two peaks were again believed to be due to the acyl species $CH_3\overset{\overset{O}{\|}}{C}Co(CO)_4$. The other three peaks which should also have been present were thought to be too weak to be detected due to the low concentration of the acyl species.

(e) Reaction of $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ with methyl iodide in methanol at -40°C.

Dicobalt octacarbonyl (0.3 g, 1 mmol) was dissolved in methanol (40 ml) and stirred for about 3 hours, until the pink solution due to $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ had been formed. This solution was then cooled to -40°C in an acetone/dry ice bath, and a solution of methyl iodide in methanol was slowly added. Then hexane (20 ml) was syringed into the system to extract any hydrocarbon-soluble materials and allowed to slowly warm to room temperature.

Infra-red examination of the carbonyl stretching frequency region of the spectrum in a cooled cell initially showed two peaks at $2018_{(w)}$ and $1900_{(vs)}$ cm^{-1} due to $Co(CO)_4^-$. When the methyl iodide was added these two peaks rapidly shrank and new peaks appeared at $2105_{(w)}$ and $2020_{(m)}$ cm^{-1}. After 20 minutes the peaks at 2018 and 1900 cm^{-1} had completely disappeared and the only peaks observable in the methanol were at $2105_{(w)}$ and $2020_{(m)}$ cm^{-1}. The hexane layer was examined at this stage and this showed peaks at $2105_{(w)}$, $2035_{(m)}$ and $2020_{(s)}$ cm^{-1} believed to be due to

$CH_3Co(CO)_4$. These peaks persisted as long as the solution was kept cool but rapidly weakened when the system was allowed to warm to room temperature. New peaks appeared at $2110_{(w)}$, $2050_{(w)}$, $2030_{(m)}$, $2007_{(m)}$, $1955_{(w)}$, $1935_{(w)}$ and $1710_{(w)}$ cm^{-1} but not all of these persisted. Eventually the peaks due to $CH_3Co(CO)_4$ disappeared and were replaced by peaks at $2110_{(w)}$, $2050_{(m)}$, $2030_{(m)}$, $2007_{(s)}$ and $1710_{(w)}$ cm^{-1}, which could all be assigned to $CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4$.

(f) Reaction of dicobalt octacarbonyl with methyl iodide in methanol.

A small amount of dicobalt octacarbonyl (0.3 g, 1 mmol) was added to methanol (30 ml) and allowed to dissolve to form the red/black solution. However the solution was not permitted enough time for much of the $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ species to form before addition of methyl iodide (0.3 g, 2 mmol). The mixture was then stirred rapidly and the colour slowly changed from red/black to a brown coloured solution. The brown solution remained unchanged for several hours. The system was evaporated "in vacuo" and a black deposit formed. Analysis gave Co, 30.4; I, 70.4%. ["CoI" requires Co, 31.7; I, 68.3%]. The black solid was dissolved in methanol, filtered and the solution evaporated to form a black solid. [Co, 19.1; I, 81.9%; CoI_2 requires Co, 18.8; I, 81.2%].

Infra-red observations of the carbonyl stretching frequency region of the spectrum provided some useful information. Initially several carbonyl peaks could be seen at $2075_{(m)}$, $2030_{(m)}$, $1900_{(m)}$ and $1860_{(m)}$ cm^{-1}. On addition of methyl iodide these peaks were observed to change and shift rapidly within 5 minutes to peaks at $2106_{(m)}$, $2025_{(m)}$, $2007_{(m)}$, $1955_{(m)}$, $1940_{(m)}$ and $1720_{(w)}$ cm^{-1}. Most of these peaks persisted throughout the rest of the solution experiment, except for those at $1955_{(m)}$ and

$1940_{(m)}$ cm^{-1} which slowly weakened and disappeared. The loss of these two absorptions meant that the only peaks left were at $2106_{(m)}$, $2025_{(m)}$, $2007_{(m)}$ and $1720_{(w)}$ cm^{-1} which correspond approximately to those attributed to the species $CH_3\overset{O}{\|}{C}Co(CO)_4$. Unfortunately the peaks in the region of 2040 cm^{-1} were very difficult to observe due to a methanol absorption.

(g) Reaction of dicobalt octacarbonyl with methyl iodide in hexane.

Orange crystals of dicobalt octacarbonyl (0.6 g, 2 mmol) were dissolved in 50 ml of hexane and the solution was gently stirred. A solution of methyl iodide was prepared, also in hexane (20 ml), and half of this was added to the dicobalt octacarbonyl solution. The solution colour did not appear to change on addition of the methyl iodide. The remainder of the methyl iodide solution was therefore syringed into the system and the reaction left stirring for several hours. The solution again appeared unchanged in colour but now small black particles were seen to be suspended in the system. The dark red/black hexane solvent was evaporated down and the black residue produced dried under vacuum. A dark grey solid was produced on drying. Analysis of the solid gave Co, 25.9; C, 7.9; I, 55.7% [CoI_2 requires Co, 18.8; I, 81.2%]. The solid was washed with methanol and formed a brown solution with a dark grey insoluble deposit. The brown solution was evaporated down and a black solid deposited. Analysis gave Co, 19.1; I, 80.4% [CoI_2 requires Co, 18.8; I, 81.2%]. The insoluble grey deposit was examined by infra-red as a nujol mull and showed peaks at $2067_{(m)}$, $2058_{(m)}$, $2040_{(w)}$, $2030_{(w)}$ and $1855_{(m)}$ cm^{-1} consistent with $Co_4(CO)_{12}$. [Found Co, 42.4; C, 24.8%, $Co_4(CO)_{12}$ requires Co, 41.3; C, 25.2%].

The carbonyl stretching frequency region of the infra-red spectrum of the system was studied throughout the reaction. Initially, before addition of the methyl iodide solution all that was observed were the peaks due to dicobalt octacarbonyl, $2073_{(s)}$, $2046_{(s)}$, $2029_{(s)}$, $1866_{(m)}$ and $1858_{(m)}$ cm^{-1}. As the methyl iodide was added the bridging carbonyl peaks were seen to reduce rapidly in intensity and new peaks appeared in the region of the terminal carbonyl stretching frequencies, at $2107_{(w)}$, $2007_{(s)}$ and $1720_{(w)}$ cm^{-1}. These peaks are believed to be due to $CH_3\overset{\overset{O}{\|}}{C}Co(CO)_4$ and the two other peaks expected for the acyl species at $2050_{(m)}$ and $2025_{(m)}$ cm^{-1} are masked by the terminal carbonyl stretching bands of dicobalt octacarbonyl. The peaks due to the acyl species persisted for several hours but eventually disappeared. More methyl iodide was added and the peaks due to dicobalt octacarbonyl were further reduced and again $CH_3\overset{\overset{O}{\|}}{C}Co(CO)_4$ was formed and persisted for some hours. The spectrum of dicobalt octacarbonyl was found to have disappeared, but new peaks had appeared in the bridging and terminal-carbonyl stretching frequency regions. These peaks were found at $2067_{(s)}$, $2058_{(s)}$, $2040_{(w)}$, $2030_{(w)}$ and $1865_{(s)}$ cm^{-1} and corresponded to those of $Co_4(CO)_{12}$.[56]

(h) Reaction of $Co(CO)_4^-$ and dicobalt octacarbonyl with sodium iodide in methanol.

(i) A solution of $PPN^+Co(CO)_4^-$ (0.3 g, 0.4 mmol) in methanol (50 ml) was stirred with sodium iodide (0.1 g, 0.6 mmol).

(ii) A solution of dicobalt octacarbonyl (0.6 g, 2 mmol) in methanol (50 ml) was stirred for about three hours. Sodium iodide (0.5 g, 3 mmol) was added to the resulting pink solution of $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ and the mixture rapidly stirred.

(iii) A solution of sodium iodide (0.5 g, 3 mmol) in methanol (50 ml) was prepared, dicobalt octacarbonyl (0.3 g, 1 mmol) was added and the system stirred rapidly. The red/black colour of dicobalt octacarbonyl in methanol was observed initially and this converted over a period of ∿ 2 hours to a pink solution.

The colour of systems i and ii remained unchanged upon the addition of sodium iodide. No evolution of gas from the system was noted nor was any formation of suspension or precipitate observed, even on warming to ∿ 50°C.

Infra-red examination of the carbonyl stretching frequency region was performed on these two systems. Both solutions showed only peaks due to $Co(CO)_4^-$ which remained unchanged throughout the experiment.

Infra-red study of system iii showed initially bands due to the bridging and terminal carbonyl groups of dicobalt octacarbonyl. These absorptions rapidly disappeared and two new peaks at $2018_{(w)}$ and $1900_{(s)}$ cm^{-1} were observed. These were assigned to the species $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$, and remained unchanged for the duration of the experiment.

Thus the presence of the iodide seems to have no effect upon the systems except possibly to increase the rate of formation of the ionic species $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ from dicobalt octacarbonyl.

5.2.2. Discussion

Research in recent years has led to the synthesis of many stable compounds containing alkyl groups σ-bonded to transition metals. In general these new compounds contained, in addition to the alkyl group, a cyclopentadienyl ring and/or carbon monoxide as substituents, which were regarded as the factor stabilising the metal-alkyl bond.

Alkyl and acyl metal carbonyls are in general volatile substances that are usually solid at room temperature. Care is necessary, however, in subliming acyl derivatives if high purity is required since decarbonylation can occur to some extent.

Although many transition metal alkyl- and acyl-compounds are very stable to oxidation and are reasonably thermally stable, the corresponding cobalt compounds show much lower stabilities and are usually only stable at temperatures below 0°C. Few alkyl- and acyl-cobalt tetracarbonyls have been isolated in a pure state; in many cases they have been converted into the more stable tricarbonyl triphenylphosphine derivatives and isolated as such.

The thermal stability of the cobalt compounds can also be increased by substituting perfluoro groups for the acyl- and alkyl-groups. Thus, although $Me\overset{O}{\overset{\|}{C}}Co(CO)_4$ starts to decompose at -20°C and decarbonylates to $CH_3Co(CO)_4$ at even lower temperatures, the corresponding perfluoro derivative, $CF_3Co(CO)_4$ is a reasonably stable liquid at room temperature, in an inert atmosphere. The thermal stability of perfluoro alkyl or acyl cobalt tetracarbonyls has been attributed to the inductive effect of the fluorine atoms, which withdraw negative charge from the cobalt atom.[94-96]

Pure alkyl and acyl cobalt tetracarbonyls are yellow to red, low-melting compounds which are soluble in most organic solvents. They react with some hydroxylic solvents, but not with ethers or hydrocarbons. The alkyl and acyl cobalt tetracarbonyls generally decompose well below 0°C. Methyl cobalt tetracarbonyl decomposes at -35°C,[75] and acetyl cobalt tetracarbonyl at -20°C. The decomposition of these compounds appears to be a second-order (or perhaps higher) process because the materials are much more stable in the vapourphase or in dilute solutions than they are in the pure state. The acyl cobalt tetracarbonyls are relatively stable in 0.1 M solution, even at room temperature; complete decomposition requires many hours or even days at these concentrations. The presence of an atmosphere of carbon monoxide also helps to stabilise the acyl cobalt tetracarbonyls. The alkyl cobalt tetracarbonyls are rapidly converted by a carbon monoxide atmosphere into the acyl cobalt tetracarbonyls. This equilibrium reaction is far on the side of the acyl derivative even at pressures of carbon monoxide below one atmosphere. The alkyl cobalt tetracarbonyls decompose rapidly even in dilute solution at 0°C.[93]

All reactions involving alkyl- or acyl -cobalt tetracarbonyls must be carried out in the absence of air, as the compounds are oxidised quite rapidly to cobalt oxides by oxygen.

The reaction of ionic salts of cobalt hydrocarbonyl with alkyl halides, alkyl sulphonates, dialkyl sulphates or other alkylating agents is one of the established methods for formation of the alkyl cobalt tetracarbonyl. If the above reaction is carried out under an atmosphere of carbon monoxide the acyl species is formed.

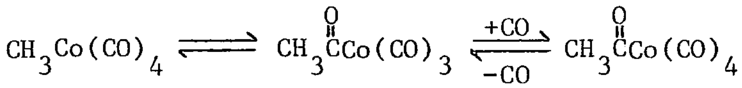
The reaction of both $PPN^+Co(CO)_4^-$ and $Na^+Co(CO)_4^-$ with methyl iodide followed this particular outline and at -40°C it was possible to observe the carbonyl bands of the methyl cobalt tetracarbonyl species clearly. The use of the $PPN^+Co(CO)_4^-$ salt however was far more convenient than the corresponding sodium salt as it did not have to be generated afresh before reaction. There appeared to be no difference in the carbonyl peaks of the products except that the $PPN^+Co(CO)_4^-$ produced much clearer spectra. Both reactions produced peaks at $2105_{(w)}$, $2035_{(m\ w)}$ and $2020_{(s)}$ cm^{-1} and these were assigned to the species $CH_3Co(CO)_4$ (peaks at $2104_{(w)}$, $2035_{(m)}$ and $2018_{(s)}$ cm^{-1} [66]). The alkyl species decomposed as the solvent was removed in an attempt to isolate it. The reaction follows the scheme:

$$M^+Co(CO)_4^- + MeI \longrightarrow M^+I^- + MeCo(CO)_4$$

Where $M = PPN^+$ or Na^+.

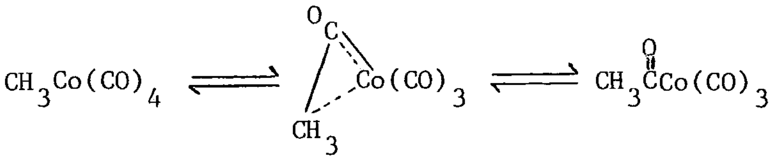
At room temperature the reaction of $PPN^+Co(CO)_4^-$ with methyl iodide follows a modified course as the initial product $CH_3Co(CO)_4$ in unstable at room temperature. Hence no infra-red peaks due to this species were observed in the spectra. However, some of the peaks observed in the spectra, those at $2110_{(w)}$, $2050_{(m\ w)}$, $2030_{(m)}$, $2010_{(m)}$ and $1710_{(w)}$ cm^{-1} were assigned to the acyl compound $CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4$ (peaks at $2107_{(w)}$, $2048_{(m)}$, $2026_{(m)}$, $2007_{(s)}$ and $1715_{(m)}$ cm^{-1}). The carbon monoxide necessary for forming this compound must be generated by the decomposition of some methyl cobalt tetracarbonyl. This is possible as room temperature is far above its decomposition temperature of $-35^{o}C$. The remaining methyl cobalt tetracarbonyl then consumed this free carbon monoxide in forming the acyl species.

The alkyl cobalt tetracarbonyls are believed to be in rapid equilibrium with acyl cobalt tricarbonyls as an intermediate in the formation of the acyl cobalt tetracarbonyls:[76]

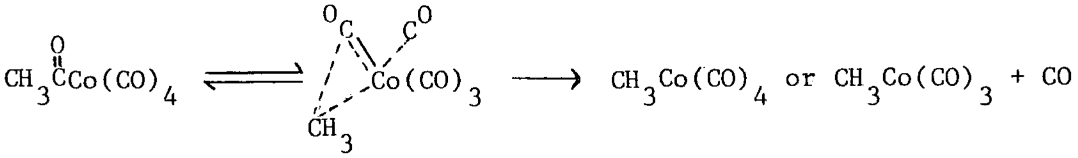


$$CH_3Co(CO)_4 \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}Co(CO)_3 \underset{-CO}{\overset{+CO}{\rightleftharpoons}} CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4$$

A transition state therefore must exist where the methyl group is partially bound to both the CO and the metal.[77,78]



It is also quite possible that a similar transition state with another carbon monoxide partially bonded to the cobalt is formed when acyl cobalt tetracarbonyls dissociate.



The reaction in methanol at room temperature was found to be very difficult to observe as the relative insolubility of $PPN^+Co(CO)_4^-$ meant that only low concentrations of products were obtained. Thus only the two strongest peaks of the acyl species were detectable, though the reaction is believed to take the same course.

The results obtained for $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ in methanol agree with those discussed earlier. At -40°C the species present in solution was the alkyl cobalt tetracarbonyl. On warming the peaks from the alkyl species weakened and were replaced by peaks due to the acyl species. Again temporary peaks were noted at 1955 and 1935 cm^{-1} but these could not be positively assigned.

Dicobalt octacarbonyl reacts with methyl iodide in methanol at room temperature and immediately produces strong absorptions due to the $CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4$ species. Elemental analysis of the solid produced on evaporation of the methanol gave Co, 30.4; I, 70.4% which corresponds to Co:I, 1:1. Recrystallisation of the solid from methanol gave CoI_2. This implied that methyl iodide reacted with dicobalt octacarbonyl to form acyl cobalt tetracarbonyl and evaporation down of the solution formed a mixture of metallic cobalt and cobalt (II) iodide. As equal molar quantities of cobalt and iodine atoms were consumed the ratio of dicobalt octacarbonyl reacting with methyl iodide appears to be 1:2. The acyl cobalt tetracarbonyl species was formed from the corresponding alkyl species by insertion of carbon monoxide. Therefore the reaction probably follows a scheme similar to this:-

$$Co_2(CO)_8 + MeI \longrightarrow MeCo(CO)_4 + ICo(CO)_4$$

$$2ICo(CO)_4 + 2MeI \longrightarrow 2MeCo(CO)_4 + 2I_2 \longrightarrow C_2H_6 + 2CoI_2 + 8CO$$

$$MeCo(CO)_4 + CO \longrightarrow Me\overset{O}{\overset{\|}{C}}Co(CO)_4$$

The reaction of methyl iodide with dicobalt octacarbonyl in hexane appears to follow a different course. The products isolated on evaporation of the system were found to be $Co_4(CO)_{12}$ and CoI_2. Acyl cobalt tetracarbonyl was produced during the reaction and appears to have decomposed to form the tetracobalt dodecacarbonyl found in the final solid product. This illustrates a difference between the reaction of methyl iodide with dicobalt octacarbonyl in the two solvents hexane and methanol. The reaction in the hexane solvent is believed to occur as outlined below:-

$$Co_2(CO)_8 + MeI \longrightarrow MeCo(CO)_4 + ICo(CO)_4$$

$$2ICo(CO)_4 + 2MeI \longrightarrow 2CoI_2 + C_2H_6 + 8CO$$

$$4MeCo(CO)_4 + 4CO \longrightarrow 4Me\overset{O}{\overset{\|}{C}}Co(CO)_4 \longrightarrow Co_4(CO)_{12} + 2C_2H_6 + 8CO$$

However no conclusive evidence was obtained for the evolution of ethane from the reaction.

A mixture of cobalt tetracarbonylate anion and iodide ion appears not to react at all. The studies of systems involving salts of the tetracarbonyl cobaltate showed no change in the infra-red solution spectra and no change in colour of the solution was noted. The studies were performed over relatively long periods of time but still no changes were observed.

The reaction of dicobalt octacarbonyl with methanol appears to be unaffected by the presence of iodide ions in solution in methanol. The dicobalt octacarbonyl slowly reacts with the methanol to form the $Co(MeOH)_6^{2+}$ and $Co(CO)_4^-$ species, as shown by the infra-red solution spectra. The only change that can be attributed to the iodide ion is that the time required for the formation of the cobalt ionic species is reduced.[79] It is possible that the iodide ion acts as a catalyst for the reaction of dicobalt octacarbonyl with methanol to form $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$.

5.3. High Pressure Study of the Cobalt/Methanol/Iodide System

5.3.1. Experimental

The basic experimental details are again very similar to those described in Chapter 3. The study was performed in the same high pressure infra-red cells, and the analysis of products was routinely performed by G.L.C. The physical conditions used were varied in order to find their influence upon the course of the reaction. The solid iodides used in the reactions were each placed in the bomb together with the cobalt acetate tetrahydrate, and then methanol was added to the mixture. (When methyl iodide was involved in the study this was mixed with the methanol before addition to the cobalt acetate tetrahydrate, already in the bomb.) The bomb was then purged with nitrogen before pressurising with 1:1 CO/H_2 synthesis gas to a pressure of $\sim$ 140 Atm, and stirred as quickly as possible. The temperature was raised to the selected level (180 - 220°C) which caused the gas pressure to rise to about 200 Atm. The reaction was allowed to run for 2 hours while the pressure was maintained at 200 Atm. When the run was completed the system was allowed to cool overnight to room temperature and the bomb was depressurised slowly the next day. The resultant products were syringed from the bomb and analysed.

The results of varying some of the reaction parameters of the iodide promoted homologation of methanol are discussed with reference to the yield and selectivity of some important products.

5.3.2. Discussion

(a) Effect of different iodides upon the cobalt/methanol/iodide system.

The results of this study are collected in Table 5.1. The first observation is that the iodide promoted system is in general more efficient than the standard cobalt/methanol system. The yields of the four major products (see Table 5.1 , exp. 2) are substantially increased, especially that of the acetate formation.

The alkali and alkaline earth metal iodides examined showed remarkable similarity, producing virtually the same product ratios and selectivities. The counter cations appear to have no detectable influence upon the course of the reaction.

Other iodides studied produced different quantities of the various products. Cobalt (II) iodide was found to be a relatively poor catalyst, producing a reduced yield of ethanol though the yields of the acetates were found to be unchanged. Thus this shows that cobalt (II) iodide is less effective as a catalyst than, for example, a mixture of cobalt acetate and sodium iodide. This can be rationalised if the ratio of iodide to cobalt is an important factor in determining reaction products. The experiment employing cobalt (II) iodide as a catalyst had intrinsically twice the iodide: cobalt ratio than the other experiments, (Table 5.1 , exp. 51). This was confirmed by studies using cobalt (II) acetate and potassium iodide in various ratios, (Table 5.2).

Iron (II) iodide was used as a promoter with cobalt acetate in the reaction but the yields of all the products were reduced. The presence of the iron in the system has the effect of suppressing the reaction throughout the product spectrum.

Methyl iodide has been recommended as a promoter for the homologation reaction by several authors.[27,28] However the study undertaken here shows it to be less effective than alkali metal iodides. With methyl iodide the yield and selectivity of the by-products, the acetates and acetaldehyde, is unchanged in comparison with the alkali metal iodide promoted systems,

Table 5.1.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	Reaction Time (hr.)	Temperature (^oC)	Pressure (Atm)	Iodide conc. (moles)	Iodide Type	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
44	0.56	7×10^{-3}	2	185	200	7×10^{-3}	LiI	Yield	8.3	7.8	2.0	1.9
								Selectivity	29.9	28.1	7.2	7.0
45	0.56	7×10^{-3}	2	185	200	7×10^{-3}	NaI	Yield	8.5	8.4	2.2	2.1
								Selectivity	32.7	32.3	8.5	8.1
46	0.56	7×10^{-3}	2	185	200	7×10^{-3}	KI	Yield	9.2	7.9	2.0	1.9
								Selectivity	33.8	29.0	7.3	7.0
47	0.56	7×10^{-3}	2	185	200	7×10^{-3}	CsI	Yield	8.7	8.5	1.8	2.3
								Selectivity	34.5	33.7	7.1	9.1
48	0.56	7×10^{-3}	2	185	200	7×10^{-3}	CaI_2	Yield	8.2	8.0	1.9	2.0
								Selectivity	32.6	31.7	7.5	7.9
49	0.56	7×10^{-3}	2	185	200	7×10^{-3}	FeI_2	Yield	3.2	3.0	0.8	0.7
								Selectivity	30.4	28.5	7.6	6.7
50	0.56	7×10^{-3}	2	185	200	7×10^{-3}	MeI	Yield	7.9	8.1	1.8	1.0
								Selectivity	28.2	31.9	7.1	3.9
51	0.56		2	185	200	14×10^{-3}	CoI_2	Yield	4.6	7.6	2.0	1.7
								Selectivity	18.0	29.6	7.8	6.8
2	0.56	7×10^{-3}	2	185	200	-	-	Yield	4.5	2.8	0.1	0.3
								Selectivity	30.2	25.2	0.5	2.0

but the yield and selectivity of ethanol is reduced. However the methyl iodide promoted system still produces a catalyst which is more effective at generating ethanol than the unpromoted reaction.

(b) Effect of iodide concentration upon the cobalt/methanol/iodide system.

The effect of iodide concentration is recorded in Table 5.2. The iodide concentration is varied in the ratio range 1:3 - 3:1, iodide to cobalt, by addition of potassium iodide to the reaction (the potassium ion has no effect on the reaction). The results are illustrated graphically in Fig. 5.1 and Fig. 5.2 in terms of percentage yield and selectivity.

The best ratio of cobalt to iodide for producing ethanol can clearly be seen to be approximately 2:1. In fact any ratio above 1:1 would appear to be a useful combination for generating ethanol with the least quantity of by-products. The yields of the by-products acetaldehyde and ethyl acetate increase steadily as the iodide concentration increases. The yield of methyl acetate follows approximately the same pattern, but at the highest concentrations of iodide the yield is found to decrease, as the overall conversion of methanol also decreases. Ethanol shows the reverse relationship with the cobalt iodide ratio. At higher concentrations of iodide the yield of ethanol is greatly reduced and this agrees with results obtained in Table 5.1 , exp. 51, for cobalt (II) iodide. At cobalt/iodide ratios of 3:1 - 1:1 the yield and selectivity to ethanol is maximised and reaches its highest value at 2:1. This value will give the best ethanol yield and selectivity for the iodide promoted system and will also give relatively low yields of the by-products.

Further investigation of higher iodide or cobalt concentrations has not been performed as the overall conversion of methanol was decreasing at

Table 5.2.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	Reaction Time (hr.)	Temperature (^oC)	Pressure (Atm)	Iodide conc. (moles)	Ratio (moles) $CoAc_2 4H_2O:KI$	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
52	0.56	7×10^{-3}	2	185	200	14×10^{-3}	1:2	Yield	4.2	7.8	2.1	1.8
								Selectivity	16.4	30.4	8.0	7.0
53	0.56	7×10^{-3}	2	185	200	21×10^{-3}	1:3	Yield	3.4	6.4	3.0	2.1
								Selectivity	16.5	31.1	14.6	10.2
54	0.56	7×10^{-3}	2	185	200	3.5×10^{-3}	2:1	Yield	10.3	7.5	1.9	1.4
								Selectivity	36.0	26.3	6.7	4.9
55	0.56	7×10^{-3}	2	185	200	2.3×10^{-3}	3:1	Yield	8.7	6.0	1.7	0.8
								Selectivity	33.4	23.0	6.5	3.1
46	0.56	7×10^{-3}	2	185	200	7.0×10^{-3}	1:1	Yield	9.2	7.9	2.0	1.9
								Selectivity	33.8	29.0	7.3	7.0

Effect of Iodide concentration

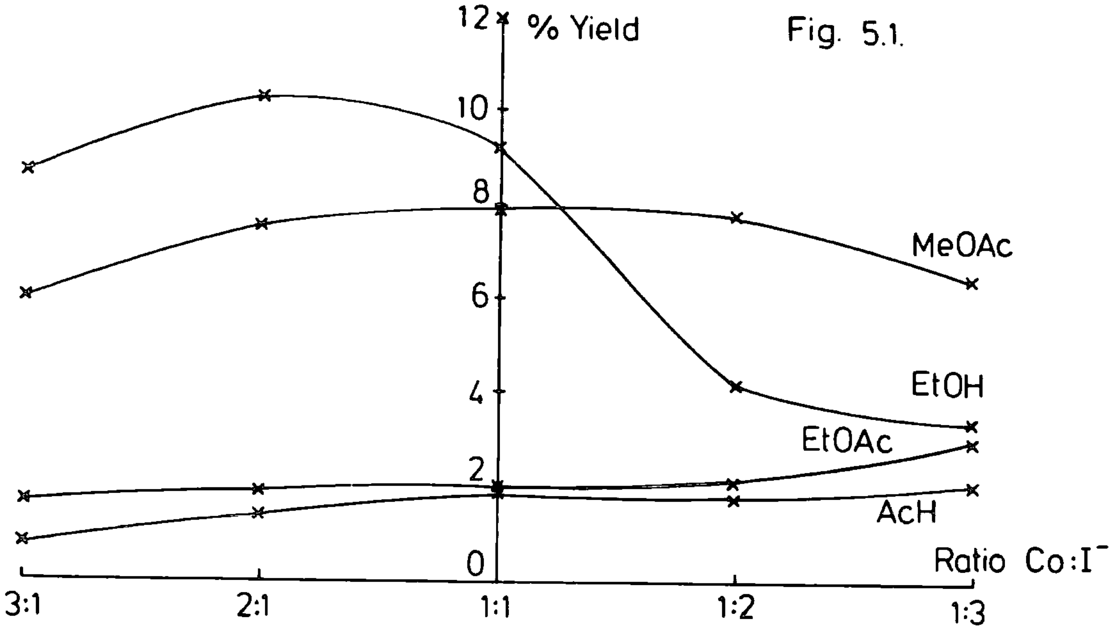


Fig. 5.1.

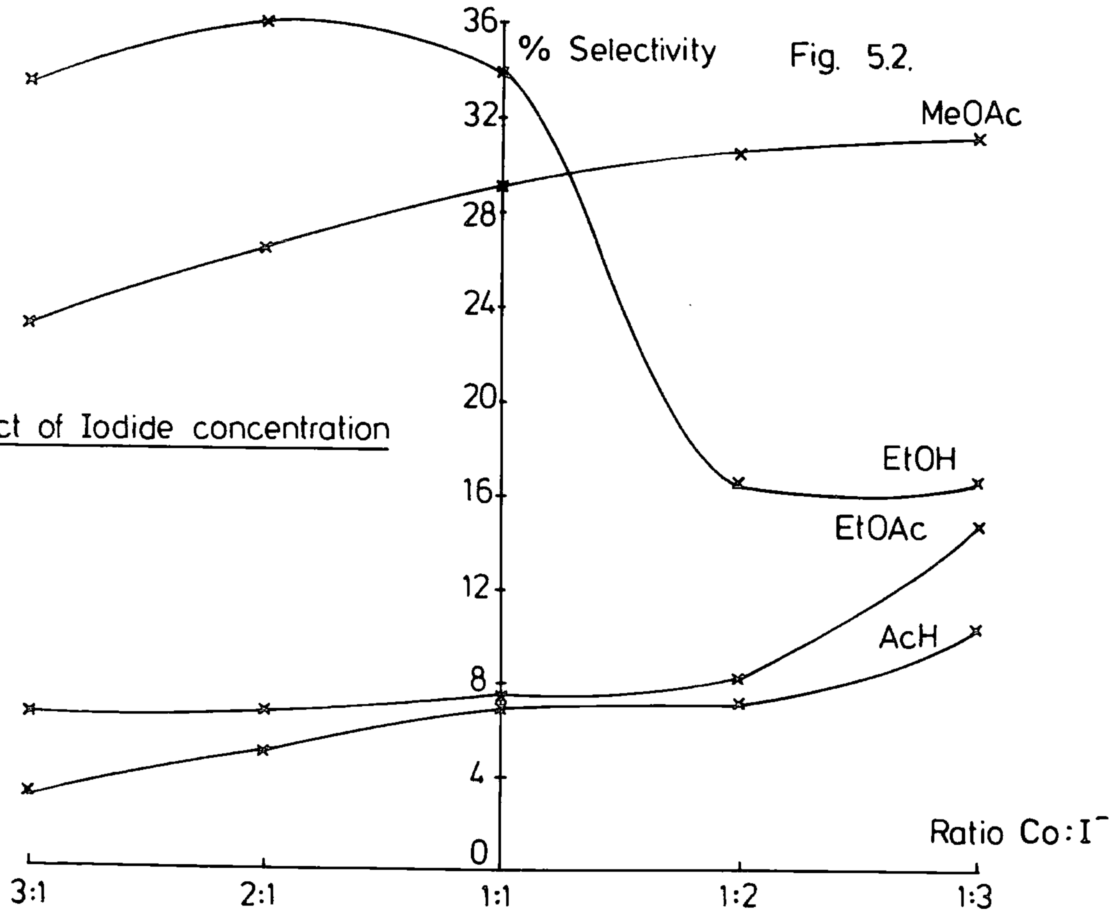


Fig. 5.2.

Effect of Iodide concentration

the extreme values examined and this trend was thought likely to continue.

(c) Effect of temperature on the cobalt/methanol/iodide system.

The system has been examined in the temperature range 165 - 220°C and the results are presented in Table 5.3. The study has been done at a 1:1 cobalt/iodide ratio again using potassium iodide as the iodide source. The percentage yields and selectivities are illustrated graphically in Fig. 5.3 and Fig. 5.4. The yield of ethanol passed through a maximum at 185°C of ∿ 9%, falling sharply to 3% at 220°C. The decrease in yield of ethanol was accompanied by a decrease in yield of all the major products and in the conversion of methanol itself. At higher reaction temperatures (200 - 220°C) a black deposit was found on the walls of the bomb which was believed to be cobalt metal. Thus it seems likely that the lower conversion of methanol at higher temperatures is due to loss of active catalyst by the plating out of cobalt metal, due to the thermal instability of the catalyst.

At lower temperatures (165 - 175°C) the yields of all the products after 2 hours were found to be reduced compared with 185°C. This can be regarded as due to the reaction being slower at these reduced temperatures, or because only a fraction of the cobalt has been converted into active catalyst. This iodide promoted reaction seems to have the same stringent temperature limitations as the unpromoted system. The temperature must be held within the range 175 - 190°C to maximise the production of ethanol and to minimise the thermal degradation of the catalyst.

The selectivities do not vary much throughout the temperature range studied and closely follow the same patterns as yields of the major products.

Table 5.3.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	Reaction Time (hr.)	Pressure (Atm)	Iodide conc. (moles)	Iodide Type	Temperature (^oC)	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
46	0.56	7×10^{-3}	2	200	7×10^{-3}	KI	185	Yield	9.2	7.9	2.0	1.9
								Selectivity	33.8	29.0	7.3	7.0
56	0.56	7×10^{-3}	2	200	7×10^{-3}	KI	165	Yield	5.1	4.3	0.9	2.1
								Selectivity	27.5	23.2	4.8	11.3
57	0.56	7×10^{-3}	2	200	7×10^{-3}	KI	175	Yield	8.1	6.8	1.6	2.0
								Selectivity	32.0	26.9	6.3	7.9
58	0.56	7×10^{-3}	2	200	7×10^{-3}	KI	200	Yield	5.0	4.2	1.9	1.3
								Selectivity	28.8	24.2	10.9	7.5
59	0.56	7×10^{-3}	2	200	7×10^{-3}	KI	220	Yield	3.2	2.7	1.4	0.5
								Selectivity	28.0	23.6	11.9	4.0

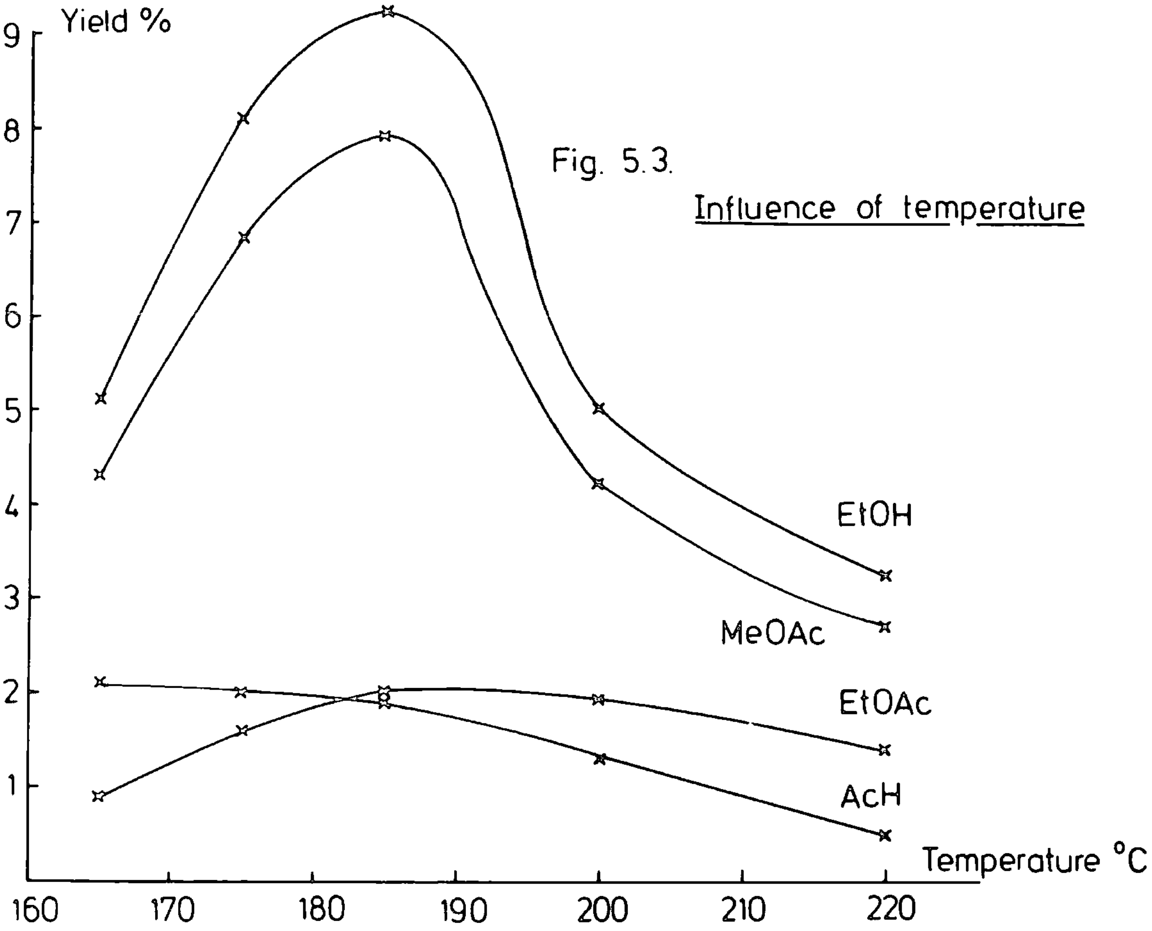


Fig. 5.3.

Influence of temperature

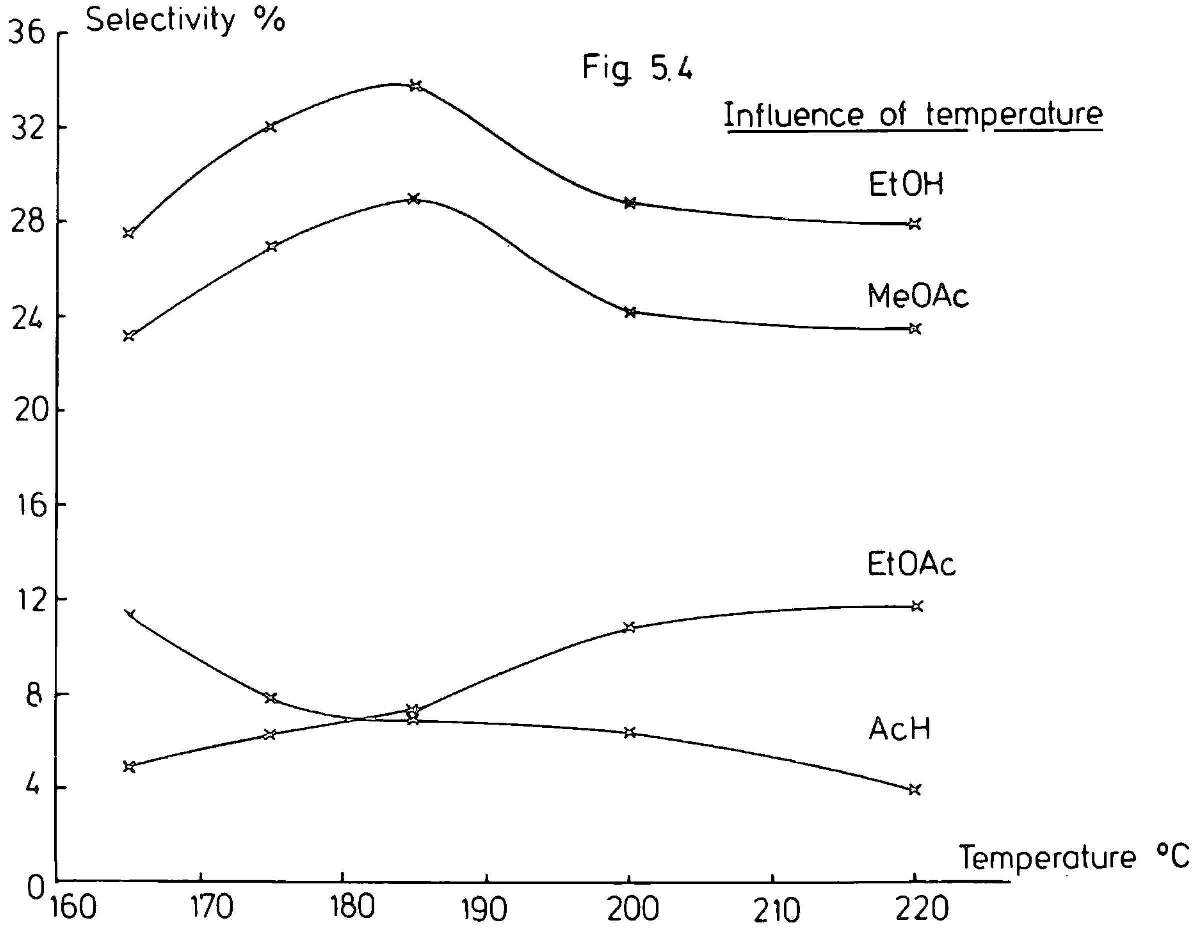


Fig. 5.4

Influence of temperature

5.4. High Pressure Infra-Red Study of the Cobalt/Methanol/Iodide System.

5.4.1. Experimental

These high pressure studies were all performed in the same cells as those used for the product distribution studies but the infra-red facility was utilised to follow the course of the reactions and to identify any intermediate species. It was found that the reaction was reasonably efficient, when promoted by iodide. The infra-red spectrum of the solution quickly became complicated by strong absorptions due to the many organic products. Unfortunately these absorptions were found to obscure and mask those due to the intermediate catalytic species. Therefore it was found to be essential to record infra-red spectra, at the maximum temperature, as quickly as possible before the absorptions due to the organic products became too intense and interfered with the spectra of the catalysts being investigated.

The materials added to the cell, dicobalt octacarbonyl, iodide and methanol, were inserted in a particular order. The iodide was first dissolved in or mixed with the methanol and this solution/mixture was syringed into the bomb. The bomb was then flushed with nitrogen before the addition of the dicobalt octacarbonyl as a solid. The bomb was then flushed once again with nitrogen, sealed and pressurised to the level selected with the appropriate gas or gas mixture.

The infra-red spectra were recorded regularly as the temperature was raised, from an initial temperature of $\sim 20^{\circ}C$, in increments of $\sim 50^{\circ}C$ to the final required reaction temperature; at each interval time (15 minutes) was allowed for the system to reach equilibrium before the spectra were recorded.

Once the examination of the system at the maximum temperature had been completed, the bomb was allowed to cool slowly to room temperature overnight, before the gas pressure was released. Once the bombs were opened a sample of the liquid was removed and examined by infra-red and G.L.C. methods to determine the organic reaction products and assign the infra-red absorptions obtained while the system was under catalytic conditions.

5.4.2. Discussion

(a) Study of the system under nitrogen pressure only.

A series of reactions were studied with nitrogen (100 Atm) only above the solutions. The pressure of nitrogen above the solutions appeared not to influence the reactions that occurred. The systems reacted initially as in the low pressure studies but on raising the temperature loss of carbon monoxide occurred as the carbonyl species decomposed.

Dicobalt octacarbonyl and potassium iodide in methanol were examined under nitrogen pressure and the peaks generated in the reaction were observed with increase in temperature. The only peaks observed in the spectra were at $2018_{(w)}$ and $1900_{(s)}$ cm^{-1} due to $Co(CO)_4^-$ ion. The iodide ion was not observed to have any effect on the reaction of dicobalt octacarbonyl to form $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$. With increase in temperature these peaks were found to reduce rapidly in intensity and disappeared at ∿ 100°C. On opening the bomb a black/grey deposit was noted on the walls, believed to be metallic cobalt.

Dicobalt octacarbonyl was also reacted with methyl iodide in methanol under nitrogen pressure and showed infra-red peaks at $2107_{(w)}$, $2050_{(m)}$, $2025_{(m)}$, $2007_{(m)}$ and $1720_{(w)}$ cm^{-1}, and these are assigned to the species $CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4$. These were all found to weaken slowly as the temperature was raised and at ∿ 100°C, the absorptions were found to have completely disappeared.

The reactions under nitrogen pressure of 100 Atm therefore follow the established pattern; the nitrogen is unable to stabilize the species produced at elevated temperature, and they decompose below 100°C by loss of carbon monoxide.

(b) Study of the system under carbon monoxide pressure.

A series of reactions were performed under a carbon monoxide pressure of 100 Atm and investigated by infra-red analysis to determine the species present at the reaction temperature.

Dicobalt octacarbonyl and potassium iodide were used in a ratio $^{Co}/I = 1$. The initial absorptions due to the species $Co(CO)_4^-$ weakened slowly as the temperature was raised, but even at the maximum temperature (185°C) the 1900 cm^{-1} band was still clearly visible. New peaks were also observed at $2107_{(w)}$, $2050_{(w)}$, $2025_{(w)}$, $2005_{(m)}$ and $1720_{(w)}$ cm^{-1} and are assigned to $CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4$.[81] These appear at ∿ 170°C and remain weak throughout the experiment.

Higher concentrations of iodide ion (ratio of $^{Co}/I = \frac{1}{2}$) have also been examined, the iodide being supplied both in the form of potassium iodide and cobalt iodide. When the reaction was performed with potassium iodide under these conditions the peaks due to $Co(CO)_4^-$ were found to disappear at ∿ 170°C. However the weak peaks due to the $CH_3\overset{O}{\overset{\|}{C}}Co(CO)_4$ species were still observed to form at this temperature. When cobalt iodide was used, both as the source of the catalyst and of the promoter, (Table 5.1., exp. 51), the reaction followed much the same route. The only significant difference was the lack of the absorptions due to the $Co(CO)_4^-$ anion as this was not observed to be formed when CoI_2 was used.

With methyl iodide as the source of iodide the reaction followed a slightly different course. Initially the carbonyl stretching frequencies corresponding to the species $CH_3\overset{\overset{O}{\|}}{C}Co(CO)_4$ were observed and as the system was warmed to 185°C, these absorptions slowly weakened but did not disappear. At no time in the studies using methyl iodide was the $Co(CO)_4^-$ ion detected. This was the only significant difference between the use of a metal iodide and methyl iodide.

The solutions were extracted and examined by chromatography and infrared to assess the amount of conversion of methanol. It was found that the methanol was virtually unchanged and very little carbonylation had taken place under these physical conditions and using carbon monoxide alone. (The normal conditions required for the straight carbonylation of methanol with a cobalt catalyst to form acetic acid and its derivatives are $\sim$ 700 Atm and 250°C.)

(c) Study of the system under synthesis gas pressure.

A further series of reactions were studied under a synthesis gas pressure of 200 Atm (comprised of 100 Atm H_2, 100 Atm Co)[82] using dicobalt octacarbonyl with potassium iodide or methyl iodide. In some experiments cobalt iodide was used as the source of both the catalyst and promoter.

Similar results were observed with the synthesis gas as were found with only the carbon monoxide present. Initially with dicobalt octacarbonyl and potassium iodide ($^{Co}/I = 1$) the only absorptions noted were due to the species $Co(CO)_4^-$. As the temperature was slowly raised the absorptions due to $Co(CO)_4^-$ weakened but even at 185°C the 1900 cm^{-1} band was clearly observable. At $\sim$ 170°C new peaks were seen to develop at $2107_{(w)}$, $2050_{(m)}$, $2025_{(m)}$, $2005_{(m)}$ and $1720_{(w)}$ cm^{-1} and these were assigned to the species $CH_3\overset{\overset{O}{\|}}{C}Co(CO)_4$, and remained weak throughout the experiment.

Using potassium iodide, ($^{Co}/I = \frac{1}{2}$), the initial peaks due to $Co(CO)_4^-$ were found to weaken as the temperature was increased and completely disappeared at $\sim 175^{\circ}C$. However the weak peaks due to $CH_3\overset{\overset{O}{\|}}{C}Co(CO)_4$[83] were still observed to develop at $\sim 160^{\circ}C$ and persist to $185^{\circ}C$. When cobalt iodide was used both as the source of the catalyst and the promoter a weak absorption due to the $Co(CO)_4^-$ ion was noted and the only other peaks that appeared in the carbonyl stretching frequency region were weak and were assigned to $CH_3\overset{\overset{O}{\|}}{C}Co(CO)_4$.

When methyl iodide was used as the source of iodide $({}^{Co}/I = 1)$ the reaction was slightly changed. Initially at room temperature the absorptions due to the acyl species were observed and as the system was slowly heated to $185^{\circ}C$ they weakened but did not disappear. No bands were observed in the spectra of the reaction that could be assigned to the cobalt tetracarbonylate anion. This was the major difference between the reactions with metal iodide and with methyl iodide as promoter.

It was found essential to record the infra-red spectra quickly, once the temperature of the system approached $\sim 170^{\circ}C$, as the organic materials formed in the reaction began to produce obscuring absorptions in the carbonyl stretching frequency region. The homologation reaction of methanol was found to be relatively efficient under these conditions with the presence of the iodide promoter in the system.

The iodide appears to function in two roles: (1) as an activator of methanol probably via formation of methyl iodide, and (2) as an agent that removes the $Co(CO)_4^-$ ion. High ${}^{I}/Co$ ratios lead to loss of soluble cobalt carbonyls over a period of time. This may occur through formation of cobalt metal and/or non carbonyl cobalt complexes[27] e.g. $[Co(OAc)_2I_2]^{2-}$, $[Co(CH_3OH)_xI_y]^{n+}$. Low ${}^{I}/Co$ ratios are more favourable, since insufficient iodide is available to completely remove the active form of cobalt, yet enough iodide is present to form methyl iodide, which apparently reacts more readily than methanol with the active cobalt carbonyl.

CHAPTER SIX

AN EXAMINATION OF THE IODINE PROMOTED COBALT/METHANOL REACTION SYSTEM

6.1. Introduction

This chapter is concerned with the influence of elemental iodine on the cobalt catalysed homologation of methanol. The use of elemental iodine as a promoter for the reaction has been suggested by many authors.[84] Iodine is believed to enhance both the yield and selectivity of the major products of the reaction.[85,86] Several possible reaction schemes have been proposed for the involvement of the iodine in the system, and the objective of this work is to clarify the reasons for the increased efficiency.

6.2. Low Pressure Study of the Dicobalt Octacarbonyl/Iodine/Methanol System

6.2.1. Experimental

(a) Reaction of dicobalt octacarbonyl with iodine in methanol.

Crystals of dicobalt octacarbonyl (0.6 g, 2 mmol) were added to methanol (40 ml) and the mixture was stirred rapidly. A solution of iodine (1.0 g, 4 mmol) in methanol (60 ml) was slowly added causing the red/black colour to weaken. The addition of the iodine solution was accompanied by gas evolution which ceased when the red/black colour changed to brown; no precipitate or undissolved material was observed. The system was evaporated to dryness "in vacuo" and a black solid was formed. This solid was washed with hexane to remove excess iodine, dried and submitted for analysis. The black residue was a very fine, air reactive powder converting to a green solid in contact with air or moisture. Elemental analysis gave Co, 19.1; I, 80.4% (CoI_2 requires Co, 18.8; I, 81.2%).

Infra-red examination of the carbonyl stretching frequency region initially showed peaks at $2073_{(s)}$, $2046_{(s)}$, $2027_{(s)}$, $1866_{(m)}$ and $1858_{(m)}$ cm^{-1}. As the iodine solution was slowly added these peaks all slowly weakened and disappeared and no new peaks in the carbonyl stretching frequency region were observed to be formed. Infra-red study of the black solid, as a nujol mull, also showed no carbonyl peaks.

(b) Reaction of $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ with iodine in methanol.

Orange/brown crystals of dicobalt octacarbonyl (0.3 g, 1 mmol) were dissolved in methanol (20 ml) and the mixture was stirred rapidly for 4 hours. The characteristic pink solution of $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ was observed to form after approximately 3 hours. Iodine crystals (0.25 g, 1 mmol) were added to the pink solution. Immediate gas evolution occurred on addition of the iodine, and the pale pink changed to a brown coloured solution. An equal quantity of iodine was then added to the now brown solution, further gas evolution occurred and the solution became still darker brown. The system was stirred overnight and no further change was observed. The methanol was evaporated "in vacuo", the black residue was washed with hexane to remove any excess iodine, dried under vacuum and sent for analysis. On contact with air or moisture the black solid converted to a green solution. Analysis gave Co, 19.4; I, 81.9%, (CoI_2 requires Co, 18.8; I, 81.2%).

Solution infra-red study of the carbonyl stretching frequency region showed, for the pink solution, peaks at $2018_{(w)}$ and $1900_{(vs)}$ cm^{-1}. The addition of the first portion of iodine to the system caused both peaks to weaken considerably, the 2018 cm^{-1} peak disappeared completely and the originally very strong 1900 cm^{-1} peak became only medium-strong. When the second portion of iodine was added to the system the peak at 1900 cm^{-1} was found to weaken and disappear and no new peaks were observed to be formed. The only peaks remaining in this region under study were due to the methanol solvent at 2125 and 2040 cm^{-1}. Infra-red study of the black solid, as a nujol mull, showed no carbonyl peaks.

(c) Reaction of $Na^{+}Co(CO)_4^{-}$ with iodine in T.H.F.

Dicobalt octacarbonyl (0.3 g, 1 mmol) in T.H.F. was reacted with sodium amalgam, as outlined in section 5.2.1., to form the sodium cobalt tetracarbonylate salt. Iodine (0.76 g, 3 mmol) was added and the buff coloured solution rapidly became brown. After stirring at room temperature for ½ hour, the system was evaporated under reduced pressure and a grey/black solid was deposited. This solid was washed with hexane to remove any excess iodine, dried under vacuum, and sent for analysis. Elemental analysis gave Co, 13.0; I, 81.1; Na, 5.3%, (CoI_2 + NaI requires Co, 12.7; I, 82.3; Na, 5.0%). No attempt was made to separate the two materials.

The system was examined by solution infra-red spectroscopy of the carbonyl stretching frequency region. The sodium tetracarbonylate salt showed one strong peak at 1900 cm^{-1}. This peak was observed to rapidly weaken and disappear as the iodine was added. No other peaks were observed at any stage in the reaction, except for a solvent peak at 1967 cm^{-1}.

(d) Reaction of $PPN^{+}Co(CO)_4^{-}$ with iodine in methanol.

A small amount of $PPN^{+}Co(CO)_4^{-}$ (0.28 g, 0.4 mmol) was dissolved in methanol (60 ml) to form a buff coloured solution, and iodine (0.25 g, 1 mmol), also dissolved in methanol (20 ml), was slowly added. The original buff coloured solution changed to a brown solution, evolution of gas was noted and a brown precipitate was also formed. The mixture was evaporated to approximately 20 ml by pumping and this induced more precipitation. This brown material was separated by filtration, dried under vacuum and sent for analysis. Elemental analysis gave H, 3.2; C, 46.7; P, 6.9; N, 1.4; I, 40.1%.

The filtrate, a brown solution, was evaporated to dryness "in vacuo" and a black solid was formed. This material was first washed with hexane, which acquired a very faint purple tinge, and then dried, before being sent for analysis. The black solid was air and moisture sensitive and converted rapidly to a green solid on contact with either. Elemental analysis gave Co, 18.4; I, 80.7% (CoI_2 requires Co, 18.8; I, 81.2%).

Infra-red study of carbonyl stretching frequency region initially showed only a single peak of medium intensity at 1900 cm^{-1}. This peak weakened and disappeared as the iodine solution was added, and no new peaks developed. Infra-red analysis of both the brown and black materials, as nujol mulls, showed no peaks due to carbonyl groups. However the brown solid did show many other (non-carbonyl) peaks and these resembled closely those produced by $PPN^+Co(CO)_4^-$ and PPN^+Cl^- in nujol mulls. This indicated that the brown species probably contained the PPN^+ ion. ^{31}P n.m.r. studies of the brown solid gave a single signal at -21.1 ppm and this corresponded exactly to the ^{31}P signal obtained with a solution of PPN^+Cl^- in dichloromethane, indicating that the same cation was present in both materials.

(e) Reaction of dicobalt octacarbonyl with iodine in hexane.

Crystals of dicobalt octacarbonyl (0.3 g, 1 mmol) were dissolved in hexane (40 ml) and solid iodine (0.5 g, 2 mmol) was slowly added to the red/black solution. A gas was observed to be evolved and the hexane solution was observed to change colour from red/black to faintly purple. At the same time as the colour change occurred a black solid was observed to deposit from the solution. The hexane was removed by syringe and the black solid dried under vacuum before being sent for analysis. The black solid was air and moisture sensitive converting to a green solution on standing. Elemental analysis gave Co, 18.3; I, 80.4% (CoI_2 requires

Co, 18.8; I, 81.2%).

The reaction was observed by solution infra-red examination of the carbonyl stretching frequency region. Initially a large number of peaks were observed at $2073_{(s)}$, $2046_{(s)}$, $2029_{(s)}$, $1866_{(m)}$ and $1858_{(m)}$ cm^{-1} due to the stretching of the terminal and bridging carbonyl groups of dicobalt octacarbonyl. As the iodine was slowly added to the system these peaks began to weaken, especially those at 1866 and 1858 cm^{-1} (due to the bridging carbonyl stretching frequencies). All the carbonyl peaks were observed to disappear when the addition of iodine was complete and no peaks other than those due to dicobalt octacarbonyl had been observed in the reaction.

(f) Reaction of dicobalt octacarbonyl with iodine in hexadecane.

Crystals of dicobalt octacarbonyl (0.3 g, 1 mmol) were dissolved in hexadecane (40 ml) and the dark red solution was rapidly stirred for 2 hours. Solid iodine (0.5 g, 2 mmol) was slowly added to the dark red solution, the solution changed to a more purple colour and a black solid was observed to deposit. This purple solution was stirred for a further 2 hours and the colour faded until only a faint purple tinge coloured the hexadecane. The solvent was syringed off and the black solid was washed with hexane before being dried under vacuum and sent for analysis. The black solid was air and moisture sensitive converting rapidly to a green solution on standing. Elemental analysis gave Co, 18.6; I, 80.8%, (CoI_2 requires Co, 18.8; I, 81.2%).

The system was examined by infra-red spectroscopy of the carbonyl stretching frequency region (2200 - 1700 cm^{-1}). Initially a large number of peaks were observed at $2073_{(s)}$, $2046_{(s)}$, $2029_{(s)}$, $1866_{(m)}$ and $1858_{(m)}$ cm^{-1} due to the stretching of the terminal and bridging carbonyl groups of dicobalt octacarbonyl. As the iodine was added to the solution all the carbonyl peaks began to reduce slowly in intensity. The peaks due to dicobalt octacarbonyl finally disappeared and were replaced by peaks at $2068_{(s)}$, $2059_{(s)}$, $2041_{(w)}$, $2031_{(w)}$ and $1866_{(m)}$ cm^{-1} due to the species $Co_4(CO)_{12}$. The carbonyl peaks due to the tetracobalt dodecacarbonyl persisted for about two hours after the addition of iodine but eventually these peaks also weakened and disappeared. No other carbonyl peaks were observed in this reaction. Infra-red examination of the black solid, as a nujol mull, showed no carbonyl absorptions.

6.2.2. Discussion.

The reaction of iodine with sodium tetracarbonyl cobaltate appears to be relatively straightforward. The presence of the iodine in the system destroys the $Co(CO)_4^-$ ion by evolving carbon monoxide and forming cobalt (II) iodide.[75] The counter ion to the $Co(CO)_4^-$ reacts also to form the iodide species. Thus for $Na^+Co(CO)_4^-$ and $[Co(MeOH)^{2+}][Co(CO)_4^-]_2$ the reaction proceeds as follows:-

$$2Na^+Co(CO)_4^- + 3I_2 \xrightarrow{\text{In THF}} 2NaI + 2CoI_2 + 8CO$$

$$[Co(MeOH)_6^{2+}][Co(CO)_4^-] + 3I_2 \xrightarrow{\text{In MeOH}} 3CoI_2 + 6MeOH + 8CO$$

The reaction of iodine with the $PPN^+Co(CO)_4^-$ is slightly different probably due to the increased size of the cation. The reaction follows a modified course:-

$$2PPN^+Co(CO)_4^- + 5I_2 \xrightarrow{\text{In MeOH}} 2PPN^+I_3^- + 2CoI_2 + 8CO$$

The polyiodide ion I_3^- is a well known species in inorganic chemistry[87,88] and accounts for the increased solubility of I_2 in water on addition of KI. In non-aqueous media such as CH_3OH or CH_3CN, its stability is substantially higher. The I_3^- ion is linear but not necessarily structurally or electronically symmetrical in the solid state and is stabilised by large cations.[89,90]

The reaction of iodine with the $Co(CO)_4^-$ anion has been suggested and investigated as a possible method of quantitatively determining the $Co(CO)_4^-$ concentration of solutions.[91] This method was also proposed to be useful in the quantitative determination of $HCo(CO)_4$ and dicobalt octacarbonyl.

Dicobalt octacarbonyl reacts with iodine in methanol as described previously to form cobalt (II) iodide.

$$Co_2(CO)_8 + 2I_2 \longrightarrow 2CoI_2 + 8CO$$

Interestingly a report[50] in the literature outlines a procedure for generating the species $ICo(CO)_4$ using the same reaction method, and reports the carbonyl stretching frequencies of the product as $2115_{(m)}$, $2050_{(m)}$ and $2046_{(vs)}$ cm^{-1}. Our solution infra-red spectroscopic investigation of the reaction in methanol failed to show any of these peaks.

The report indicated that cetane, (hexadecane), a long chain hydrocarbon solvent had been used in the reaction and so our study of the reaction was further continued in hexane and hexadecane solvents.

Dicobalt octacarbonyl was found to react with iodine in hexane in much the same way as in methanol solvent. The product extracted from the system was cobalt (II) iodide. Infra-red examination of the reaction showed none of the reported absorptions for $ICo(CO)_4$, the peaks due to dicobalt octacarbonyl were destroyed rapidly by the iodine, those due to the bridging carbonyl groups weakening most rapidly.

The final investigation into the reaction of dicobalt octacarbonyl with iodine was performed in hexadecane (cetane) solution. Again the solid produced from the reaction was identified as cobalt (II) iodide and no other solid was obtained. The infra-red examination of this reaction showed absorptions due initially to dicobalt octacarbonyl but on addition of the iodine the absorptions were quickly reduced in intensity. However as the peaks due to dicobalt octacarbonyl weakened the absorptions due to the tetracobalt dodecacarbonyl were observed to appear. The peaks due to the $Co_4(CO)_{12}$ species persisted for approximately 2 hours in the presence of iodine in solution. This implied that the $Co_4(CO)_{12}$ was much more resistant to attack by iodine than dicobalt octacarbonyl. The fact that tetracobalt dodecacarbonyl was observed must be due to the solvent used. The hexadecane is a relatively viscous medium and this probably assisted the formation of $Co_4(CO)_{12}$ from $Co_2(CO)_8$ by resisting such rapid attack by iodine as was possible in hexane solution. The $Co_4(CO)_{12}$ is also far less soluble in hydrocarbons than $Co_2(CO)_8$, so it is possible that some $Co_4(CO)_{12}$ was deposited as a solid and this was thus protected to some extent from iodine attack. It is thus conceivable that the iodine slowly attacked the $Co_4(CO)_{12}$ in solution which was then slowly replaced by dissolution of $Co_4(CO)_{12}$ from the deposited solid. All the carbonyl stretching absorptions observed in this reaction are assigned to either dicobalt octacarbonyl or tetracobalt dedecacarbonyl, and thus still no peaks have been observed due to the reported $ICo(CO)_4$ species even under the conditions reported in the literature. The only other halogen compound reported is the unstable phosphine substituted cobalt tricarbonyl $ClCo(PPh_3)(CO)_3$.[92]

6.3. High Pressure Study of the Cobalt/Iodine/Methanol System

6.3.1. Experimental

The basic experimental details are very similar to those described in preceding chapters. The study was performed in the same high-pressure vessels, and the analysis of products was routinely performed by G.L.C. The physical conditions used were varied in order to find their influence upon the course of the reaction. The iodine used in the reactions was placed in the bomb as a solid, together with the cobalt acetate tetrahydrate and then methanol was added to the mixture. The bomb was purged with nitrogen before pressurising with 1:1 Co/H_2 synthesis gas to a pressure of $\sim$ 140 Atm, and the reactants stirred as rapidly as possible by a magnetic "flip-flop" agitator. The temperature of the system was then raised to the selected level (180 - 220^{o}C) causing the gas pressure to rise to about 200 Atm. The reaction was allowed to run for two hours while the pressure was maintained at $\sim$ 200 Atm by injection of further 1:1 Co/H_2 synthesis gas when required. When the run was completed the system was allowed to cool overnight to room temperature and the bomb was depressurised slowly the next day. The resultant reaction mixture was syringed from the bomb and analysed.

The results of varying some of the reaction conditions of the iodine promoted homologation of methanol are discussed below with reference to the yield and selectivity of some important products.

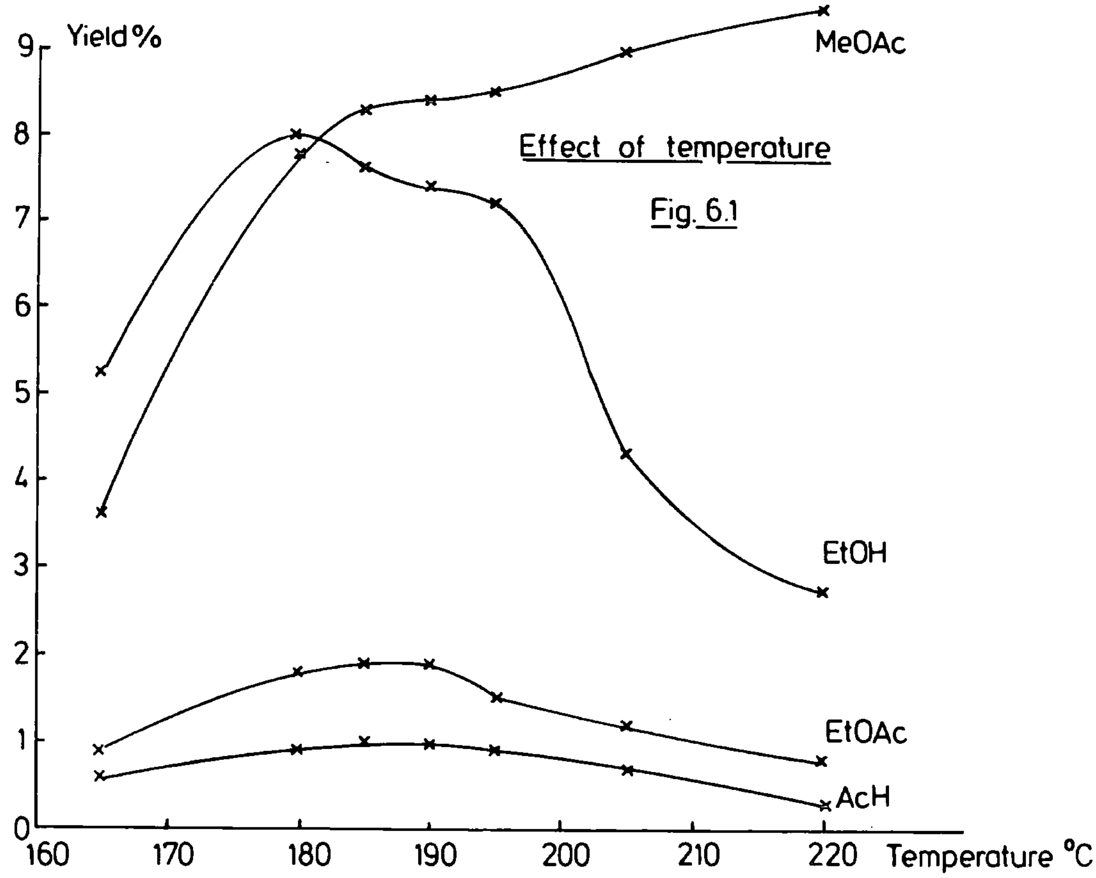
6.3.2. Discussion

(a) Influence of temperature.

The influence of temperature on the iodine promoted methanol homologation reaction is recorded in Table 6.1. The variation of yield with temperature is presented graphically in Fig. 6.1. and shows several interesting features. The yield of ethanol was found to pass through a maximum at $\sim$ 180^{o}C and decrease rapidly outside the narrow temperature range 180 - 200^{o}C. The decrease in ethanol formation at lower temperatures is accompanied by a decrease in yield of all the major products. This can be regarded as due to the reaction being substantially slower at these lower

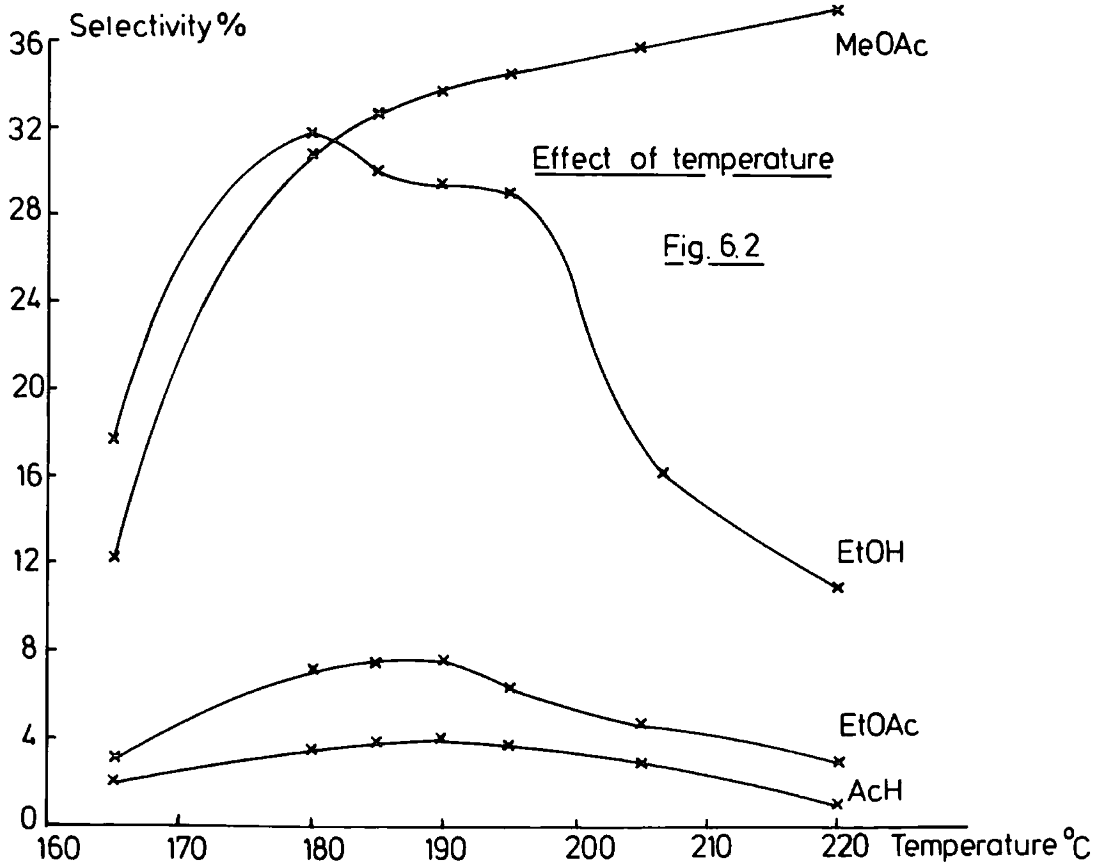
Table 6.1.

Expt. No.	MeOH (moles)	Co(OAc)$_2$ 4H$_2$O (moles)	Temperature (^{o}C)	Pressure (Atm)	Reaction Time (hr.)	Iodine (I$_2$) (moles)	Ratio Co:I	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
56	0.56	7.0×10^{-3}	185	200	2	3.5×10^{-3}	1:1	Yield	7.6	8.3	1.9	1.0
								Selectivity	29.9	32.6	7.4	3.9
57	0.56	7.0×10^{-3}	195	200	2	3.5×10^{-3}	1:1	Yield	7.2	8.5	1.5	0.9
								Selectivity	29.1	34.4	6.1	3.6
58	0.56	7.0×10^{-3}	205	200	2	3.5×10^{-3}	1:1	Yield	4.3	9.0	1.2	0.7
								Selectivity	17.0	35.7	4.8	2.8
59	0.56	7.0×10^{-3}	190	200	2	3.5×10^{-3}	1:1	Yield	7.4	8.4	1.9	1.0
								Selectivity	29.5	33.5	7.6	4.0
60	0.56	7.0×10^{-3}	180	200	2	3.5×10^{-3}	1:1	Yield	8.0	7.8	1.8	0.9
								Selectivity	31.7	30.9	7.1	3.5
61	0.56	7.0×10^{-3}	220	200	2	3.5×10^{-3}	1:1	Yield	2.7	9.5	0.8	0.3
								Selectivity	10.8	38.0	3.2	1.2
62	0.56	7.0×10^{-3}	165	200	2	3.5×10^{-3}	1:1	Yield	5.2	3.6	0.9	0.6
								Selectivity	17.7	12.2	3.1	2.0



Effect of temperature

Fig. 6.1



Effect of temperature

Fig. 6.2

temperatures or because only a fraction of the cobalt has been converted into active catalyst. In this region also, ethanol is the major product of the reaction whereas at higher temperatures > $180^{o}C$, methyl acetate is found to be the preferred product at the expense of the ethanol.

It was observed in Chapter 3, that at higher reaction temperatures the yield of ethanol was found to decrease. The instability of the catalyst at these elevated temperatures was suggested as the explanation for this behaviour and was supported by the fact that cobalt metal was observed plated out on the walls of the bomb. This explanation can be applied also in the iodine promoted system as cobalt metal was again found to be deposited on the walls of the bomb. The iodine thus imparts no extra thermal stability to the catalyst. This loss of catalyst at higher temperatures can explain the fall in the yield of ethanol but not the substantial increase in formation of methyl acetate. The increased yield of methyl acetate at higher temperatures can possibly be explained by, the increased rate of a competing reaction even though less catalyst is available or the higher temperature reduces the solubility of hydrogen and hence makes reduction less likely. Conversely, the reaction may occur by a heterogeneous catalytic mechanism.

(b) Influence of cobalt/iodine ratio.

The effects of varying the cobalt/iodine ratio have been studied and are recorded in Table 6.2. The ratio referred to here is the molar proportion of (cobalt atoms:iodine atoms). The results of the experiments are illustrated in Fig. 6.3. and Fig. 6.4. The yield of ethanol is observed to reach a maximum at the ratio of 1:1. This value would seem to represent the best proportion of cobalt to iodine. The yields of the by-products methyl acetate and acetaldehyde increase steadily as the iodine

Table 6.2.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	Temperature (^oC)	Pressure (Atm)	Reaction Time (hr.)	Iodine (I_2) (moles)	Ratio Co:I	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
56	0.56	7.0×10^{-3}	185	200	2	3.5×10^{-3}	1:1	Yield	7.6	8.3	1.9	1.0
								Selectivity	29.9	32.6	7.4	3.9
63	0.56	7.0×10^{-3}	185	200	2	1.75×10^{-3}	2:1	Yield	5.7	4.2	1.0	0.5
								Selectivity	30.8	21.3	5.4	2.7
64	0.56	7.0×10^{-3}	185	200	2	7.0×10^{-3}	1:2	Yield	4.1	9.0	2.6	2.2
								Selectivity	21.0	45.2	13.1	10.9
65	0.56	7.0×10^{-3}	185	200	2	2.33×10^{-3}	3:2	Yield	7.1	6.8	1.6	0.8
								Selectivity	31.0	30.0	7.0	3.5
66	0.56	7.0×10^{-3}	185	200	2	5.25×10^{-3}	2:3	Yield	6.0	8.5	2.1	1.5
								Selectivity	25.2	35.7	8.8	6.3

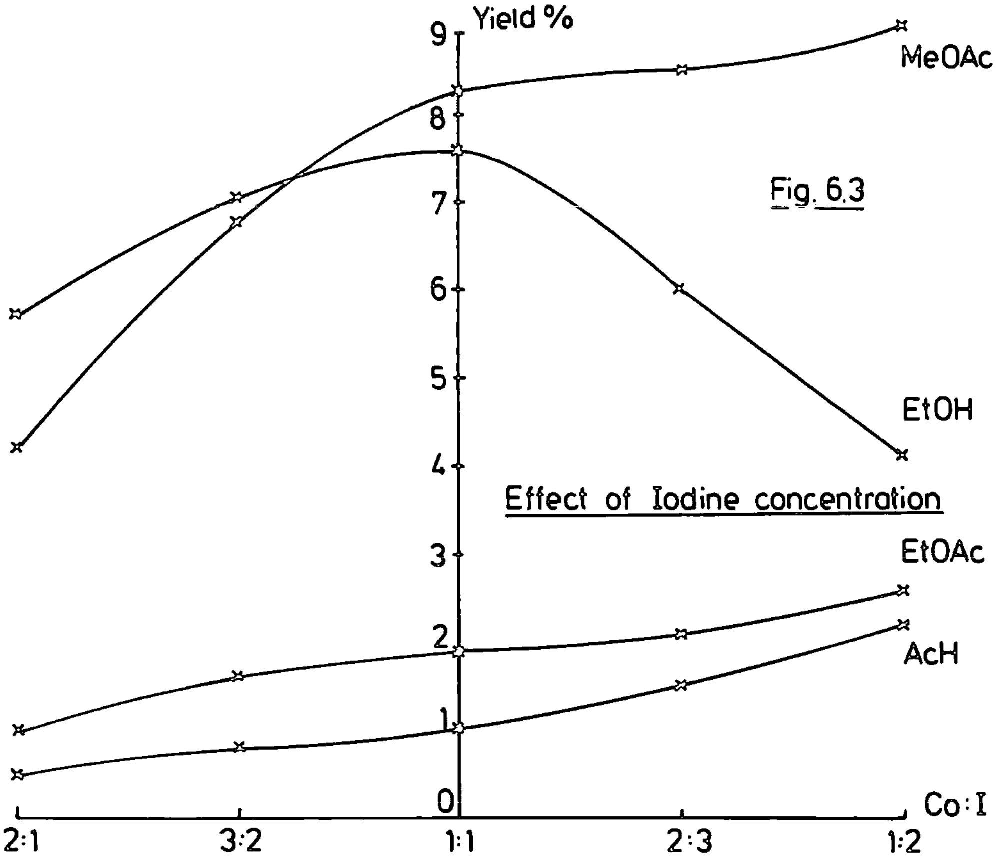


Fig. 6.3

Effect of Iodine concentration

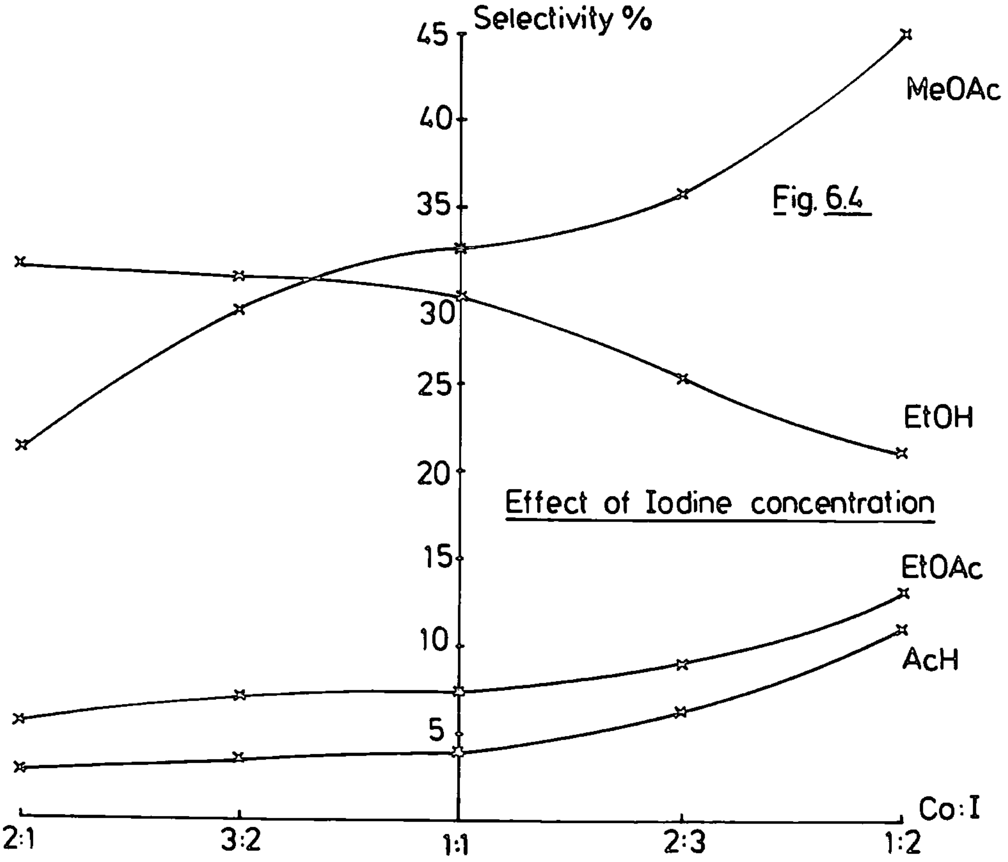


Fig. 6.4

Effect of Iodine concentration

concentration increases. Ethanol yield decreases both at high and at low iodine concentration, although at low iodine ratios this is accompanied by a decrease in yield of all products. The yield of methyl acetate with iodine concentration follows the same pattern as that observed in 5.3.2. where iodide was used in the reactions. The selectivities of the major products show approximately the same features as the yields, at high iodine ratio methyl acetate is the preferred product and at low iodine concentration ethanol is preferred.

6.4. High Pressure Infra-Red Study of the Cobalt/Methanol/Iodine System

6.4.1. Experimental

These high pressure studies were all performed in the same cells used for the autoclave reactions but the infra-red facility was utilised to follow the course of the reactions and to identify any intermediate species. It was found that the reaction was reasonably efficient, when promoted by iodine. Hence the infra-red spectrum of the solution quickly became complicated by strong absorptions due to the many organic products. Unfortunately these absorptions were found to obscure and mask those due to the intermediate catalytic species. Therefore it was found to be essential to record infra-red spectra, at maximum temperature, as quickly as possible before the absorptions due to the organic products became too intense and interfered with the spectra of the catalysts being investigated.

The materials added to the cell, dicobalt octacarbonyl, iodine and methanol were added in a particular order. The iodine, dissolved in the methanol, was syringed into the bomb. The bomb was then flushed with nitrogen before the addition of the dicobalt octacarbonyl as a solid. The cell was then flushed once again with nitrogen, sealed and pressurised to the level selected with the appropriate gas or gas mixture.

The infra-red spectra were recorded regularly as the temperature was raised from an initial temperature of ∿ 20°C, in increments of ∿ 50°C to the final required reaction temperature; at each interval time (15 min.) was allowed for the system to reach equilibrium before the spectra were recorded.

Once the examination of the system at the maximum temperature had been completed, the bomb was allowed to cool slowly to room temperature overnight, before the gas pressure was released. Once the bombs were opened a sample of the liquid was removed and examined by infra-red and G.L.C. methods to determine the organic reaction products. Such information aided the interpretation of the infra-red spectra.

6.4.2. Discussion.

(a) Study of the cobalt/iodine/methanol system under nitrogen pressure.

An examination of dicobalt octacarbonyl and iodine in methanol under nitrogen pressure (∿ 100 Atm) indicated that none of the carbonyl species was stable in the presence of iodine, regardless of the nitrogen pressure. The starting materials examined were, dicobalt octacarbonyl, $PPNCo(CO)_4$ and $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$. The investigation centred on observation of the carbonyl stretching frequency region with increase in temperature. No new carbonyl stretching absorptions were detected in any of the systems examined the iodine rapidly destroyed any carbonyl species present. On opening the bomb a brown liquid was usually extracted consisting mainly of cobalt iodide in methanol.

(b) The cobalt/iodine/methanol system under carbon monoxide pressure.

The study consisted of observation, by infra-red spectroscopy, of the carbonyl stretching frequency region (2300 - 1600 cm^{-1}) as the temperature was slowly raised.

The starting materials for this investigation were dicobalt octacarbonyl (or $PPN^+Co(CO)_4^-$) and iodine in methanol. In effect cobalt iodide was formed in solution by the time measurements were made, and hence no carbonyl absorptions were observed at room temperature. The temperature was slowly raised and the infra-red spectrum of the system observed continually. The cells were heated to 180°C before any absorptions due to carbonyl species were observed. At this temperature however, weak peaks began to develop at $2110_{(w)}$, $2025_{(w)}$, $2010_{(w)}$ and $1720_{(w)}$ cm^{-1} assigned to the species $CH_3\overset{\overset{O}{\|}}{C}Co(CO)_4$.[77,66] Also at 180°C, a weak peak developed at 1900 cm^{-1}, believed due to $Co(CO)_4^-$. This peak persisted to 190°C and its intensity weakened rapidly, whereas the absorptions assigned to $CH_3\overset{\overset{O}{\|}}{C}Co(CO)_4$ slowly increased in intensity.

The cells were allowed to cool slowly to room temperature, the absorptions decreased in intensity as the temperature fell and disappeared at approximately 170°C. The cells were opened at room temperature and the resultant brown solution extracted and analysed by G.L.C. The solution was found to contain methyl acetate but only in low quantities, indicating that a very small amount of carbonylation of the methanol had taken place. The pressures and temperatures used in this experiment (100 Atm, 200°C) were low compared with those necessary for efficient carbonylation to take place (600 Atm, 250°C).

(c) The cobalt/iodine/methanol system under synthesis gas pressure.

The reaction system of dicobalt octacarbonyl and iodine in methanol was studied under 140 Atm pressure of a 1:1 Co/H_2 gas mixture. The cells were slowly heated to 185°C and the infra-red spectrum of the system recorded.

Initially no absorptions in the carbonyl stretching frequency region were detected and no change in the spectra was observed until the temperature of the cells reached 165°C. At this temperature weak peaks began to develop at $2110_{(w)}$, $2025_{(w)}$, $2010_{(w)}$ and $1720_{(w)}$ cm^{-1}. These absorptions strengthened as the temperature was increased to 190°C but above this temperature the peaks were observed to decrease in intensity. The absorptions were assigned to the species $CH_3\overset{\overset{O}{\|}}{C}Co(CO)_4$,[66] believed to be an important intermediate in the formation of ethanol.[93] A weak peak at 1900 cm^{-1} was observed at 170°C and assigned to $Co(CO)_4^-$ but this persisted only for a while before disappearing. No absorptions were observed that could be assigned to dicobalt octacarbonyl or to cobalt tetracarbonyl hydride. The reaction was not examined at temperatures $>$ 170°C over long periods of time as absorptions due to organic products soon developed and obscured the spectra. On cooling of the system to room temperature the carbonyl peaks were all observed to weaken and disappear. The cells were opened at room temperature and the resultant brown solution syringed out and analysed by G.L.C. The cobalt was observed to be in solution as cobalt (II) iodide.

CHAPTER SEVEN

AN EXAMINATION OF THE LIGAND STABILISED AND IODINE (OR IODIDE) PROMOTED COBALT/METHANOL REACTION

7.1. Introduction

This chapter is concerned with the influence of both a stabilising ligand (a tertiary phosphine, arsine or stibine) and a promoter (elemental iodine or alkali metal iodide) on the cobalt catalysed homologation of methanol. The stabilising ligand is believed to allow the reaction to take place both at higher temperatures and lower carbon monoxide pressures more efficiently; the promoter also enhances the reaction, thus a combination of these materials has been predicted to permit much more efficient conversion to ethanol.

Examination of the system in high pressure infra-red cells allows the effect of the additives to be studied and their influence upon the species present at reaction temperature. Measurements and other accurate information in the literature on the system are scarce[22,23,72] but several schemes have been suggested for the reaction.[3,4] One of the objectives of this work relates to the reasons for increased efficiency of the reaction when performed in the presence of these additives.

7.2. Low Pressure Study of the Dicobalt Octacarbonyl/Ligand/Iodine/Methanol Reaction

7.2.1. Experimental

(a) Reaction of $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ [97] with iodine and triphenyl phosphine.

Crystals of dicobalt octacarbonyl (0.7 g, 2 mmol) were dissolved in methanol (60 ml) and the dark red/brown solution formed was rapidly stirred for three hours until the pink solution was produced. Elemental iodine (1.04 g, 4 mmol) was slowly added to the pink solution and quickly produced a brown solution. Then to this brown solution triphenyl phosphine (2.14 g, 8 mmol) was added and a pink solution was formed. The pink solution was stirred overnight and remained unchanged. Evaporation to dryness "in vacuo" produced a brown solid which was washed with hexane to remove any excess iodine and triphenyl phosphine, and dried, before being sent for elemental analysis. Found: Co, 6.7; H, 3.3; C, 52.0; P, 7.6; I, 30.1%, ($Co(PPh_3)_2I_2$$^{109-115}$ requires Co, 7.0; H, 3.6; C, 51.6; P, 7.4; I, 30.3%).

Infra-red examination of the carbonyl stretching frequency region of the solutions showed initially in the pink solution two peaks at $2018_{(w)}$ and $1900_{(s)}$ cm^{-1} due to the species $Co(CO)_4^-$. On addition of iodine the carbonyl peaks were destroyed and no new carbonyl stretching peaks were observed to form after this stage. Infra-red analysis of the final brown solid as a nujol mull showed no carbonyl stretching peaks but showed some absorptions indicative of triphenyl phosphine ligand in the compound.

(b) Reaction of $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ with methyl iodide and triphenyl phosphine.

Dicobalt octacarbonyl (0.7 g, 2 mmol) was dissolved in dry, degassed methanol (60 ml) and the dark red/black solution was rapidly stirred. After about three hours a pink solution had formed and to this was added methyl iodide (0.36 g, 2.6 mmol) dissolved in hexane (40 ml). The system reacted slowly, the methanol changed from pink to brown in colour and the hexane layer became pale yellow. The system remained unchanged overnight. Addition of triphenyl phosphine (1.4 g, 5.3 mmol) caused the two layers to change colour slowly, the hexane becoming darker yellow and the methanol becoming pink/brown in colour. The hexane layer was removed by syringe and the methanol layer was extracted with hexane to remove any further hydrocarbon soluble material. The methanol solution was then filtered, producing a small amount of black solid, and evaporated to dryness, producing a brown residue. Both solids were washed with hexane before being sent for elemental analysis. Analysis of the black solid gave Co, 94.6; C, 2.1%, and is believed to be cobalt metal. The brown solid gave Co, 7.4; H, 3.8; C, 51.1; P, 7.7; I, 30.7% ($Co(PPh_3)_2I_2$ requires Co, 7.0; H, 3.6; C, 51.6; P, 7.4; I, 30.3%). The hexane layer was reduced in volume and placed in the freezer to encourage crystallisation. A yellow crystalline material was produced from this solution and this was extracted, dried and analysed. Elemental analysis gave Co, 13.9; H, 3.7; C, 61.1; P, 6.5% ($Me\overset{O}{\overset{\|}{C}}Co(CO)_3PPh_3$ requires Co, 13.2; H, 4.0; C, 61.6; P, 6.9%).

Infra-red examination of the reaction initially showed two peaks in the carbonyl stretching frequency region at $2018_{(w)}$ and $1900_{(s)}$ cm^{-1} due to the anion $Co(CO)_4^-$. On addition of the methyl iodide the peaks in methanol at $2018_{(w)}$ and $1900_{(s)}$ cm^{-1} were found to weaken rapidly and new peaks appeared at $2110_{(w)}$, $2050_{(m\ w)}$, $2030_{(m)}$, $2010_{(m)}$, $1955_{(w)}$, $1935_{(w)}$ and $1710_{(w)}$ cm^{-1}. The two peaks at 1955 and 1935 cm^{-1} slowly disappeared over about 40 minutes and those due to $Co(CO)_4^-$ disappeared within 2 hours. Examination of the hexane layer showed no absorptions due to the $Co(CO)_4^-$ ion, but several peaks were found to develop at $2107_{(w)}$, $2050_{(m)}$, $2025_{(m)}$, $2005_{(m\ s)}$ and $1718_{(w)}$ cm^{-1}. These peaks are assigned to the species $Me\overset{O}{\overset{\|}{C}}Co(CO)_4$.[66,73] These latter absorptions persisted until the addition of triphenyl phosphine which caused the peaks to weaken and disappear and new absorptions to form at $2050_{(m)}$, $1985_{(m)}$, $1969_{(m)}$ and $1690_{(w)}$ cm^{-1}.[98] These persisted indefinitely, and are assigned to $Me\overset{O}{\overset{\|}{C}}Co(CO)_3PPh_3$.

(c) Reaction of $PPN^+Co(CO)_4^-$ with methyl iodide and triphenyl phosphine at -40°C.

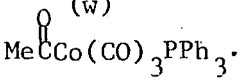
A small amount of $PPN^+Co(CO)_4^-$ (0.7 g, 1 mmol) was dissolved in dichloromethane (50 ml) and the system was stirred rapidly on an acetone/dry ice bath. A solution of methyl iodide (1 g, 7 mmol) also in dichloromethane (20 ml) was slowly added to the $PPN^+Co(CO)_4^-$ solution. The reaction proceeded as outlined in 5.2.1.(a) and the brown solution of $MeCo(CO)_4$ was formed, identified by infra-red spectroscopy. Triphenyl phosphine (0.5 g, 2 mmol) was slowly added to this solution causing the brown colour to become slightly lighter and a yellow solid product was formed. The brown solution was allowed to warm to room temperature and some of the yellow product was seen to dissolve. The yellow product was separated by filtration, washed with hexane and dried under vacuum. Elemental analysis gave Co, 13.6; H, 4.3; C, 61.0; P, 6.5% ($Me\overset{O}{\overset{\|}{C}}Co(CO)_3PPh_3$ requires Co, 13.2; H, 4.0; C, 61.6; P, 6.9%).

Infra-red study at -40^oC of the carbonyl stretching frequency region initially showed carbonyl absorptions at $2015_{(w)}$ and $1900_{(s)}$ cm^{-1} due to the anion $Co(CO)_4^-$. On addition of the methyl iodide the spectrum changed rapidly. Within 15 minutes the peaks due to $Co(CO)_4^-$ had completely disappeared and new absorptions had formed at $2105_{(w)}$, $2035_{(m,w)}$ and $2020_{(m)}$ cm^{-1}. These new peaks were assigned to the species $MeCo(CO)_4$,[66] which has carbonyl peaks at $2104_{(w)}$, $2035_{(m)}$ and $2018_{(s)}$ cm^{-1}. The addition of triphenylphosphine to this system has a rapid effect on the infra-red absorptions. The peaks due to $MeCo(CO)_4$ disappear and new peaks are formed at $2050_{(m)}$, $1980_{(m)}$, $1960_{(m)}$ and $1690_{(w)}$ cm^{-1}. These new peaks are assigned to the species $Me\overset{O}{\overset{\|}{C}}Co(CO)_3PPh_3$.[98]

(d) Reaction of $Na^+Co(CO)_4^-$ with methyl iodide and triphenyl phosphine in THF.

An amalgam of sodium and mercury was prepared by reacting sodium metal with mercury under a nitrogen atmosphere.[74,99] The cleanest portion of this freshly prepared amalgam was taken and reacted with dicobalt octacarbonyl (0.3 g, 1 mmol) in solution in THF (50 ml). The system was stirred for about 2 hours, until the THF was colourless and then the amalgam was run off from the flask. This solution of $Na^+Co(CO)_4^-$ in THF was cooled to -40°C in an acetone/dry ice bath. A cooled solution of methyl iodide (0.3 g, 2 mmol) also in THF (20 ml) was slowly added to the rapidly stirred, cooled solution. The THF slowly began to take on a brown colouration and this darkened as the methyl iodide was added. The system remained unchanged for 2 hours and was then gently allowed to warm to room temperature. Then a solution/suspension of triphenyl phosphine (0.5 g, 2 mmol) in THF (20 ml) was added to the brown solution. This mixture was rapidly stirred and the brown colour faded to a pale brown and a brown/yellow solid was noted to deposit from the solution. The system was placed in the freezer to encourage crystallisation and further yellow solid was observed to form. This solid was separated by filtration, washed with hexane and dried under vacuum before being sent for analysis. Elemental analysis gave Co, 13.6; H, 3.7; C, 60.9; P, 14.6% ($\mathrm{Me\overset{O}{\overset{\|}{C}}Co(CO)_3PPh_3}$ requires Co, 13.2; H, 4.0; C, 61.6; P, 14.3%).

Infra-red analysis in the carbonyl region of the spectrum initially showed only those peaks due to dicobalt octacarbonyl: $2073_{(s)}$, $2046_{(s)}$, $2029_{(s)}$, $1866_{(m)}$ and $1858_{(m)}$ cm^{-1}. As the reaction with the amalgam occurred the absorptions due to dicobalt octacarbonyl slowly reduced in intensity and were eventually replaced by a single peak at $1900_{(m)}$ cm^{-1}, due to $Co(CO)_4^-$. Lowering the temperature of the system to -40°C had no effect on the infra-red spectrum. On addition of methyl iodide the peak at 1900 cm^{-1} slowly disappeared and was replaced by new absorptions at $2105_{(w)}$, $2035_{(m\ w)}$ and $2029_{(s)}$ cm^{-1} due to the species $MeCo(CO)_4$. The spectrum changed on warming to give peaks at $2110_{(w)}$, $2050_{(m\ w)}$, $2030_{(m)}$, $2010_{(m)}$ and $1715_{(w)}$ cm^{-1} due to the formation of $\mathrm{Me\overset{O}{\overset{\|}{C}}Co(CO)_4}$.[66] When triphenyl phosphine was added the spectrum slowly changed as these absorptions were destroyed and new peaks formed at $2050_{(m)}$, $1980_{(m)}$, $1960_{(m)}$, $1690_{(w)}$ cm^{-1}. These new absorptions are assigned to the species



$\mathrm{Me\overset{O}{\overset{\|}{C}}Co(CO)_3PPh_3}$.[98]

(e) Reaction of $[Co(CO)_3PPh_3]_2$ with methyl iodide in methanol.

A small amount of the red/brown solid $[Co(CO)_3PPh_3]_2$ (0.8 g, 1 mmol) was suspended in methanol (40 ml) and the mixture was stirred rapidly. Methyl iodide (0.7 g, 5 mmol) in methanol (20 ml) was added to this system and the system observed for two hours. No reaction was observed to take place. The system was fitted with a condenser and heated at reflux temperature (65 - 68°C) for a further 2 hours. Again no reaction was observed to occur. The system was then sealed in a Carius tube and heated to 110°C for 4 hours. The red/brown suspended solid was observed to have reacted to form a solution that was violet at 110°C and brown/pink at room temperature. The solution was cooled to liquid nitrogen temperature, the tube opened, evacuated, refilled with nitrogen and allowed to warm to room temperature. The brown/pink solution was reduced in volume and a brown precipitate formed. The precipitate was separated by filtration, washed with hexane and dried. Elemental analysis gave Co, 6.8; H, 3.8; C, 51.0; P, 7.1; I, 30.0% ($Co(PPh_3)_2I_2$ requires Co, 7.0; H, 3.6; C, 51.6; P, 7.4; I, 30.3%). The filtrate, a brown solution, was evaporated and produced a black solid which was also washed with hexane. The black material was dried under vacuum and sent for elemental analysis. Analysis gave Co, 19.3; I, 81.7% (CoI_2 requires Co, 18.8; I, 81.2%).

Infra-red solution spectroscopy in the carbonyl stretching frequency region initially showed no carbonyl absorptions. The $[Co(CO)_3PPh_3]_2$ was in suspension and was not detected in the spectra. No change was observed in the spectrum as the system was refluxed. The infra-red spectrum of the brown/pink solution from the Carius tube was examined and showed only one absorption at 1730 cm^{-1} which was not due to the methanol solvent. No absorptions were observed in the terminal or doubly bridging metal carbonyl stretching frequency regions, indicating that the product in solution was not a carbonyl species.

(f) Reaction of $[Co(CO)_3PPh_3]_2$ with iodine in methanol.

A suspension of the red/brown $[Co(CO)_3PPh_3]_2$[54] (0.8 g, 1 mmol) was prepared in methanol (40 ml) and the system was rapidly stirred. Black crystals of iodine (0.5 g, 2 mmol) were dissolved in methanol (20 ml) and the resulting brown solution was slowly added to the suspension. The system was examined at room temperature for three hours and no reaction was observed to take place. The reaction vessel was fitted with a condenser and the mixture refluxed (at 65 - 67°C) for 2 hours. Reaction occurred to form the brown solution. The system was permitted to cool to room temperature and the volume reduced by half "in vacuo". A brown precipitate formed and was separated by filtration. The solid was washed with hexane to remove free iodine and triphenylphosphine, dried and sent for analysis. Elemental analysis gave Co, 7.3; H, 3.4; C, 52.1; P, 7.7; I, 30.4% ($Co(PPh_3)_2I_2$[110,112] requires Co, 7.0; H, 3.6; C, 51.6; P, 7.4; I, 30.3%). The brown filtrate was evaporated "in vacuo" and a black solid was formed. This material was washed with hexane to remove residual iodine. The residue was dried under vacuum and submitted for elemental analysis. Analysis gave Co, 18.2; I, 81.6% (CoI_2 requires Co, 18.8; I, 81.2%).

The reaction was examined spectroscopically in the carbonyl stretching frequency region of the infra-red spectrum. Initially at room temperature no carbonyl absorptions were detected as the $[Co(CO)_3PPh_3]_2$ was in suspension not in solution. No carbonyl absorptions were observed as the system reacted and therefore the carbonyl complex either produced insoluble intermediates, or they were destroyed very rapidly if reaction occurred in solution. The spectrum of the brown solution was also taken at room temperature and no peaks assignable to carbonyl stretching frequencies were detected.

7.2.2. Discussion

The reaction of $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ with iodine proceeded as explained in 6.2.1., and cobalt (II) iodide was formed in solution. The addition of triphenyl phosphine to the solution produced a change in colour from brown to pink, and evaporation of the solvent produced a brown solid, identified as $Co(PPh_3)_2I_2$.[109-115]

Divalent cobalt forms numerous complexes of various stereochemical types, where octahedral and tetrahedral ones are the most common. Co^{II} forms tetrahedral complexes more readily than any other transition-metal ion. This is in accord with the fact that for a d^7 ion, ligand-field stabilisation energies disfavour the tetrahedral configuration, relative to the octahedral one, to a smaller extent than for any other d^n $(1 \leqslant n \leqslant 9)$ configuration, although it should be carefully noted that this argument is only valid in the comparison of one metal ion to another, and not for assessing the absolute stabilities of the configurations for any particular ion.

As the stability difference between octahedral and tetrahedral Co^{II} complexes is small, there are several cases in which the two stereochemical types with the same ligand are both known, and may be in equilibrium.

Tetrahedral complexes, $[CoX_4]^{2-}$ are generally formed with mono-dentate anionic ligands, such as Cl^-, Br^-, I^-, SCN^- and N_3^-; with a combination of two such ligands and two neutral ligands (L) pseudotetrahedral neutral complexes of the type CoL_2X_2 are formed e.g. $Co(PPh_3)I_2$.

With methyl iodide and $[Co(MeOH)_6^{2+}][Co(CO)_4^-]_2$ the reaction follows the pattern established in 6.2.1.: the species cobalt (II) iodide is formed in methanol together with the acyl species, $\mathrm{Me\overset{\overset{O}{\|}}{C}Co(CO)_4}$, which was extracted into the hexane solvent. On addition of triphenyl phosphine to this system, the pseudotetrahedral product $Co(PPh_3)_2I_2$ is formed in the methanol and the species $\mathrm{Me\overset{\overset{O}{\|}}{C}Co(CO)_3PPh_3}$[93] is generated in the hexane. This latter material crystallises from the hexane on cooling.

The triphenyl phosphine ligand is simply substituted into the acyl cobalt tetracarbonyl and thus one molecule of carbon monoxide is evolved:

$$\mathrm{Me\overset{\overset{O}{\|}}{C}Co(CO)_4} + \mathrm{PPh_3} \longrightarrow \mathrm{Me\overset{\overset{O}{\|}}{C}Co(CO)_3PPh_3} + \mathrm{CO} \qquad (1)$$

The reaction of methyl iodide with $PPN^+Co(CO)_4^-$ at -40°C proceeds as explained in the previous chapter, and the methyl cobalt tetracarbonyl, $MeCo(CO)_4$,[66] is generated. On addition of triphenyl phosphine the acyl cobalt tricarbonyl phosphine compound is formed, without loss of carbon monoxide:[93,108]

$$\mathrm{MeCo(CO)_4} + \mathrm{PPh_3} \xrightarrow{-40^{\circ}C} \mathrm{Me\overset{\overset{O}{\|}}{C}Co(CO)_3PPh_3} \qquad (2)$$

Sodium tetracarbonylcobaltate initially reacts at -40°C with methyl iodide to form the methyl cobalt tetracarbonyl and, on warming to room temperature, part of the sample of this unstable species decomposes. The generated carbon monoxide converts some of the methyl complex to the more stable acyl product ($\mathrm{Me\overset{\overset{O}{\|}}{C}Co(CO)_4}$[66]). The reaction of this acyl compound with triphenyl phosphine then proceeds as in equation (1) above.

The reaction of triphenyl phosphine with the alkyl compound is believed to occur by a migratory-insertion reaction.[103] The reaction takes place by the migration of the alkyl group to an adjacent carbonyl group forming a coordinatively unsaturated cobalt tricarbonyl species. In a separate step this intermediate tricarbonyl species adds an external ligand at the site vacated by the migrating alkyl group. In most cases that have been examined this reaction is highly stereospecific,[104-107] with alkyl groups having chirality at the metal-carbon bond, migrating with retention of configuration. The rates of these reactions and the position of equilibrium depend upon the strengths of the metal-carbon bond and of the metal-carbon monoxide bond in the original alkyl complex. First row, 3d transition metal alkyls are usually more reactive than second- and third-row 4d and 5d transition metal alkyls. Presumably this reactivity profile results from modest differences in metal-carbon bond strengths, the first-row metal carbon bonds being slightly weaker than those of the 4d and 5d metals.

Thus the reactivity of the methyl cobalt tetracarbonyl with triphenyl phosphine is such that the generation of the species $MeCo(CO)_3PPh_3$ cannot be performed simply by addition of triphenyl phosphine. Its simplest method of preparation is to react $[Co(CO)_3PPh_3]_2$ with sodium amalgam to form the salt $Na^+[Co(CO)_3PPh_3^-]$.[98] This is then reacted with methyl iodide to form the methyl species, $MeCo(CO)_3PPh_3$,[98] although care must be taken to prevent reaction of this species with any free carbon monoxide as the acyl species is then formed readily.

The compound $[Co(CO)_3PPh_3]_2$ reacts with methyl iodide at ∿ 110°C and the solid products obtained from the reaction are CoI_2 and $Co(PPh_3)_2I_2$. The change in colour of the solution from violet to pink/brown is possibly due to free iodine in solution or due to the change in configuration of the $[Co^{2+}(MeOH)_6]$ species from a tetrahedral to a octahedral configuration, although the latter possibility is much less likely. The solution infra-red of the system shows an absorption at 1730 cm^{-1} which is possibly due to an organic carbonyl compound formed from decomposition of a species such as $\mathrm{Me\overset{\overset{O}{\|}}{C}Co(CO)_3PPh_3}$ at the high reaction temperature. G.L.C. examination of this solution showed that the organic product was probably acetone.

Reaction of $[Co(CO)_3PPh_3]_2$ with iodine follows much the same pattern: the solid products obtained on evaporating the system were CoI_2 and $Co(PPh_3)_2I_2$. The reaction however was found to occur at a lower temperature and the violet solution was not observed. The infra-red solution spectra in the carbonyl stretching frequency region showed no new absorptions around 1700 cm^{-1}. This indicates that the species formed in the preceding experiment, with methyl iodide, is not produced when iodine itself rather than methyl iodide is employed.

7.3. High Pressure Study of the Cobalt/Iodine/Ligand/Methanol System

7.3.1. Experimental

The basic experimental details are very similar to those described in Chapter 3. The study was performed in the same high pressure infra-red cells, and the analysis of products was routinely performed by G.L.C. The physical conditions used were varied in order to find their influence upon the course of the reaction. The iodine (or iodide) employed in the reactions was placed in the bomb together with the ligand and the cobalt (II) acetate tetrahydrate, and then methanol was added to the mixture.

The bomb was purged with nitrogen before pressurising with 1:1 CO/H_2 synthesis gas to a pressure of approximately 140 Atm, and was stirred as quickly as possible. The temperature was raised to the selected level (170 - 220^{o}C) causing the gas pressure to increase to about 200 Atm. The reaction was allowed to run for 2 hours while the pressure was maintained at 200 Atm. When the run was completed the system was allowed to cool overnight to room temperature and the bomb was depressurised slowly the next day. The resultant products were syringed from the bomb and analysed.

The results of varying some of the reaction parameters of the iodine/ iodide promoted and ligand stabilised homologation of methanol are discussed with reference to the yield and selectivity of some important reaction products.

Catalyst.

The catalyst used in these experiments consisted of cobalt (II) acetate tetrahydrate plus a promoter (iodine or iodide) and a stabilising ligand (phosphine, arsine or stibine). This combination is designed to take advantage of both the extra thermal stability and enhanced selectivity to ethanol of the catalyst, provided by the stabilising ligand and the promoting effect of the iodine (or iodide).

7.3.2. Discussion

(a) Effect of temperature on the cobalt/methanol/iodine/phosphine system.

The reaction has been examined in the temperature range 170 - 225°C and the results are presented in Table 7.1. The study has been performed at a 1:1 cobalt:ligand ratio, and a 1:1 cobalt atoms:iodine atoms ratio using elemental iodine as the promoter. The percentage yields and selectivities are illustrated graphically in Fig. 7.1. and Fig. 7.2. The yield of ethanol passed through a maximum at 205°C of ∿ 15%, falling to 6% at 225°C. The decrease in yield of ethanol was accompanied by a decrease in yield of all the major products, and in the conversion of methanol itself. At higher reaction temperatures (210 - 225°C) a black deposit was

Table 7.1.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	PPh_3 (moles)	Iodine (I_2) (moles)	Reaction Time (hr.)	Pressure (Atm)	Temp. (^oC)	Ratio Co:Ligand	Ratio Co:I	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
67	0.56	7.0×10^{-3}	7.0×10^{-3}	3.5×10^{-3}	2	200	170	1:1	1:1	Yield	6.6	8.0	1.5	2.9
										Selectivity	23.6	28.5	5.2	10.3
68	0.56	7.0×10^{-3}	7.0×10^{-3}	3.5×10^{-3}	2	200	185	1:1	1:1	Yield	11.7	6.4	3.3	1.4
										Selectivity	36.5	19.0	9.2	3.6
69	0.56	7.0×10^{-3}	7.0×10^{-3}	3.5×10^{-3}	2	200	195	1:1	1:1	Yield	14.1	6.1	4.0	1.2
										Selectivity	42.5	18.4	12.1	3.6
70	0.56	7.0×10^{-3}	7.0×10^{-3}	3.5×10^{-3}	2	200	205	1:1	1:1	Yield	15.0	6.0	5.0	1.0
										Selectivity	45.8	17.8	14.8	3.0
71	0.56	7.0×10^{-3}	7.0×10^{-3}	3.5×10^{-3}	2	200	215	1:1	1:1	Yield	12.7	5.4	4.3	1.0
										Selectivity	41.9	17.9	14.7	3.3
72	0.56	7.0×10^{-3}	7.0×10^{-3}	3.5×10^{-3}	2	200	225	1:1	1:1	Yield	6.0	4.3	1.9	0.7
										Selectivity	29.9	21.1	9.3	3.4

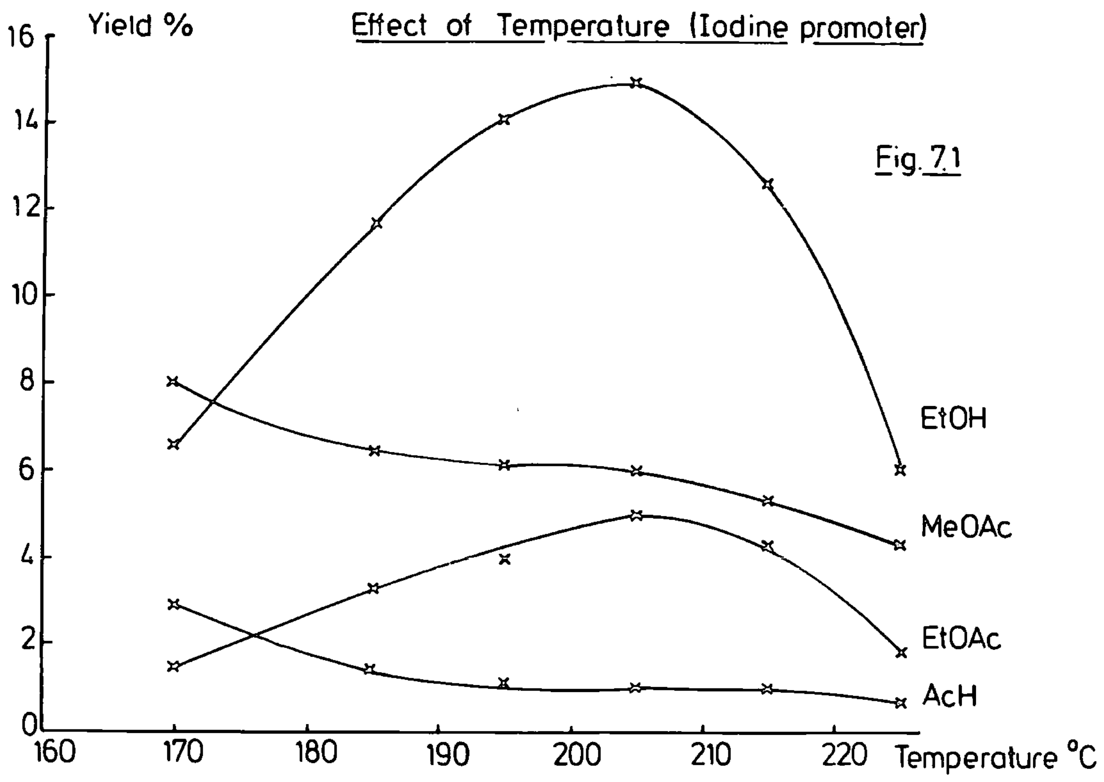

Effect of Temperature (Iodine promoter)

Fig. 7.1

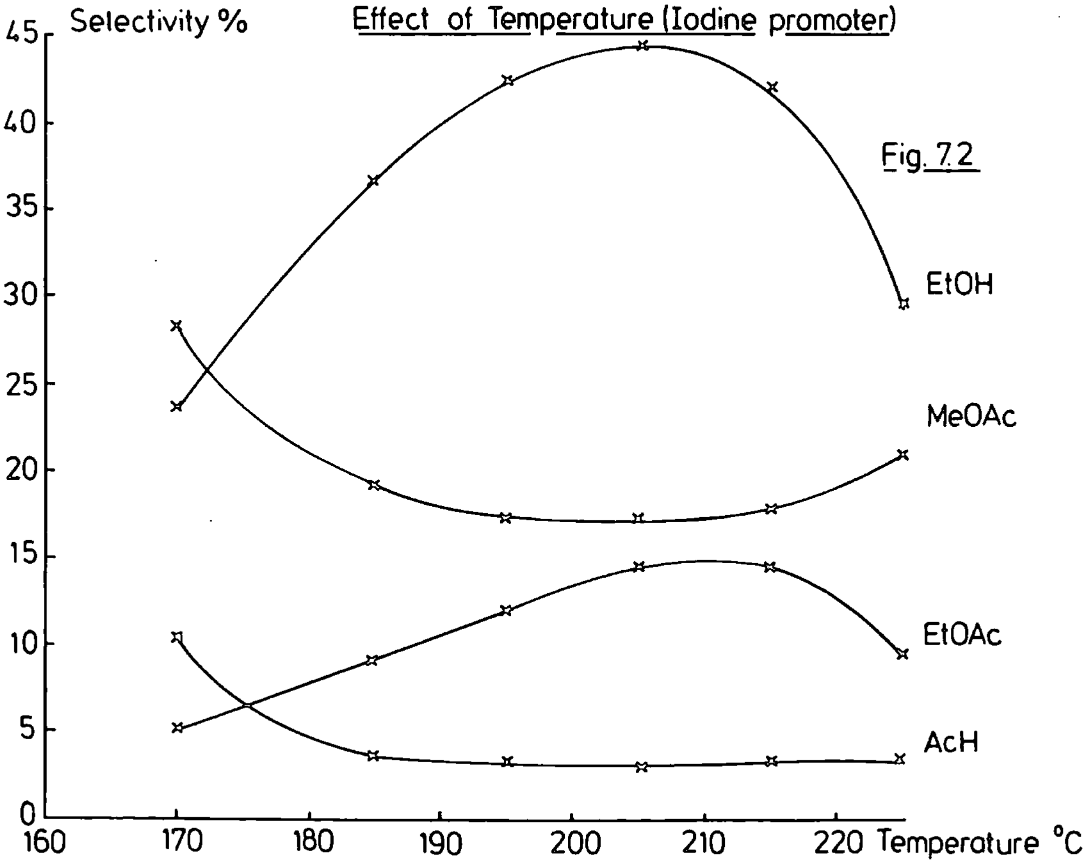

Effect of Temperature (Iodine promoter)

Fig. 7.2

found on the walls of the bomb which was believed to be cobalt metal. Thus it seems likely that the lower conversion of methanol at higher temperatures is due to the loss of active catalyst by the plating out of cobalt metal, as the catalyst is thermally unstable at these elevated temperatures i.e. the stabilising ligand thus allows the reaction to be run at 205°C (compared with 185°C for the unstabilised system) though at still higher temperatures the catalyst is once again decomposed.

At lower temperatures (170 - 195°C) the yields of ethanol and ethyl acetate were found to be reduced compared with those at 205°C. This can be regarded as due to the homologation reaction being slower at these reduced temperatures, or because only a fraction of the cobalt has been converted into active catalyst. The formation of methyl acetate and acetaldehyde is enhanced at the lower temperatures possibly due to less efficient reduction of the acetaldehyde to ethanol.

The selectivities follow closely the same pattern as the yields of the major products except for the selectivity to methyl acetate which increases at high temperature.

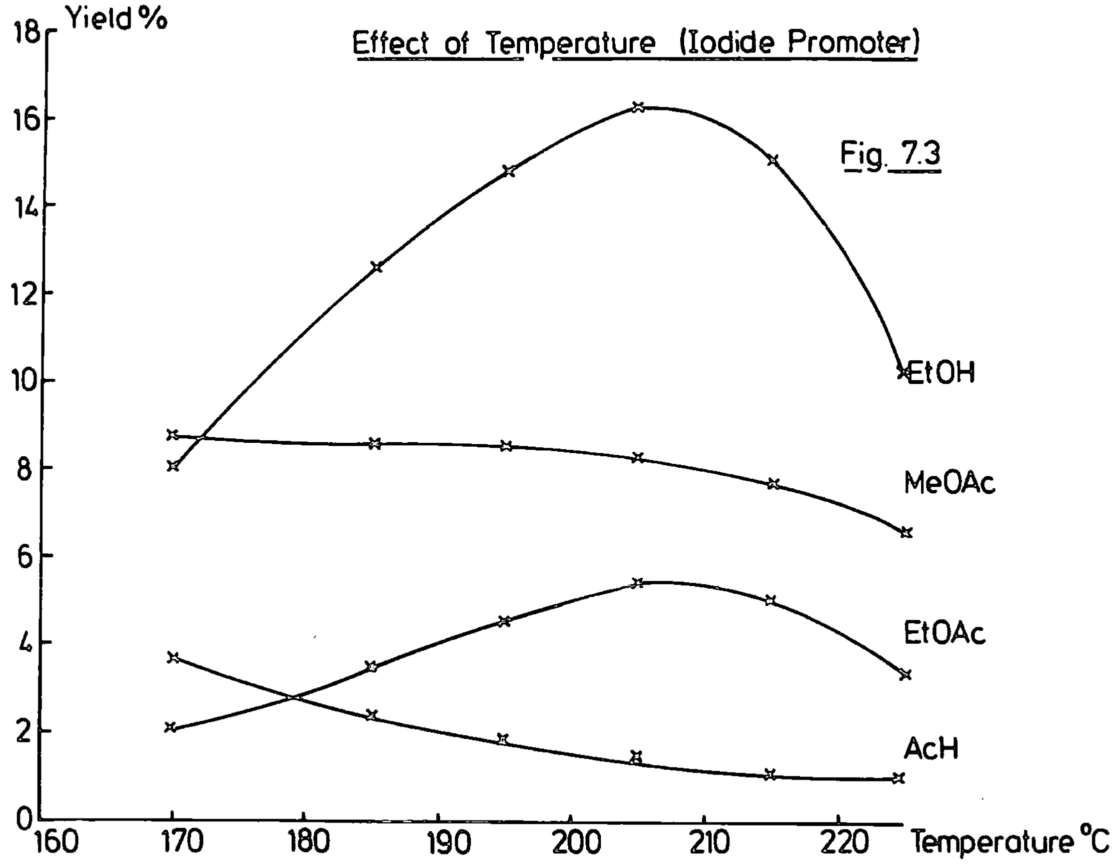
(b) Effect of temperature on the cobalt/methanol/iodide/phosphine system.

The reaction has been examined in the same temperature range (170 - 225°C) and the results are presented in Table 7.2. The study was performed at 1:1:1, cobalt:ligand:iodide ratio using potassium iodide as the promoter. The percentage yields and selectivities of the major products are illustrated graphically in Fig. 7.3. and Fig. 7.4.

The results obtained for the iodide promoter are very similar to those found when elemental iodine was employed under the same conditions. The yields of the major products were enhanced when the iodide promoter

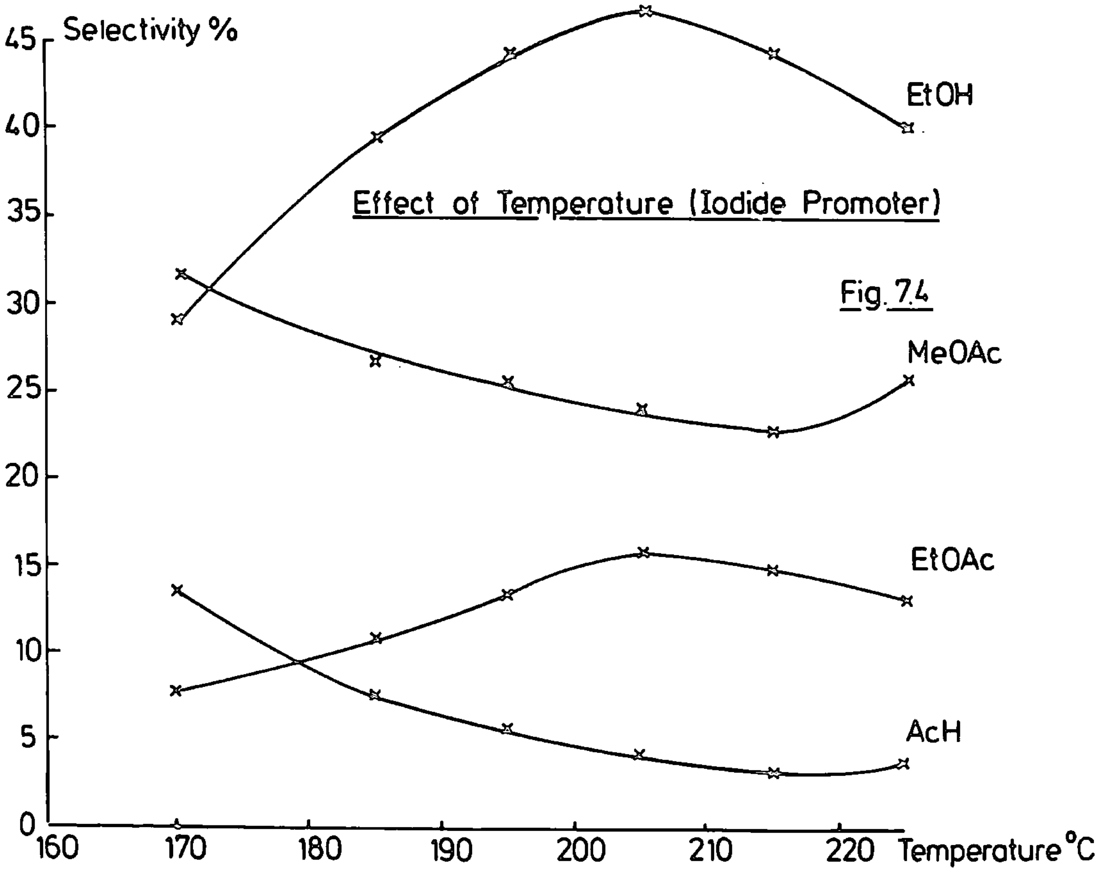
Table 7.2.

Expt. No.	MeOH (moles)	Co(OAc)$_2$ 4H_2O (moles)	PPh_3 (moles)	KI (moles)	Reaction Time (hr.)	Pressure (Atm)	Temp. (^oC)	Ratio Co:Ligand	Ratio Co:I^-	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
73	0.56	7.0×10^{-3}	7.0×10^{-3}	7.0×10^{-3}	2	200	170	1:1	1:1	Yield	8.0	8.7	2.1	3.7
										Selectivity	29.0	31.6	7.6	13.4
74	0.56	7.0×10^{-3}	7.0×10^{-3}	7.0×10^{-3}	2	200	185	1:1	1:1	Yield	12.6	8.6	3.5	2.4
										Selectivity	39.3	26.8	10.9	7.5
75	0.56	7.0×10^{-3}	7.0×10^{-3}	7.0×10^{-3}	2	200	195	1:1	1:1	Yield	14.8	8.5	4.5	1.9
										Selectivity	44.4	25.5	13.5	5.7
76	0.56	7.0×10^{-3}	7.0×10^{-3}	7.0×10^{-3}	2	200	205	1:1	1:1	Yield	16.3	8.3	5.5	1.5
										Selectivity	47.0	24.0	15.9	4.3
77	0.56	7.0×10^{-3}	7.0×10^{-3}	7.0×10^{-3}	2	200	215	1:1	1:1	Yield	15.1	7.7	5.1	1.1
										Selectivity	44.2	22.6	14.9	3.2
78	0.56	7.0×10^{-3}	7.0×10^{-3}	7.0×10^{-3}	2	200	225	1:1	1:1	Yield	10.3	6.6	3.4	1.0
										Selectivity	40.1	25.7	13.2	3.9



Effect of Temperature (Iodide Promoter)

Fig. 7.3



Effect of Temperature (Iodide Promoter)

Fig. 7.4

was used but the increase was not great. The increase in yields of the products due to the iodide promoter when compared to the iodine promoter was present throughout the temperature range studied and was also reflected in the increased selectivities.

These results illustrate that iodide is a more efficient promoter than elemental iodine for the ligand stabilised homologation of methanol. This confirms the results obtained in Chapter 5 and Chapter 6 that, in the case of the promoted reaction, iodide is a better promoter than elemental iodine.

(c) Effect of iodide concentration on the cobalt/methanol/iodine/phosphine system.

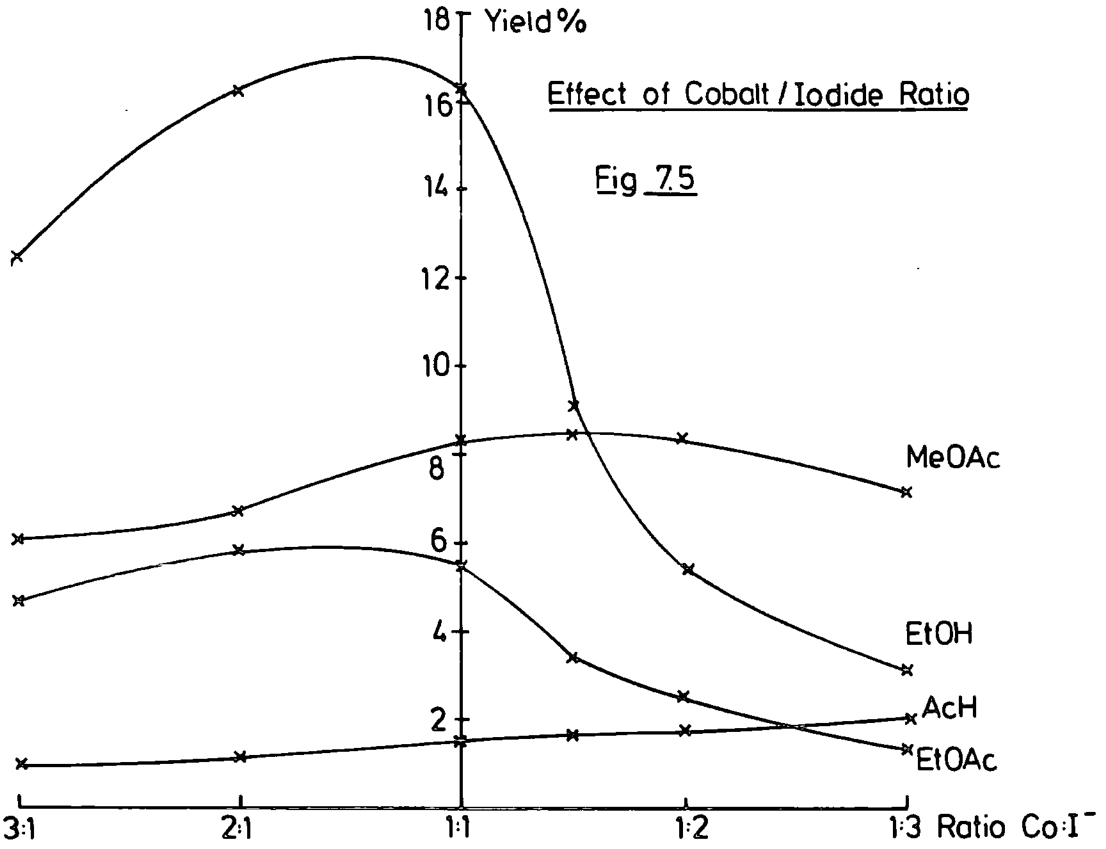
The effect of iodide concentration on the homologation reaction is recorded in Table 7.3. The iodide/cobalt ratio was varied in the range 3:1 - 1:3 by addition of potassium iodide to the reaction, as the potassium ion is believed to be inert in this system. The results obtained are illustrated graphically in Fig. 7.5. and Fig. 7.6. in terms of the percentage yield and selectivity of the four major products.

The best ratio of cobalt to iodide for producing ethanol appears to between 2:1 - 1:1. In fact any ratio of cobalt:iodide greater than 1:1 would appear to be a useful combination for generating ethanol, with the least quantity of unwanted by-products.

At higher concentrations of iodide the yield and selectivity of ethanol fall rapidly and the preferred reaction product is methyl acetate. This trend continues as the iodide concentration increases and the selectivity to methyl acetate increases still further. The yield and selectivity to acetaldehyde remain fairly low but also show a steady increase as the iodide concentration increases.

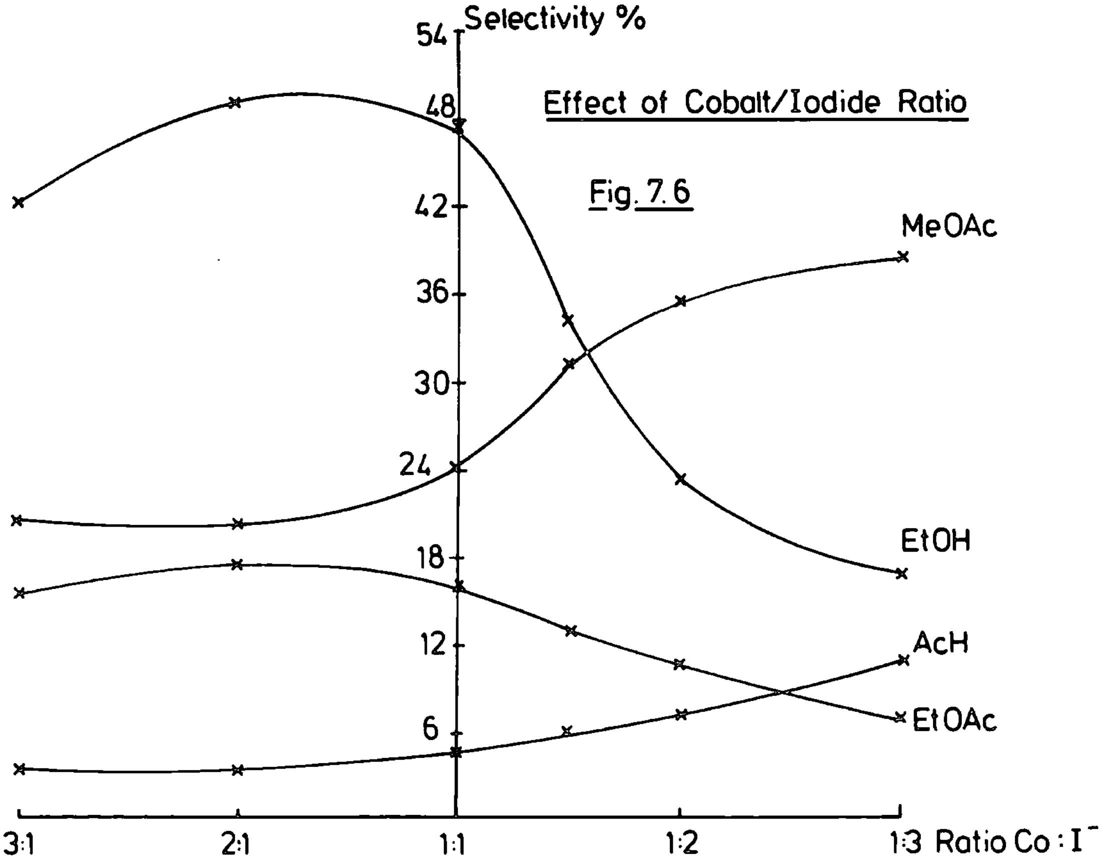
Table 7.3.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	PPh_3 (moles)	KI (moles)	Reaction Time (hr.)	Pressure (Atm)	Temp. (^oC)	Ratio Co:Ligand	Ratio $Co:I^-$	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
76	0.56	7.0×10^{-3}	7.0×10^{-3}	7.0×10^{-3}	2	200	205	1:1	1:1	Yield	16.3	8.3	5.5	1.5
										Selectivity	47.0	24.0	15.9	4.3
79	0.56	7.0×10^{-3}	7.0×10^{-3}	14.0×10^{-3}	2	200	205	1:1	1:2	Yield	5.4	8.3	2.5	1.7
										Selectivity	23.0	35.4	10.7	7.3
80	0.56	7.0×10^{-3}	7.0×10^{-3}	21.0×10^{-3}	2	200	205	1:1	1:3	Yield	3.1	7.1	1.3	2.0
										Selectivity	16.8	38.5	7.0	10.8
81	0.56	7.0×10^{-3}	7.0×10^{-3}	3.5×10^{-3}	2	200	205	1:1	2:1	Yield	16.3	6.7	5.8	1.1
										Selectivity	49.3	20.3	17.5	3.3
82	0.56	7.0×10^{-3}	7.0×10^{-3}	2.3×10^{-3}	2	200	205	1:1	3:1	Yield	12.5	6.1	4.7	1.0
										Selectivity	42.1	20.5	15.8	3.4
83	0.56	7.0×10^{-3}	7.0×10^{-3}	10.5×10^{-3}	2	200	205	1:1	2:3	Yield	9.1	8.4	3.4	1.6
										Selectivity	34.1	31.5	12.8	6.0



Effect of Cobalt / Iodide Ratio

Fig 7.5



Effect of Cobalt/Iodide Ratio

Fig. 7.6

(d) Effect of phosphine concentration on the cobalt/methanol/iodide/ phosphine system.

The effect of the phosphine concentration on the reaction is presented in Table 7.4. The triphenyl phosphine/cobalt ratio was varied in the range 2:1 - 1:2 and the reaction products, yields and selectivities are recorded in Fig. 7.7.

The phosphine concentration appeared to have very little effect upon the yield of methyl acetate and acetaldehyde. The yield of ethanol and ethyl acetate appeared unaffected by the phosphine concentration, provided the ratio of cobalt/phosphine was between 1:1 to 1:2. However at lower concentrations of phosphine the reaction was found to be less effective and the yields of ethanol and ethyl acetate were reduced substantially. This is probably due to a combination of loss of catalyst at this elevated temperature as insufficient stabilising ligand is present, and the lower catalytic activity of the iodide-only promoted species compared with the promoted and stabilised species.

The selectivities of the four major products showed a very similar pattern, though at higher ligand concentration there was a general decrease in selectivity of all the major products as the product spectrum broadened and more of the minor by-products were produced. The most efficient cobalt/ligand ratio for generating ethanol from this system is thus 1:1.

(e) Effect of ligand type on the cobalt/methanol/iodide/ligand system.

The effect of changing the ligand type on the reaction is assessed for the ligands tri-n-butylphosphine, triphenyl arsine and triphenyl stibine and is reported in Table 7.5.

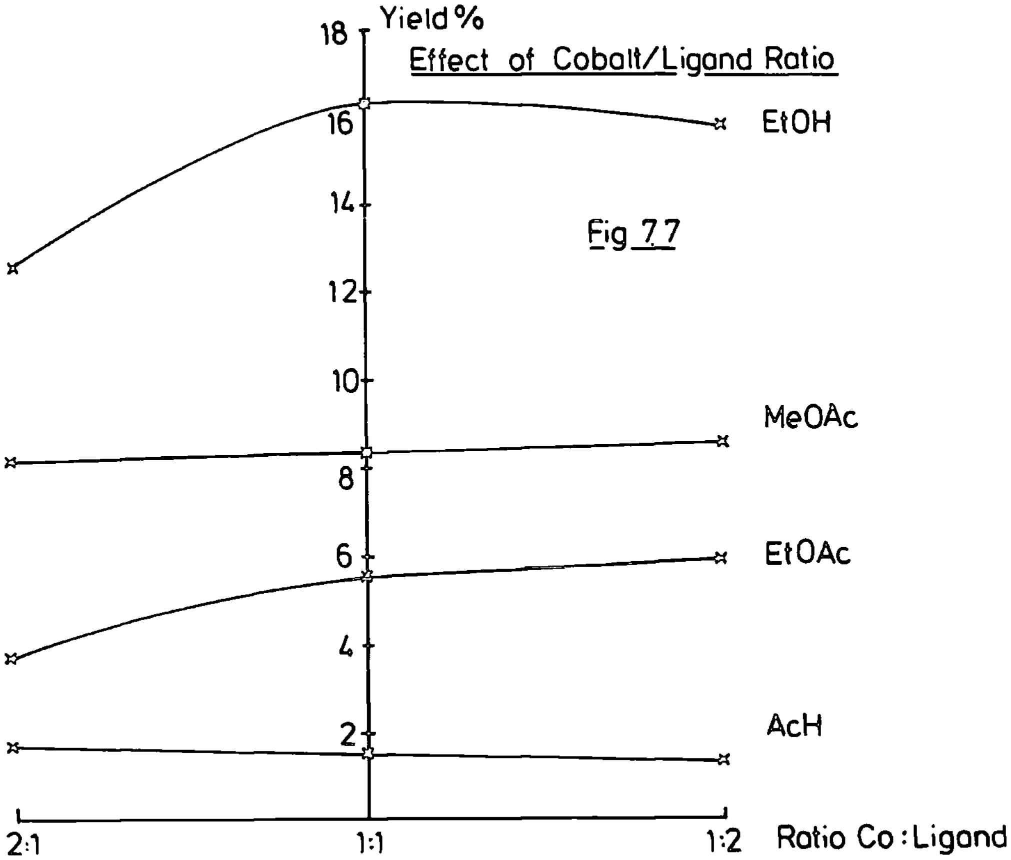
The use of tri-n-butylphosphine enhanced the activity of the catalyst

Table 7.4.

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	PPh_3 (moles)	KI (moles)	Reaction Time (hr.)	Pressure (Atm)	Temp. (^oC)	Ratio Co:Ligand	Ratio $Co:I^-$	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
76	0.56	7.0×10^{-3}	7.0×10^{-3}	7.0×10^{-3}	2	200	205	1:1	1:1	Yield	16.3	8.3	5.5	1.5
										Selectivity	47.0	24.0	15.9	4.3
84	0.56	7.0×10^{-3}	14.0×10^{-3}	7.0×10^{-3}	2	200	205	1:2	1:1	Yield	15.8	8.6	5.9	1.3
										Selectivity	40.3	21.9	15.0	3.3
85	0.56	7.0×10^{-3}	3.5×10^{-3}	7.0×10^{-3}	2	200	205	2:1	1:1	Yield	12.6	8.1	3.7	1.7
										Selectivity	34.0	21.9	10.1	4.6

Table 7.5

Expt. No.	MeOH (moles)	$Co(OAc)_2$ $4H_2O$ (moles)	Ligand (moles)	KI (moles)	Reaction Time (hr.)	Pressure (Atm)	Temp. (^oC)	Ratio Co:Ligand	Ratio $Co:I^-$	Products	Ethanol %	Methyl Acetate %	Ethyl Acetate %	Acetaldehyde %
86	0.56	7.0×10^{-3}	7×10^{-3} $P(C_4H_9)_3$	7.0×10^{-3}	2	200	205	1:1	1:1	Yield	17.0	8.5	5.8	1.7
										Selectivity	49.3	24.7	16.8	4.9
87	0.56	7.0×10^{-3}	7×10^{-3} $AsPh_3$	7.0×10^{-3}	2	200	205	1:1	1:1	Yield	2.6	12.5	1.3	5.1
										Selectivity	6.1	29.3	3.0	12.0
88	0.56	7.0×10^{-3}	7×10^{-3} $SbPh_3$	7.0×10^{-3}	2	200	205	1:1	1:1	Yield	3.3	10.4	1.5	6.2
										Selectivity	8.2	25.7	3.7	15.3



Effect of Cobalt/Ligand Ratio

Fig 7.7

Effect of Cobalt/Ligand Ratio

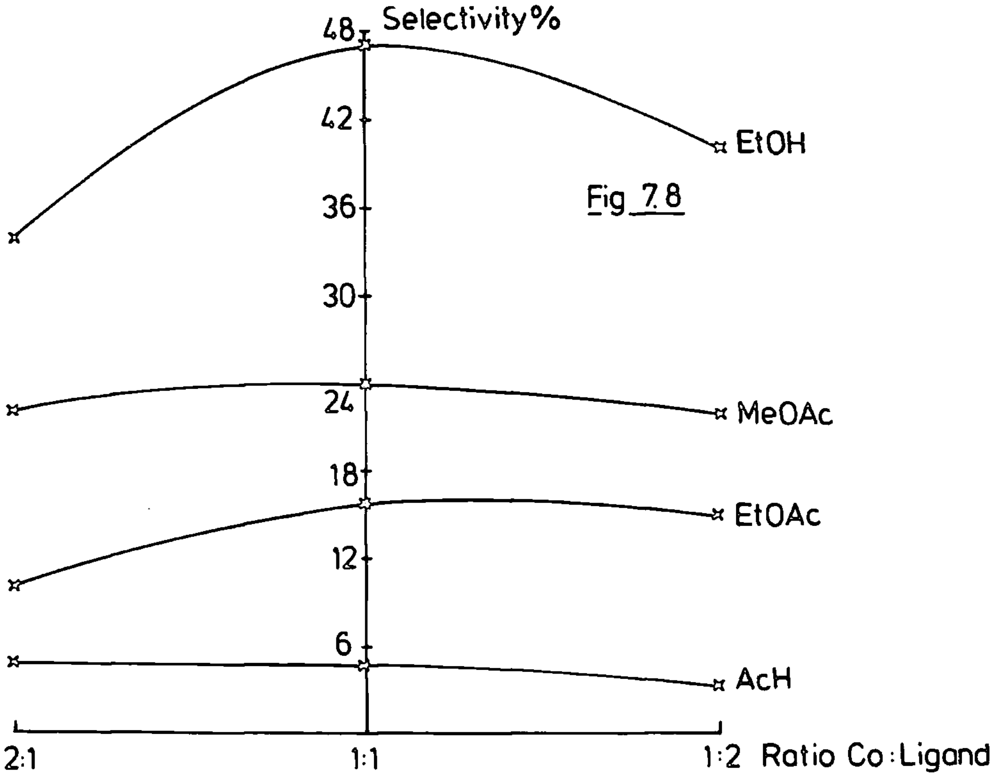


Fig 7.8

and an increased yield was observed for all the products. This provides evidence for the belief that by careful choice of phosphine type the proportion of ethanol to by-products may be increased.

The ligands triphenyl arsine and triphenyl stibine have a markedly different influence upon the homologation reaction. The yield of ethanol is reduced greatly and the two major products of the reaction are now methyl acetate and acetaldehyde. Studies performed by colleagues at British Petroleum Research Centre indicate that at lower temperatures, $\sim 180^{o}C$, the reaction of methanol under these conditions (iodide promoter and arsine or stibine ligand) may enable acetaldehyde to be synthesised very efficiently.

7.4. High Pressure Infra-Red Study of the Cobalt/Methanol/Ligand/Iodine System

7.4.1. Experimental

The reactions were all performed in the same cells used for the autoclave studies, but the infra-red facility was utilised to follow the course of the reaction. It was found that these systems were fairly efficient and quickly produced a wide range of organic materials. It was found necessary to examine the system at the maximum reaction temperature only for $\sim \frac{1}{2}$ hour as the spectra of the catalytic species soon became obscured by absorptions due to the organic materials.

The materials added to the cell, dicobalt octacarbonyl, ligand, iodine (or iodide) and methanol, were inserted in a particular order. The ligand and iodine (or iodide) were first dissolved/suspended in the methanol and this mixture was syringed into the bomb. The bomb was then flushed with nitrogen before addition of the dicobalt octacarbonyl as a solid. The bomb was flushed once again with nitrogen, sealed and pressurised to the level selected with the appropriate gas or gas mixture.

The infra-red spectra were recorded regularly as the temperature was raised from room temperature in increments of approximately 30°C to the final selected reaction temperature; at each temperature, time was allowed for the system to reach equilibrium before the spectra were recorded.

Once the system had been examined at the final reaction temperature, it was allowed to cool slowly to room temperature before the gas pressure above the system was released. The infra-red spectra were taken at room temperature before depressurising the bomb, and once the gas had been released, a standard infra-red solution spectrum of the extracted liquid was run. The solution was also examined by chromatographic methods to check that the reaction products had not built up to a spectroscopically intolerable level.

7.4.2. Discussion

(a) Study of the cobalt/methanol/ligand/iodine (or iodide) system under nitrogen pressure.

A series of reactions were studied with a pressure of nitrogen (100 Atm) above the systems. The pressure of nitrogen appeared to have no detectable effect upon the reaction which proceeded to form $Co(PPh_3)_2I_2$.

Dicobalt octacarbonyl and excess triphenyl phosphine were reacted with elemental iodine under nitrogen pressure and the infra-red spectrum in the carbonyl stretching frequency region observed. No carbonyl absorptions were observed at any time as the temperature of the reaction system was raised to a maximum of 100°C. The system was allowed to cool and a brown liquid was syringed from the vessel after depressurising and opening. The brown liquid was evaporated to dryness and a brown solid was formed. This was washed with hexane to remove the excess triphenyl phosphine, dried "in vacuo" and submitted for analysis. This gave Co, 6.8; H, 3.5; C, 51.2; P, 7.8; I, 30.0% [$Co(PPh_3)_2I_2$[111] requires Co, 7.0; H, 3.6; C, 51.6; P, 7.4; I, 30.3%].

The reaction of triphenyl phosphine, dicobalt octacarbonyl and sodium iodide was also examined under nitrogen pressure. The only peaks observed were at $2000_{(m)}$ and $1900_{(s)}$ cm^{-1} and could be assigned to the species $[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-]$. With increase in temperature both of these peaks were found to reduce in intensity. By 100°C the two absorptions had completely disappeared and did not reappear on heating to 120°C. The bomb was cooled and opened and a red/brown solid was found to have deposited. The red/brown solid was washed with hexane and dried, before elemental and solid infra-red analysis. These gave Co, 14.3; H, 3.4; C, 62.7; P, 7.8; [$[Co(CO)_3PPh_3]_2$ requires Co, 14.6; H, 3.7; C, 62.2; P, 7.7%]: carbonyl absorptions at $1970_{(sh)}$, $1950_{(s)}$ and $1900_{(w)}$ cm^{-1}. These analyses showed the red/brown solid to be the dimer $[Co(CO)_3PPh_3]_2$.[38]

(b) Study of the system under carbon monoxide pressure.

A series of reactions were performed under carbon monoxide pressure of approximately 100 Atm and investigated to reveal the species present at the reaction temperature.

Excess triphenyl phosphine and dicobalt octacarbonyl were reacted with iodine under carbon monoxide pressure. The system however showed no absorptions that could be attributed to carbonyl groups as the iodine rapidly attacked the dicobalt octacarbonyl. As the temperature approached 170°C weak carbonyl absorptions appeared at $2050_{(w)}$, $1980_{(w)}$, $1970_{(w)}$ and $1690_{(w)}$ cm^{-1} believed due to $Me\overset{\overset{O}{\|}}{C}Co(CO)_3PPh_3$. These peaks strengthened as the temperature was raised and a further peak at $1900_{(w)}$

cm^{-1} also appeared. The peak at 1900 cm^{-1}, believed due to $Co(CO)_4^-$, did not persist but slowly disappeared. When the system was allowed to cool to room temperature all the absorptions due to carbonyl groups were observed to disappear. On releasing the gas pressure and opening the bomb a brown solution was found. Evaporation of this brown solution produced a brown solid which was washed with hexane and sent for analysis. This gave Co, 6.7; H, 3.4; C, 52.1; P, 7.2; I, 30.1% $[Co(PPh_3)_2I_2$[109] requires Co, 7.0; H, 3.6; C, 51.6; P, 7.4; I, 30.3%].

The same study was performed using sodium iodide in place of elemental iodine and the reaction was observed as above. The only peaks observed were at $2000_{(m)}$ and $1900_{(s)}$ cm^{-1} and could be assigned to the species $[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-]$. As the temperature was gradually increased both of these absorptions were found to reduce slightly in intensity. As the bomb temperature reached 170°C weak carbonyl absorptions appeared at $2050_{(w)}$, $1980_{(w)}$, $1970_{(w)}$ and $1690_{(w)}$ cm^{-1} believed to be due to $Me\overset{O}{\overset{\|}{C}}Co(CO)_3PPh_3$. These peaks strengthened as the temperature was raised to 185°C and the absorption at 1900 cm^{-1} also strengthened. All these peaks were found to persist at this temperature.

When the system was cooled to room temperature the peaks all weakened substantially. However on releasing the carbon monoxide pressure these absorptions were found to rapidly disappear and, on extracting the mixture, most of the cobalt was found to be in the form of $[Co(CO)_3PPh_3]_2$.[55,67] The remainder appeared to have deposited as cobalt metal on the walls of the cell.

(c) Study of the system under synthesis gas pressure.

A series of reactions were performed under a synthesis gas pressure of 200 Atm (100 Atm H_2, 100 Atm CO) using dicobalt octacarbonyl with a ligand and iodine or iodide promoter.

Excess triphenyl phosphine and dicobalt octacarbonyl were reacted with iodine under synthesis gas pressure. The reaction initially showed no absorptions that could be assigned to carbonyl groups, as the elemental iodine had destroyed the dicobalt octacarbonyl. However as the temperature approached $170^{\circ}C$ weak carbonyl absorptions appeared at $2050_{(w)}$, $1980_{(w)}$, $1970_{(w)}$ and $1690_{(w)}$ cm^{-1}, believed to be due to $\mathrm{Me}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Co(CO)_3PPh_3}$.[108] These carbonyl stretching absorptions strengthened as the temperature was raised and a peak at $1900_{(m)}$ cm^{-1} also appeared. The peak at 1900 cm^{-1}, believed to be due to $Co(CO)_4^-$, strengthened for ∿ 25 minutes and then slowly began to disappear.

When the system was slowly allowed to return to room temperature all the carbonyl stretching absorptions were observed to weaken and disappear. The gas pressure was released and a brown solution was syringed from the vessel. A brown solid was formed on evaporation of this solution, which was washed with hexane and sent for analysis. Found: Co, 7.4; H, 3.8; C, 51.0; P, 7.1; I, 30.0% [$Co(PPh_3)_2I_2$ requires Co, 7.0; H, 3.6; C, 51.6; P, 7.4; I, 30.3%].

The same study was performed using sodium iodide in place of elemental iodine and the reaction followed as before. Initially the only peaks observed were at $2000_{(m)}$ and $1900_{(s)}$ cm^{-1}, due to the salt $[Co(CO)_3(PPh_3)_2^+][Co(CO)_4^-]$. The temperature of the cell was increased and these absorptions were observed to weaken. As the bomb reached ∿ $170^{\circ}C$ weak carbonyl absorptions were detected at 2050, 1980, 1970 and 1690 cm^{-1} which were assigned to $\mathrm{Me}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Co(CO)_3PPh_3}$. These peaks increased in intensity as the temperature approached 185°C. The 1900 cm^{-1} peak also strengthened, though the one at 2000 cm^{-1} weakened still further at this temperature. All these absorptions were found to persist.

The system was allowed to cool to room temperature and all the absorptions persisted, although all were reduced in intensity. On releasing the synthesis gas pressure these absorptions were found to disappear and on syringing the mixture from the cell most of the cobalt was found to be in the form of $[Co(CO)_3PPh_3]_2$.[55]

The study was also performed with triphenyl arsine and triphenyl stibine as the ligand employed. The infra-red spectra showed analogous species to be present; however the intensities of the absorptions due to the species $Me\overset{O}{\overset{\|}{C}}Co(CO)_3XPh_3$[93] were much reduced.

Comparison of spectra observed in the case of synthesis gas pressure and in that of carbon monoxide pressure only showed very little difference; no absorptions due to the species $HCo(CO)_3L$ or $HCo(CO)_4$[100-102] were observed. The presence of hydrogen however did cause the spectra to be obscured rapidly by absorptions due to organic by-products of the homologation reaction.

CHAPTER EIGHT

A DISCUSSION OF THE COBALT CATALYSED HOMOLOGATION REACTION OF METHANOL

8.1. Introduction

In this chapter the major mechanism proposed for the homologation reaction of methanol is considered and the various steps of the mechanism are discussed with reference to the results obtained here, and elsewhere. The mechanism is then modified to rationalize the influence of stabilising ligands and promoters. Various routes to some of the major by-products are also proposed and examined against a background of known and established organic chemistry.

The steric and electronic influences of the substituents of the tertiary valent phosphine, arsine and stibine ligands are considered and the resultant modified ligand-metal bonding, is discussed.

Solvent effects on the reaction are noted and explained with reference to solubility of synthesis gas and phase transfer catalysis. High pressure infra-red studies of two phase systems are reported briefly.

Finally the results obtained are used to construct a modified mechanism for the homologation reaction, taking into account the effects of promoters and stabilisation upon the system.

8.2. Discussion

The detailed mechanism for the homologation reaction has been under discussion for many years. Wender[2,116] has proposed a six step basic mechanism for the formation of ethanol. These six steps consist of:-

(1) Reduction of dicobalt octacarbonyl by hydrogen;

(2) Protonation of the methanol;

(3) Formation of the methyl-cobalt bond;

(4) Migration of a methyl group from cobalt to a carbonyl carbon;

(5) Reduction of the acyl intermediate;

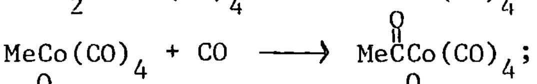
(6) Reduction of acetaldehyde to ethanol.

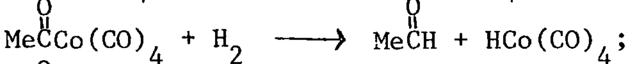
The mechanism can therefore be outlined in equations as below:-

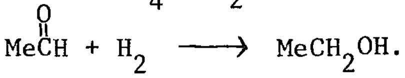
(1) $Co_2(CO)_8 + H_2 \longrightarrow 2HCo(CO)_4$;

(2) $HCo(CO)_4 + MeOH \longrightarrow Me\overset{+}{O}H_2 + Co(CO)_4^-$;

(3) $Me\overset{+}{O}H_2 + Co(CO)_4^- \longrightarrow MeCo(CO)_4 + H_2O$;

(4) 
$MeCo(CO)_4 + CO \longrightarrow Me\overset{O}{\overset{\|}{C}}Co(CO)_4$;

(5) 
$Me\overset{O}{\overset{\|}{C}}Co(CO)_4 + H_2 \longrightarrow Me\overset{O}{\overset{\|}{C}}H + HCo(CO)_4$;

(6) 
$Me\overset{O}{\overset{\|}{C}}H + H_2 \longrightarrow MeCH_2OH$.

The approach utilised in this discussion will be to evaluate critically the details of each step. This approach will allow comparisons and analogies to be drawn with other better known reaction schemes.

Stepwise examination of mechanism

Step 1. Production of hydridotetracarbonylcobalt (I)

We have observed the carbonyl absorptions of both bridged and non-bridged isomers of dicobalt octacarbonyl in hexane solution.[117,152] Under a pressure of 200 Atm of synthesis gas and at 130°C the absorptions of cobalt tetracarbonyl hydride were detected to form from such a solution of dicobalt octacarbonyl. This confirms the observations of Orchin and coworkers.[118] More detailed rate studies in n-heptane have suggested that a series of equilibria exist between dicobalt octacarbonyl, hydrogen and carbon monoxide:[119,120]

$$Co_2(CO)_8 \rightleftharpoons Co_2(CO)_7 + CO$$

$$H_2 + Co_2(CO)_7 \rightleftharpoons H_2Co_2(CO)_7$$

$$H_2Co_2(CO)_7 \rightleftharpoons HCo(CO)_4 + HCo(CO)_3$$

$$HCo(CO)_3 + CO \rightleftharpoons HCo(CO)_4$$

A direct reduction, which is formally the sum of these equations, is also inferred to compete with the above:

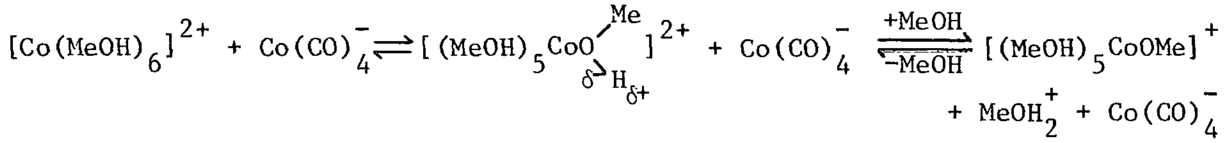
$$Co_2(CO)_8 + H_2 \longrightarrow 2HCo(CO)_4$$

The effect of solvent on the reduction of dicobalt octacarbonyl by hydrogen is of fundamental importance to the homologation reaction. However, for this reaction where the usual solvent is an alcohol, an intervening factor must be considered. This is the known disproportionation of dicobalt octacarbonyl in methanol at room temperature and ambient pressure:[40]

$$3Co_2(CO)_8 + 12MeOH \longrightarrow 2[Co(MeOH)_6]^{2+} + 4Co(CO)_4^- + 8CO$$

The reduction of dicobalt octacarbonyl by hydrogen to produce the hydride can only take place if this disproportionation is reversible under a high pressure of carbon monoxide. However our results obtained from high pressure infra-red studies did not detect any absorptions in the carbonyl stretching frequency region under these conditions that could be assigned to dicobalt octacarbonyl. The only carbonyl stretching absorptions present in the spectra were assigned to the cobalt tetracarbonylate anion, $(Co(CO)_4^-)$. This indicates that the disproportionation reaction is not reversible to any great extent. Orchin et al[121] claim that the disproportionation is reversible but this is not substantiated by this work. Our infra-red studies[123] indicate that neither dicobalt octacarbonyl nor cobalt tetracarbonyl hydride are present in detectable quantities under homologation conditions. Consequently these results cast doubts upon the importance of the hydride compound in the catalytic system, unless the hydride is present in such low concentrations that it is not detected by the infra-red spectroscopy. The hydride may still be an important species for the unpromoted homologation reaction of methanol but if present it must only exist in solution in extremely small quantities.

It has also been postulated that methanol coordinated to the cobalt (II) ion would have its hydrogen-oxygen bonds activated towards displacement of hydrogen. Thus the formation of $HCo(CO)_4$ by reduction of dicobalt octacarbonyl with hydrogen would be no longer necessary:-



$$[\mathrm{Co(MeOH)_6}]^{2+} + \mathrm{Co(CO)_4^-} \rightleftharpoons [\mathrm{(MeOH)_5Co}\overset{\mathrm{Me}}{\underset{\delta-\,\mathrm{H}^{\delta+}}{\mathrm{O}}}]^{2+} + \mathrm{Co(CO)_4^-} \underset{-\mathrm{MeOH}}{\overset{+\mathrm{MeOH}}{\rightleftharpoons}} [\mathrm{(MeOH)_5CoOMe}]^{+} + \mathrm{MeOH_2^+} + \mathrm{Co(CO)_4^-}$$

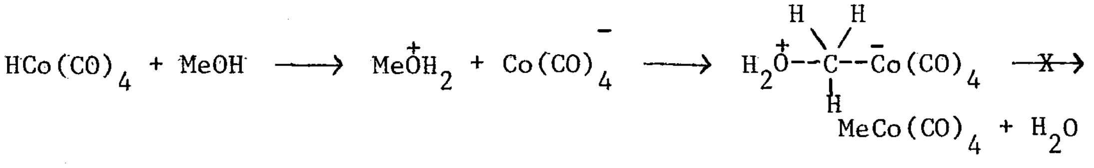
However our pH studies of solutions containing these ions showed a pH change, on mixing, that was fully explained by dilution effects. No change in pH could be assigned to the generation of the acidic hydride species. Hence we do not regard this as a likely mechanism.

Step 2. Activation of the carbon-oxygen bond of methanol.

Cobalt tetracarbonyl hydride is a very acidic metal hydride. Titration of this hydride in methanol solution has shown that it is as strong an acid in this solvent as are either nitric or hydrochloric acids in methanol.[122] It was suggested that solutions of this hydride should therefore be sufficiently acidic to protonate methanol, and then displacement of water from this "methanonium" ion by the tetracarbonyl cobaltate anion should occur to form a carbon-cobalt bond. Recent evidence has ruled out the formation of the methyl cation from protonated methanol in even the strongest of Lewis acids,[124] and hence the S_N1 reaction route is eliminated:

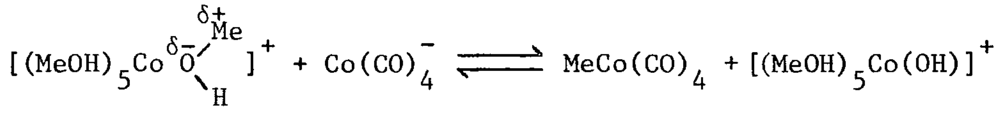
$$\mathrm{HCo(CO)_4} + \mathrm{MeOH} \longrightarrow \mathrm{Me\overset{+}{O}H_2} + \mathrm{Co(CO)_4^-} \not\longrightarrow \mathrm{Me^+} + \mathrm{H_2O} + \mathrm{Co(CO)_4^-}$$

Reaction by a S_N2 process remained feasible but an examination of $HCo(CO)_4$ in methanol solution by infra-red spectroscopy provided no support for this hypothesis:



$$\mathrm{HCo(CO)_4} + \mathrm{MeOH} \longrightarrow \mathrm{Me\overset{+}{O}H_2} + \overset{-}{\mathrm{Co(CO)_4}} \longrightarrow \mathrm{H_2\overset{+}{O}}\text{--}\underset{\mathrm{H}}{\overset{\mathrm{H\ \ H}}{\mathrm{C}}}\text{--}\overset{-}{\mathrm{Co}}\mathrm{(CO)_4} \not\longrightarrow \mathrm{MeCo(CO)_4} + \mathrm{H_2O}$$

A more likely explanation for the formation of $MeCo(CO)_4$ is that at high temperatures and pressures, methanol in the coordination sphere of the cobalt (II) cation will have its carbon-oxygen bonds activated towards displacement as follows:



$$[(MeOH)_5Co\overset{\delta-}{O}(\overset{\delta+}{Me})(H)]^+ + Co(CO)_4^- \rightleftharpoons MeCo(CO)_4 + [(MeOH)_5Co(OH)]^+$$

If this is indeed the case such a route would demand that the disproportionation reaction of dicobalt octacarbonyl occurs at elevated temperature and pressure and that the equilibrium lies well to the right, in order for there to be Co^{2+} and $Co(CO)_4^-$ ions present for the displacement reaction to take place. In fact our observations show no sign of this reaction being reversible, and ample concentrations of both Co^{2+} and $Co(CO)_4^-$ have been observed to be present. The formation of the methylcobalt species via activation of methanol coordinated to Co^{2+} ion seems to be the most likely route, according to our results.

In the iodide or iodine promoted system other modes of activation are available. Methanol can react in an S_N2-type process to afford methyl iodide from the equilibria:

$$MeOH + I^- \rightleftharpoons MeI + OH^-$$

$$Me\overset{+}{O}H_2 + I^- \rightleftharpoons MeI + H_2O$$

The methyl iodide can then function as the active methylating species[125] on the $Co(CO)_4^-$ ion. This, however is only the pathway for the promoted system. Homologation takes place without the presence of a promoter albeit less efficiently, probably by the route outlined above.

The presence of iodine as a promoter has been examined by Mizoroki[27,126] using a high temperature and high pressure u.v. cell. For methanol/acetic acid mixtures cobalt (II) ions were proposed to be present as $[Co(AcO)_{4-n}I_n]^{2-}$ for n = 1-4. While we have investigated methanol only systems, analogous species such as $[I_2Co(MeOH)_n]$ (n = 2 or 4) and $[ICo(MeOH)_5]^+$ may prove to be present for the system without acetic acid and may influence the activation of methanol. The presence of the iodide ion may influence the dicobalt octacarbonyl disproportionation reaction under the conditions studied. However our observations from high-pressure infra-red spectroscopy showed no absorptions that could be assigned to new carbonyl species. (Species such as those proposed above would not be detected by this technique.)

Step 3. Formation of the methyl-cobalt bond.

Several mechanisms of formation of methyl cobalt tetracarbonyl have been proposed. One of the more likely schemes involving the activation of coordinated methanol has already been discussed for the non-promoted reaction.

The nucleophilicity of carbonyl transition metal anions is well documented. The acidity of $HCo(CO)_4$ renders its anion, $Co(CO)_4^-$, essentially non-basic, but it is still quite nucleophilic.[79,127] Literature values for the nucleophilicity of $Co(CO)_4^-$ indicate that it is comparable to the methoxide ion[56] and such an ion is nucleophilic enough to react with most alkylating agents. The alkyl species formed, $MeCo(CO)_4$, is very unstable under reaction conditions with respect to decomposition and alkyl migration.[73] Thus for the iodide promoted reaction the S_N2 nucleophilic displacement reaction is likely:

$$MeI + Co(CO)_4^- \longrightarrow MeCo(CO)_4 + I^-$$

This agrees with our observations of the reaction under low temperature conditions and the subsequent rapid formation of the acyl-cobalt species.

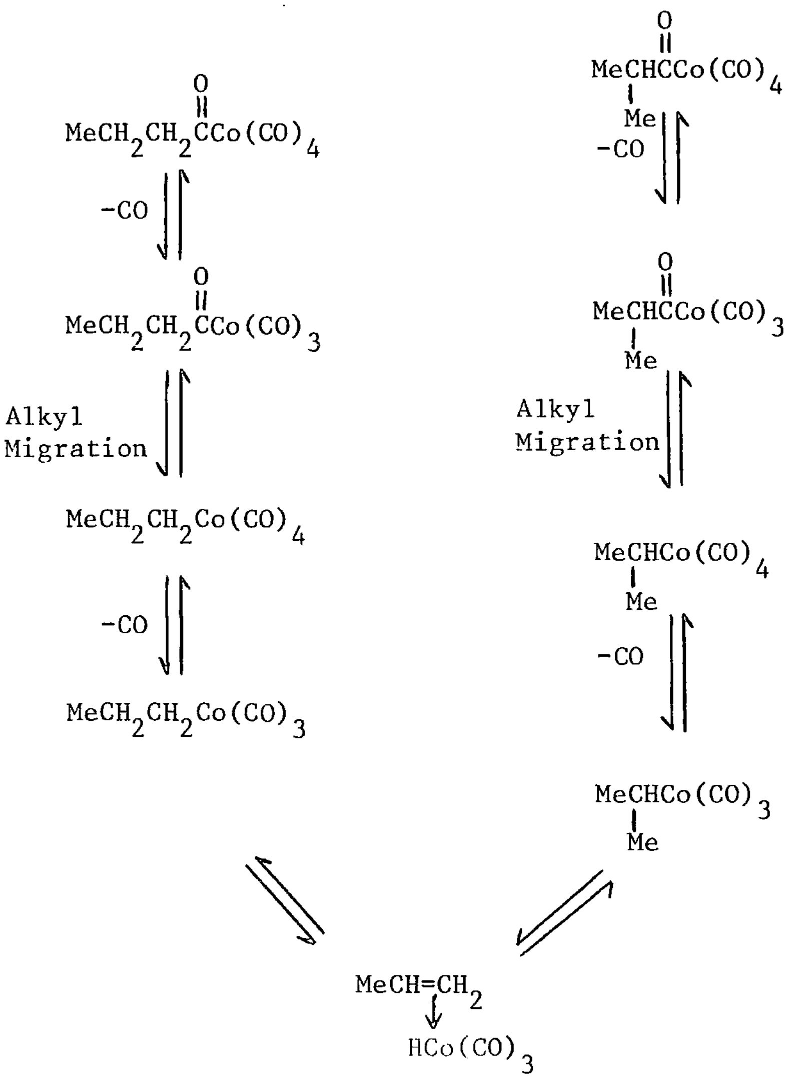
Step 4. Methyl migration from cobalt to a carbonyl carbon.

Migration of the alkyl group is known to take place readily. Indeed Heck and Breslow[93] developed a synthesis of acyl cobalt tetracarbonyls based on this premise. Our studies have shown the existence in substantial quantities of $\mathrm{Me\overset{\overset{O}{\|}}{C}Co(CO)_4}$ and $\mathrm{Me\overset{\overset{O}{\|}}{C}Co(CO)_3PPh_3}$ under homologation conditions for the unstabilised and ligand stabilised systems respectively. Theoretical studies have been made of the energetics and stereochemistry of the methyl migration reaction. A molecular orbital approach,[128] leads to a path whereby the methyl group firstly pseudorotates from its more stable axial position to an equatorial position in the trigonal bipyramidal structure of $\mathrm{MeCo(CO)_4}$. This is the principal barrier to methyl migration and is estimated to be about 13 Kcal $\mathrm{mol.^{-1}}$ An ab initio approach has arrived at a value of 8 Kcal $\mathrm{mol^{-1}}$ for this process.[129,161]

The results from our investigations show that the alkyl-cobalt species very rapidly converts to the acyl-cobalt species even under mild conditions. Indeed at high temperatures and pressures only the acyl-cobalt species is detected.

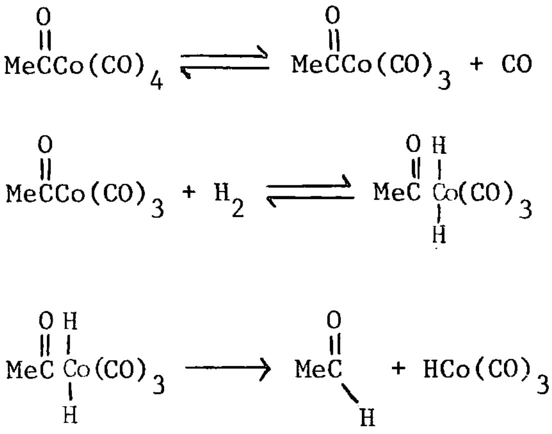
Substitution of a tertiary phosphine for a carbonyl ligand increases the stability of these molecules towards loss of carbon monoxide. These substituted compounds have been isolated and have been observed to undergo a stoichiometric methyl migration.[130,131] In general our results show that the phosphine ligand imparts thermal stability to the compound, but substantially reduces its catalytic activity, although the selectivity to ethanol does show some improvement.

The equilibrium between alkyl- and acyl-cobalt tetracarbonyls has been well established[64,76,78,83] and the reaction has been the subject of many review articles.[132-134] However when higher alcohols are employed in the homologation reaction isomerisation of the alkyl species is believed to occur due to the alkyl-acyl equilibrium.[156-9]



Step 5. Reduction of acyl transition metal complex.

Both hydrogen and $HCo(CO)_4$ could function as the reducing agent for acyl cobalt tetracarbonyls. Reduction by hydrogen would involve loss of carbon monoxide, oxidative addition of hydrogen and reductive elimination of acetaldehyde:

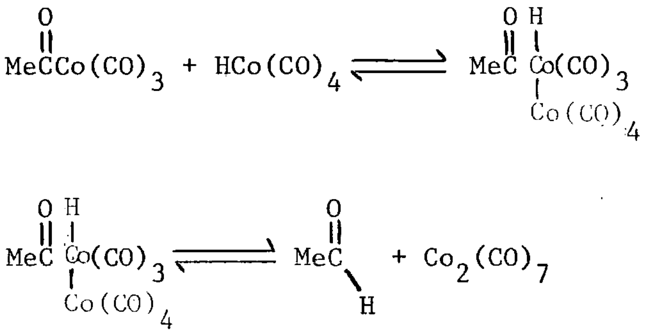


$$\mathrm{Me\overset{O}{\overset{\|}{C}}Co(CO)_4 \rightleftharpoons Me\overset{O}{\overset{\|}{C}}Co(CO)_3 + CO}$$

$$\mathrm{Me\overset{O}{\overset{\|}{C}}Co(CO)_3 + H_2 \rightleftharpoons Me\overset{O}{\overset{\|}{C}}\,\underset{H}{\overset{H}{Co}}(CO)_3}$$

$$\mathrm{Me\overset{O}{\overset{\|}{C}}\,\underset{H}{\overset{H}{Co}}(CO)_3 \longrightarrow Me\overset{O}{\overset{\|}{C}}H + HCo(CO)_3}$$

Our results favour this reduction of the acyl species by hydrogen: the alternative method, reduction by cobalt tetracarbonyl hydride, is believed to be much less likely as no evidence has been obtained for the presence of the hydride under homologation conditions. Reduction by $HCo(CO)_4$ would involve the same sequence, with $HCo(CO)_4$ in place of hydrogen:



$$\mathrm{Me\overset{O}{\overset{\|}{C}}Co(CO)_3 + HCo(CO)_4 \rightleftharpoons Me\overset{O}{\overset{\|}{C}}\,\underset{Co(CO)_4}{\overset{H}{Co}}(CO)_3}$$

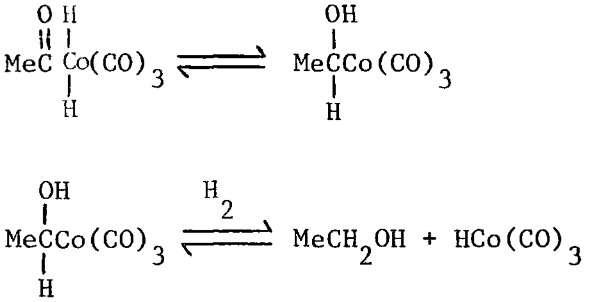
$$\mathrm{Me\overset{O}{\overset{\|}{C}}\,\underset{Co(CO)_4}{\overset{H}{Co}}(CO)_3 \rightleftharpoons Me\overset{O}{\overset{\|}{C}}H + Co_2(CO)_7}$$

Heck, in his review article,[135] cites evidence that both hydrogen and cobalt tetracarbonyl hydride reduce acyl cobalt tetracarbonyls to aldehydes. Recent articles[136,137] and reviews[138,3] on the subject appear to prefer the hydrogen route.

Step 6. Reduction of acetaldehyde to ethanol.

The reaction of acetaldehyde to form ethanol can be considered to occur by reduction with hydrogen or cobalt tetracarbonyl hydride.[154,155] Our studies again favour the hydrogen route as the metal-hydride has not been detected in the reaction system.

Alternatively the two reduction stages can be accomplished whilst the organo group remains attached to the metal:



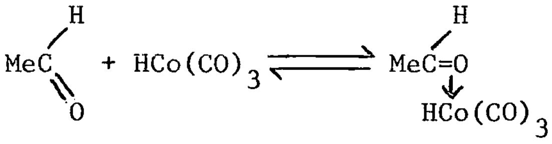
$$\mathrm{Me\overset{\overset{O}{\|}}{C}\,\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{Co}}(CO)_3 \rightleftharpoons Me\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}Co(CO)_3}$$

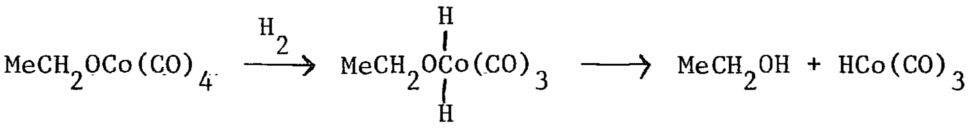
$$\mathrm{Me\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}Co(CO)_3 \overset{H_2}{\rightleftharpoons} MeCH_2OH + HCo(CO)_3}$$

The reduction of free acetaldehyde has been studied under high pressure and high temperature conditions as part of investigations into the hydroformylation reaction.

The mechanism proposed by Marko[139] for the reduction of aldehydes includes the tricarbonyl-cobalt species $HCo(CO)_3$, as the rate was inversely dependent upon carbon monoxide pressure:

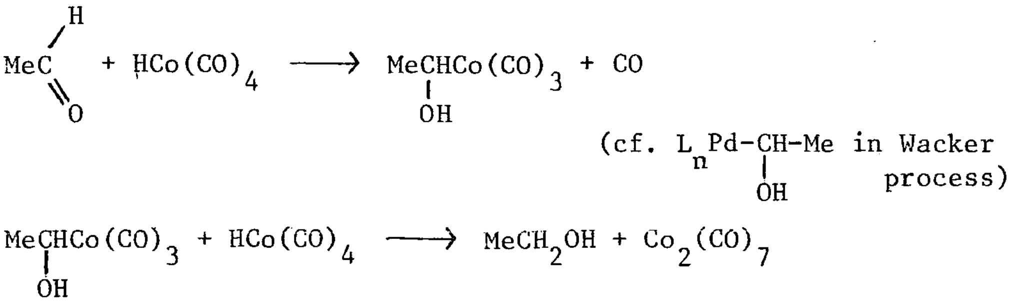
$$\mathrm{HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO}$$





$$\mathrm{MeCH_2OCo(CO)_4 \xrightarrow{H_2} MeCH_2O\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{Co}}(CO)_3 \longrightarrow MeCH_2OH + HCo(CO)_3}$$

A further study of the reduction of aldehydes has also been reported.[140] A similar inverse dependence of rate on carbon monoxide pressure was observed and a scheme involving a different coordinatively unsaturated species was proposed:



$$\mathrm{MeC(H){=}O} + \mathrm{HCo(CO)_4} \longrightarrow \underset{\mathrm{OH}}{\mathrm{MeCHCo(CO)_3}} + \mathrm{CO}$$

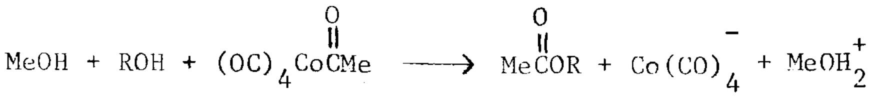
(cf. $\underset{\mathrm{OH}}{\mathrm{L_nPd\text{-}CH\text{-}Me}}$ in Wacker process)

$$\underset{\mathrm{OH}}{\mathrm{MeCHCo(CO)_3}} + \mathrm{HCo(CO)_4} \longrightarrow \mathrm{MeCH_2OH} + \mathrm{Co_2(CO)_7}$$

These two schemes differ significantly from one another. The inverse dependence of rate on carbon monoxide pressure does provide fairly strong evidence for the involvement of cobalt tricarbonyl hydride. The nature of its involvement and of that of hydrogen seem the main questions. However under homologation conditions the presence of these proposed hydride species seems to be very unlikely, and hence reduction by hydrogen at the metal centre appears to be strongly favoured.

By-products from the homologation reaction

A discussion is presented of the various pathways whereby some side-products may be generated. Reactions leading to the production of the various acetates encompass several possible routes. The nucleophilic attack of methanol or ethanol on the acyl intermediate is probably the most likely:

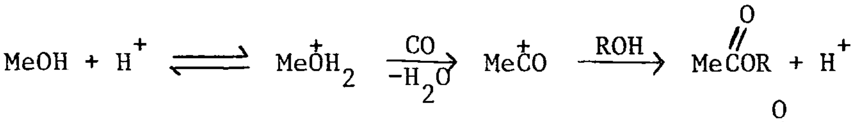


$$\mathrm{MeOH} + \mathrm{ROH} + \mathrm{(OC)_4Co}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Me} \longrightarrow \mathrm{Me}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR} + \mathrm{Co(CO)_4^-} + \mathrm{MeOH_2^+}$$

R = -Me or -Et

The presence of water in the products of the homologation reaction suggests that some acetic acid should also be formed by this pathway. Any acetic acid formed under these conditions is likely to be esterified.

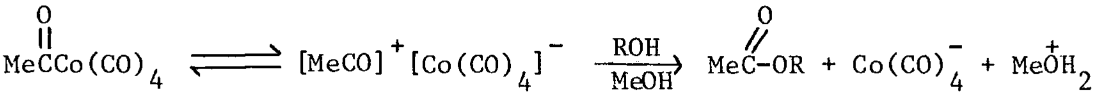
Esters can also arise under these conditions by routes involving acylium ion intermediates. One such route is the acid-catalysed carbonylation of alcohols known as the Koch-Haaf reaction:



$$MeOH + H^+ \rightleftharpoons Me\overset{+}{O}H_2 \xrightarrow[-H_2O]{CO} Me\overset{+}{C}O \xrightarrow{ROH} Me\overset{O}{\overset{/\!/}{C}}OR + H^+$$

This could possibly be a route to the acyl species, $Me\overset{O}{\overset{\|}{C}}Co(CO)_4$, which is in competition with its formation via the metal-alkyl species.

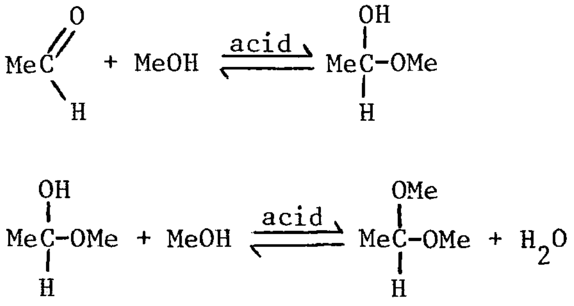
Alternatively, the acyl intermediate in these reactions would ionise



$$Me\overset{O}{\overset{\|}{C}}Co(CO)_4 \rightleftharpoons [MeCO]^+[Co(CO)_4]^- \xrightarrow[MeOH]{ROH} Me\overset{O}{\overset{/\!/}{C}}\text{-}OR + Co(CO)_4^- + Me\overset{+}{O}H_2$$

The ionic intermediate, $[MeCO]^+[Co(CO)_4]^-$, is the transition metal analogue of the intermediate in an aluminium chloride catalysed acylation, i.e. $[MeCO]^+[AlCl_4]^-$. In effect the alcohols present become acylated. In fact, carboxyalkylation of alcohols has been found to be catalysed by the cobalt tetracarbonyl anion and a potential preparative technique based on this reaction has been developed.[141]

Acetals have been isolated from the homologation reaction under conditions of ∿ 150°C. These compounds are most likely formed by the normal acid catalysed route to acetals utilizing some of the acetaldehyde formed in the reaction.



$$Me\overset{O}{\overset{/\!/}{C}}\text{-}H + MeOH \xrightleftharpoons{acid} Me\overset{OH}{\underset{H}{C}}\text{-}OMe$$

Hemiacetal

$$Me\overset{OH}{\underset{H}{C}}\text{-}OMe + MeOH \xrightleftharpoons{acid} Me\overset{OMe}{\underset{H}{C}}\text{-}OMe + H_2O$$

Acetal

At 200°C such acetals may well react quickly in an acid-catalysed process to provide a carbonium ion intermediate which can be reduced to the corresponding ether:

$$MeCH(OR)_2 \xrightarrow{H_2} Me\overset{+}{C}H\text{-}OR \xrightarrow{H_2} MeCH_2\text{-}OR$$

$R = -Me, -Et$

This route however does not explain the formation of dimethyl ether. This is believed to form via the normal dehydration of two molecules of methanol. A similar pathway could also account for the other ethers detected, but this would necessitate the formation of a primary carbonium ion where as the route from the acetal involves the resonance stabilised carbonium ion, $Me\overset{+}{C}H-OR \longleftrightarrow MeCH=\overset{+}{O}R$.

Transition metals exhibit a strong tendency to form compounds with trivalent phosphorous and arsenic, and to a lesser extent antimony. In homogeneous catalysis the ligands are often modified in order to change the activity or the selectivity of the catalyst, though in general tertiary phosphines are mainly employed.[142-7] However some of the trends among the group V donors deserve comment. The significance of π-bonding in phosphine ligands is controversial, but it seems likely that the heavier group-V donors are predominantly, perhaps exclusively, σ-donors. Metal-donor steric-repulsion effects increase in the order $P < As < Sb$. Steric effects of the substituents on the donor decrease in the order $P > As > Sb$.

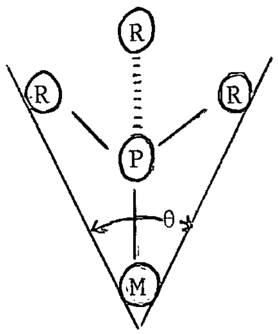
Tertiary phosphines were once thought to stabilise transition-metal alkyl derivatives partly through d-π backbonding involving filled metal d-orbitals interacting with vacant d-orbitals on phosphorus. However this issue cannot be said to be fully resolved, as for simple tertiary phosphines there seems to be no instance where dπ-dπ backbonding is required to explain the observed physical properties. However π-backbonding is likely to be significant among complexes of PF_3 and, to a lesser degree, complexes of phosphites, $(RO)_3P$. The kinetic stabilisation of metal-alkyl bonds obtained by use of phosphine ligands may simply be caused by preserving coordinative saturation at the metal and by steric shielding of the metal by bulky substituent groups, thus inhibiting kinetic paths for metal-alkyl bond breaking.

The relative tendency of phosphine and related ligands to bind to a metal are suggested by the following trend in equilibrium constants:[148]

$$W(CO)_5(amine) + L \overset{K}{\rightleftharpoons} W(CO)_5L + amine$$

K increases in the order $Ph_3Sb < Ph_3As < Ph_3P$. In this case, steric effects are probably relatively unimportant, so that this trend may reflect intrinsic affinities. Thus the exact values may vary from one complex to another, while the trend remains fairly constant.

Altering the substituents on tertiary phosphines can cause substantial changes in the chemical properties of their transition-metal complexes. Some of these effects are electronic, but steric effects are also very important. The bulky tertiary phosphine ligands distort the surrounding ligands and shield the metal, thus markedly affecting the chemistry of phosphine complexes. Also a large number of physical properties are influenced by the bulk of phosphine ligands. These have been reviewed by Tobman,[142,149] who has proposed the cone angle as a measure of steric bulk.



Schematic representation of phosphine ligand of cone angle θ

Ligand	Cone angle
PPh_3	145 ± 2
PEt_3	132 ± 4
$P(C_4H_9)_3$	130 ± 4
$P(C_6H_{11})_3$	179 ± 10
$P(t\text{-}But)_3$	182 ± 2

No cone angles for arsine or stibine ligands were found to have been reported in the literature, so unfortunately comparison down group V is not possible as yet. However our studies of reactions involving the phosphines,

PPh_3, $P(C_4H_9)_3$ and $P(C_6H_{11})_3$ indicated that the ligand with the largest cone angle $P(C_6H_{11})_3$ was the poorest additive for ethanol production. In terms of ethanol formation there was little difference between PPh_3 and $P(C_4H_9)_3$, although n-butyl phosphine is generally regarded as a more efficient ligand.

Steric and electronic factors are often strongly interrelated, so that it is difficult to separate them. For example the percentage of s-character in the phosphorus ligand electron pair should decrease as the cone angle increases. More electronegative substituents on phosphorus produce a shorter M-P bond by inducing more s-character into the M-P bond.

There are many types of phosphine ligands and some of them will undoubtedly find a role in homogeneous catalysis. According to patent literature[23] many of the more exotic phosphine ligands (e.g. the secondary and multidentate phosphine ligands) have been tested in the homologation reaction, with varying degrees of success.

The replacement of a carbon monoxide ligand by a phosphine ligand can have an enormous effect upon the chemical properties of a compound. For example the hydride $HCo(CO)_4$ has an acid dissociation constant in water approximately as strong as that of a mineral acid,[150,122] whereas for $HCo(CO)_3PPh_3$ also in water the dissociation constant is reduced by a factor of 10^{-7}. This implies that if any $HCo(CO)_3PPh_3$ was formed in the reaction, it would be observed readily by infra-red spectroscopy as the ionisation

$$HCo(CO)_3PPh_3 \rightleftharpoons H^+ + {}^-Co(CO)_3PPh_3$$

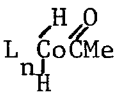
does not occur to any great extent. Our results show no evidence for this hydride, so it appears that it is not formed in the stabilised reaction. Modification of the system by addition of a phosphine ligand causes a substantial change in the reaction.

Our results indicate that the stabilised reaction is very poor at generating ethanol and this is thought to be due to the lack of Co^{2+} ions on which activation of methanol can take place. The main species observed in the stabilised reaction are $[Co(CO)_3(PR_3)_2]^+[Co(CO)_4]^-$ and $[Co(CO)_3PR_3]_2$ both of which reduce the availability of Co^{2+} ions in the system.

When tertiary arsines or stibines are used as stabilising ligands other points have to be considered.

It is highly probable that the production of ethanol from methanol and synthesis gas proceeds via the formation of acetaldehyde. Whether the compound is generated as free acetaldehyde or is still bound to the metal centre has not been determined.

$$MeOH + CO + H_2 \longrightarrow MeCHO + H_2O \xrightarrow{H_2} MeCH_2OH + H_2O$$

The addition of triphenyl arsine or triphenyl stibine inhibits this last step in the reaction resulting in a high yield of acetaldehyde. The degree of reduction of acetaldehyde to ethanol is believed to be dependent on the nature of the complex,  $L_n\overset{H}{\underset{H}{Co}}\overset{O}{C}Me$, or more specifically on the electronic or steric properties of the ligands, L. In order to come to a firmer conclusion on the mechanism a wide range of phosphines, arsines and stibines would have to be examined. However, the following points are relevant:-

(a) Hydroformylation reactions involve the conversion of an olefin and synthesis gas into an aldehyde. When this reaction is catalysed by a cobalt complex a small amount of the aldehyde product is converted to alcohol, especially at higher temperatures. The degree of reduction is increased on adding a phosphine such as PPh_3 to the reaction mixture. The species generally regarded as responsible for this reduction is $HCo(CO)_3L$ where L = CO, or PPh_3 in the stabilised reaction. If L = PPh_3 the electron density on the metal increases in comparison to L = CO, which in turn increases the hydridic character of the complex (i.e. its ability to form H^-). It is this increased hydridic character that is thought to improve the yield of alcohol.

(b) In the case of the methanol reaction a similar species may be responsible for the reduction of acetaldehyde to ethanol. The hydridic character of the complex $HCo(CO)_3L$ will increase in the order $L = CO < SbPh_3 < AsPh_3 < PPh_3$. However, although $HCo(CO)_3AsPh_3$ is slightly less hydridic than the phosphine, the difference is not great. Consequently it seems unlikely that this can explain the marked change in product spectrum when an arsine ligand is used as the modifying ligand. In addition the position of L = CO in the series is not consistent with the reducing ability of the unstabilised system (i.e. better than with an arsine or stibine). It thus appears to be an over-simplification to compare this part of the homologation with the hydroformylation reaction.

(c) There are other ways in which electronic effects can influence the reduction. For example oxidative addition of hydrogen to the complex $CH_3CH_2O\text{-}Co(CO)_{3/\text{or } 2}L$ is probably essential before the ethanol product can be formed. This could be enhanced by reduced electron density on the metal or by a non-labile metal-ligand bond (dissociation of L may be a necessary first step before oxidative addition can occur).

(d) Bulky ligands on the intermediate $L_nCoH\text{----}CH_3CHO$ will promote the elimination of acetaldehyde at the expense of further reduction. If steric factors are important in this reaction, arsines that have basicities comparable with $AsPh_3$, yet are smaller in size, should give increased ethanol yields.

Solvents

Three solvent effects have been noted so far in the study of the methanol homologation reaction:-

(a) The addition of organic acids and acid derivatives (e.g. methyl acetate) suppresses the formation of methyl and ethyl acetates and acetic acid.

(b) Immiscible solvents (e.g. chlorobenzene) improve the yield of ethanol and when added in high concentration suppress the formation of acetates.

(c) Miscible, coordinating solvents improve the ethanol yield.

The beneficial effects of organic acids and acid derivatives are believed to be due simply to equilibrium effects. The addition of, what are regarded as unwanted by-products, to the initial reaction mixture suppresses the formation of further acetates and hence assists the formation of the required product with less wastage of starting material. Also the by-product can be recycled in the system and continue to have a useful effect.

A second point applying to solvents in general is the dependence of the reaction on dissolved synthesis gas. Studies by colleagues at British Petroleum Research Centre, Sunbury have shown that the homologation reaction is strongly dependent upon the speed of stirring of the reaction and therefore to the quantity of dissolved gases. This dependence is thought to be due to the poor solubility of hydrogen in methanol, even under high pressure. Hence the reaction may be hindered by lack of readily available hydrogen. Thus a solvent, (immiscible or miscible with methanol), in which hydrogen is more soluble is able to provide a more easily accessible source of reducing agent.

A further point is worth examination for immiscible solvents; this is the possibility of phase transfer. The inert solvent phase (e.g. a hydrocarbon) will be hydrogen rich and can provide conditions in which the generation of a metal hydride species is favourable. The hydride, once formed, is able to act as an acid and ionise in the carbon monoxide rich methanol phase where carbonylation can be envisaged to occur. The acyl species eventually generated can then phase transfer back to the hydrocarbon solvent for final reduction to ethanol. This allows the more polar species to exist within the methanol phase and the non-polar species to exist in the hydrocarbon phase. The presence of methyl iodide and tertiary phosphines will encourage phase transfer by generation of methylating species such as $Ph_3\overset{+}{P}Me\overset{-}{I}$ (observed in ^{31}P n.m.r. at 22.0 ppm) which can act as phase transfer methylating agents.

High pressure infra-red studies have been performed on dicobalt octacarbonyl in a mixture of hexane and methanol under synthesis gas pressure and carbonyl stretching frequency absorptions corresponding to dicobalt octacarbonyl, cobalt tetracarbonyl hydride and $Me\overset{O}{\overset{\|}{C}}Co(CO)_4$ have been detected in the hexane layer of this non-promoted, non-stabilised system. The reaction has also been examined with a methyl iodide promoter and a phosphine stabilising ligand present, again using hexane as the inert phase, and the only carbonyl stretching frequency absorptions observed were assigned to the species $Me\overset{O}{\overset{\|}{C}}Co(CO)_3PPh_3$.

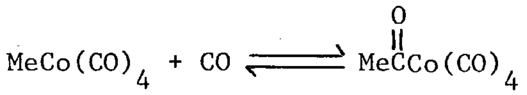
The observation of these types of species in the inert solvent is not conclusive evidence for phase transfer from the methanol, but the results indicate that this is one aspect of the reaction that requires further study and may yield useful results.

Another area of investigation that needs to be examined more closely is the possibility of including co-catalysts in the reaction system. Recent studies[160] have shown that the inclusion of a co-catalyst of ruthenium trichloride in the stabilised and promoted system enhances the yield of ethanol and substantially decreases the yield of acetates and acetaldehyde. Other co-catalysts may prove to have similar effects on the homologation reaction.

8.3. Summary

The mechanism most often advanced for the homologation reaction (shown below) implicates $HCo(CO)_4$ as the key form of cobalt reacting with MeX (X = I or OH).[56] The rest of the sequence parallels the mechanism proposed for cobalt-catalysed olefin hydroformylation.

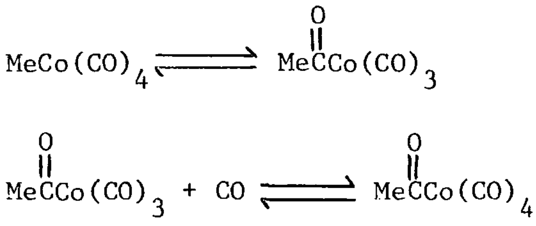
$$\mathrm{MeOH + HCo(CO)_4 + MeX \rightleftharpoons MeCo(CO)_4 + Me\overset{+}{O}H_2 + X^-} \qquad (1)$$



$$\mathrm{MeCo(CO)_4 + CO \rightleftharpoons Me\overset{O}{\overset{\|}{C}}Co(CO)_4} \qquad (2)$$

$$\mathrm{MeOH + Me\overset{O}{\overset{\|}{C}}Co(CO)_4 + H_2 \rightleftharpoons MeCHO + Me\overset{+}{O}H_2 + Co(CO)_4^-} \qquad (3)$$

Reaction (2) may also be considered as occurring in two parts, i.e.



$$\mathrm{MeCo(CO)_4 \rightleftharpoons Me\overset{O}{\overset{\|}{C}}Co(CO)_3}$$

$$\mathrm{Me\overset{O}{\overset{\|}{C}}Co(CO)_3 + CO \rightleftharpoons Me\overset{O}{\overset{\|}{C}}Co(CO)_4}$$

Similar coordinatively unsaturated species may be postulated in the other steps as well.

The results of this current study implicate $Co(CO)_4^-$ as the active form of cobalt in the homologation reaction. No $HCo(CO)_4$ and no $Co_2(CO)_8$ is observed either in methanol solution under CO/H_2 pressure, or when iodine is present. Interestingly, both species were observed at some stage during an infra-red study of the hydroformylation reaction.[151] Unlike the hydroformylation study, the infra-red study of the homologation reaction suggests that the dominant form of cobalt throughout the reaction is $[Co(MeOH)_xI_y]^{n+}[Co(CO)_4]^-_n$. Thus equation (1) may be more appropriately replaced by:

$$Co(CO)_4^- + MeX \rightleftharpoons MeCo(CO)_4 + X^-$$

$$(X = I \text{ or } OH)$$

In such a scheme, any $HCo(CO)_4$ if formed as shown in equation 3 would necessarily be present only in minute quantities, and could be envisaged either as reacting with X^- to give $Co(CO)_4^-$ and HX, or as ionising thus:-

$$HCo(CO)_4 + MeOH \longrightarrow Co(CO)_4^- + Me\overset{+}{O}H_2.$$

Iodine appears to function in two roles: (1) as an activator of methanol via methyl iodide formation, and (2) as an agent that removes the active form of cobalt, $Co(CO)_4^-$. Excess iodine and extended reaction periods lead to total loss of all soluble cobalt carbonyls. This may occur through formation of cobalt metal, and/or non-carbonyl cobalt complexes e.g. $[Co(OAc)_2I_2]^{x-}$. Low iodine/cobalt ratios are favourable since insufficient iodine is available to completely remove the active form of cobalt, yet iodide is present to form methyl iodide which apparently reacts more readily with the active cobalt carbonyl derivative. The homologation reaction proceeds in the absence of iodine but much more slowly, particularly when ligand modifiers are used. This may suggest that two different mechanisms are operative, depending upon the presence or absence of iodine.

Iodine also appears to function in these same two roles, both as an activator via methyl iodide formation and as an agent for removal of catalyst. However our results indicate that iodide promoted systems remain active for longer times than the corresponding iodine promoted systems. Thus the addition of an iodide as a promoter is generally preferable to elemental iodine.

It is interesting to speculate that the active forms of cobalt, in the absence of iodine are Co^{2+} and $Co(CO)_4^-$. However when iodine or iodide promoters are present, the reaction occurs much more efficiently, with $Co(CO)_4^-$ as the active form of catalyst. The promoters provide a different route for the formation of the metal-alkyl bond.

When a ligand such as triphenyl phosphine is present dicobalt octacarbonyl reacts to form $[Co(CO)_3(PPh_3)_2]^+[Co(CO)_4^-]$ initially. As the reaction proceeds some of the dimer $[Co(CO)_3PPh_3]_2$ undoubtedly forms, as well as a small amount of $HCo(CO)_3PPh_3$. These reactions convert virtually all of the cobalt to non-catalytic species, and thus little Co^{2+} is present for activation of the methanol. $PPN^+Co(CO)_4^-$ has been found to be a poor catalyst for the unpromoted reaction in comparison with $Co_2(CO)_8$ but in the iodide promoted system there is little difference between the two catalysts. This result appears to support the belief that the Co^{2+} ion is an important feature of the unpromoted system.

8.4. Synopsis

The methanol homologation reaction as catalysed by cobalt carbonyl has been shown to be a very complex process, highly dependent on a variety of reaction parameters and variables, such as pressure, temperature and synthesis gas composition. Ethanol is the ultimate required product though many by-products are also formed. Also the initial carbonylation product, acetaldehyde, can be obtained in high selectivity by ligand modification. Iodine and iodide are effective promoters but high I/Co ratios lead to undesirable reaction by-products and catalyst deactivation, especially with iodine. High pressure infra-red spectroscopy has given evidence implicating $Co(CO)_4^-$ as the active catalyst in the iodide promoted system, whereas the Co^{2+} ion is also believed to be important in the unpromoted system.

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APPENDIX

(a) Lectures and Seminars organised by the Department of Chemistry during the period 1979-1982

(* denotes those attended.)

*21 November 1979

Dr. J. Muller (University of Bergen),

"Photochemical Reactions of Ammonia".

28 November 1979

Dr. B. Cox (University of Stirling),

"Macrobicyclic Cryptate Complexes, Dynamics and Selectivity".

5 December 1979

Dr. G.C. Eastmond (University of Liverpool),

"Synthesis and Properties of Some Multicomponent Polymers".

*12 December 1979

Dr. C.I. Ratcliffe (University of London),

"Rotor Motions in Solids".

19 December 1979

Dr. K.E. Newman (University of Lausanne),

"High Pressure Multinuclear NMR in the Elucidation of the Mechanisms of Fast, Simple Inorganic Reactions".

*30 January 1980

Dr. M.J. Barrow (University of Edinburgh),

"The Structures of Some Simple Inorganic Compounds of Silicon and Germanium - Pointers to Structural Trends in Group IV".

*6 February 1980

Dr. J.M.E. Quirke (University of Durham),

"Degradation of Chloryphyll-a in Sediments".

23 April 1980

B. Grievson, B.Sc. (University of Durham),

"Halogen Radiopharmaceuticals".

14 May 1980

Dr. R. Hutton (Waters Associates, U.S.A.),

"Recent Developments in Multi-milligram and Multi-gram Scale Preparative High Performance Liquid Chromatography".

21 May 1980

Dr. T.W. Bentley (University of Swansea),

"Medium and Structural Effects in Solvolytic Reactions".

10 July 1980

Professor P. des Marteau (University of Heidelburg),

"New Developments in Organonitrogen Fluorine Chemistry".

*7 October 1980

Professor T. Felhner (Notre-Dame University, U.S.A.),

"Metalloboranes - Cages or Coordination Compounds"?

15 October 1980

Dr. R. Adler (University of Bristol),

"Doing Chemistry Inside Cages - Medium Ring Bicyclic Molecules".

*12 November 1980

Dr. M. Gerloch (University of Cambridge),

"Magnetochemistry is about Chemistry".

19 November 1980

Dr. T. Gilchrist (University of Liverpool),

"Nitroso Olefins as Synthetic Intermediates".

*3 December 1980

Dr. J.A. Connor (University of Manchester),

"Thermochemistry of Transition Metal Complexes".

*18 December 1980

Dr. R. Evans (University of Brisbane, Australia),

"Some Recent Communications to the Editor of the Australian Journal of Failed Chemistry".

*18 February 1981

Professor S.F.A. Kettle (University of East Anglia),

"Variations in the Molecular Dance at the Crystal Ball".

25 February 1981

Dr. K. Bowden (University of Sussex),

"The Transmission of Polar Effects of Substituents".

4 March 1981

Dr. S. Craddock (University of Edinburgh),

"Pseudo-Linear Pseudohalides".

11 March 1981

Dr. J.F. Stoddard (I.C.I. Ltd./University of Sheffield),

"Stereochemical Principles in the Design and Function of Synthetic Molecular Receptors".

17 March 1981

Professor W. Jencks (Brandsis University, Massachusetts),

"When is an Intermediate not an Intermediate"?

*18 March 1981

Dr. P.J. Smith (International Tin Research Institute),

"Organotin Compounds - A Versatile Class of Organometallic Compounds".

*9 April 1981

Dr. W.H. Meyer (R.C.A. Zurich),

"Properties of Aligned Polyacetylene".

6 May 1981

Professor M. Szware, F.R.S.,

"Ions and Ion Pairs".

10 June 1981

Dr. J. Rose (I.C.I. Plastics Division),

"New Engineering Plastics".

17 June 1981

Dr. P. Moreau (University of Montpellier),

"Recent Results in Perfluoroorganometallic Chemistry".

21 September 1981

Dr. P. Plimmer (DuPont),

"From Conception to Commercialisation of a Polymer".

14 October 1981

Professor E. Kluk (University of Katowice),

"Some Aspects of the Study of Molecular Dynamics in Simple Molecular Liquids".

28 October 1981

Dr. R.J.H. Clark (University College London),

"Resonance Raman Spectroscopy a New Technique for Chemical, Spectroscopic and Structural Studies".

*6 November 1981

Dr. W. Moddeman (Monsanto Ltd., U.S.A.),

"High Energy Materials".

18 November 1981

Professor M.J. Perkins (Chelsea College),

"Spin Trapping and Nitroxide Radicals".

25 November 1981

Dr. M. Braid (University of Newcastle),

"Intramolecular Reactions of Carbenes and Carbenoids".

*2 December 1981

Dr. G. Beamson (University of Durham),

"Photoelectron Spectroscopy in a Strong Magnetic Field".

20 January 1982

Dr. M.R. Bryce (University of Durham),

"Organic Metals".

27 January 1982

Dr. D.L.H. Williams (University of Durham),

"Nitrosation and Nitrosamines".

3 February 1982

Dr. D. Parker (University of Durham),

"Modern Methods for the Determination of Enantiomeric Purity".

*10 February 1982

Dr. D. Pethrick (University of Strathclyde),

"Conformational Dynamics of Small and Large Molecules".

17 February 1982

Professor D.T. Clark (University of Durham),

"Structure, Bonding, Reactivity and Synthesis of Surfaces as Revealed by ESCA".

24 February 1982

Dr. L. Field (University of Oxford),

"The Application of NMR Methods to the Study of Penicillin Biosynthesis".

3 March 1982

Dr. P. Banfield (I.C.I. Organics Division),

"Computer Aided Synthesis Design: A View from Industry".

*17 March 1982

Professor R.J. Hoines (University of Cambridge),

"Clustering around Ruthenium, Iron and Rhodium".

5 May 1982

Dr. G. Tennant (University of Edinburgh),

"Exploitation of the Aromatic Nitro-group in the Design of New Heterocyclic Reactions".

12 May 1982

Dr. C.D. Garner (University of Manchester),

"The Structure and Function of Molybdenum Centres in Enzymes".

19 May 1982

Professor R.D. Chambers (University of Durham),

"Fluorocarbanions - Some 'Alice in the Looking Glass' Chemistry".

*26 May 1982

Dr. A. Welch (University of Edinburgh),

"Conformational Patterns and Distortions in Carbametallaboranes".

14 June 1982

Professor C.J.M. Stirling (University College of Wales, Bangor), "How much does Strain Effect Reactivity"?

28 June 1982

Professor D.J. Burton (University of Iowa), "Some Aspects of the Chemistry of Fluorinated Phosphonium Salts and Phosphonates".

2 July 1982

Professor H.F. Koch (Ithaca College U.S.A.), "Proton Transfers to and Elimination Reactions from Localised and Delocalised Carbanions".

(b) Conferences attended during the period 1979-1982

(i) Annual Congress of the Chemical Society and the Royal Institute of Chemistry, Durham University, April 1980.

(ii) Graduate Symposium, Durham University, 1982.

(c) First year induction course

A series of one hour presentations on the services available in the Department.

(i) Departmental organisation.
(ii) Safety matters.
(iii) Electrical appliances.
(iv) Chromatography and microanalysis.
(v) Library facilities.
(vi) Atomic absorption and inorganic analysis.
(vii) Mass spectrometry.
(viii) Nuclear magnetic resonance spectroscopy.
(ix) Glassblowing technique.